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Edited by

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PREFACE

This volume consists entirely of a review, by Professor M. Witanowski and his coauthors, on nitrogen NMR. The account relates to the literature published between 1981 and 1984 and serves to both update and expand upon those presented in earlier volumes of this series, the most recent of which was Volume 11B.

I am very grateful to the authors for producing this review and for their understanding and willing cooperation during the preparation of this volume.

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G. A. WEBB
October 1985

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Nitrogen NMR Spectroscopy

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I. INTRODUCTION

In preparing this report we have it in mind to provide a full survey of the nitrogen NMR literature that has been published since our last review appeared.¹ Consequently, the period covered extends from late 1980 to the end of 1983.

Taken in conjunction with our earlier accounts,¹⁻⁴ we are thus in a position to provide a comprehensive survey of nitrogen NMR spectroscopy over a period of 33 years. The period commenced in 1950 when Proctor and Yu⁵ reported a shielding difference of 303 ppm for the two ^{14}N signals of ammonium nitrate, this being amongst the first chemical shifts to be reported for any nucleus.

During the three years currently under consideration the applications of nitrogen NMR have continued to increase and the number of publications relating to it has burgeoned. Advances have been made in both the experimental and theoretical aspects of the subject.

Both the ^{14}N and ^{15}N isotopes are commonly studied; the former in situations where either the quadrupolar relaxation rate is small, in order to provide relatively narrow signals and thus reliable nuclear shielding results, or where the factors responsible for quadrupole interactions are the main interest of the investigation.

The ^{15}N nucleus, of lower natural abundance, has sharper NMR signals which are capable of yielding nuclear shielding, spin-spin coupling and relaxation data. The less efficient nuclear relaxation processes, such as those arising from dipole-dipole, chemical shielding anisotropy or spin-rotation interactions, normally control ^{15}N relaxation.

That nitrogen NMR is an invaluable structure-determination technique for many chemists and biochemists is, in large part, due to the extent of the nitrogen chemical shift range. The importance of the lone-pair electrons in providing flexibility to the range of nitrogen chemical shifts and, to a lesser extent, that of spin-spin couplings involving nitrogen has been stressed in our previous report.¹ Since then, much interest has been aroused by the use of nitrogen nuclear shielding variations to investigate solute-solvent interactions.⁶ The nitrogen lone-pair electrons appear to be responsible for providing the shielding sensitivity to subtle molecular interactions. A similar shielding sensitivity does not appear to be experienced by a number of commonly studied NMR nuclei such as ^1H and ^{13}C .

Owing to advances in NMR instrumentation and the ubiquitous nature of nitrogen in molecular science, it seems almost certain, *ceteris paribus*, that nitrogen NMR spectroscopy will be an expanding technique for many years to come.

II. THEORY OF NITROGEN NMR PARAMETERS

The more fundamental aspects of the theory of NMR parameters have been covered in our earlier reports¹⁻⁴ and presented in some detail in a recent monograph.⁷ Consequently only a superficial account of the theoretical background to nuclear shielding and spin-spin coupling interactions appears here.

A. Calculations of nitrogen shieldings

As discussed elsewhere^{7,8} the quantum-mechanical description of nuclear shielding, in an applied magnetic field, was originally provided by Ramsey⁹ in 1950. This was almost coincidental with the observation of the first nitrogen chemical shift.⁵ There are a number of restrictions on the use of Ramsey's procedure which tend to increase in severity with molecular size. Consequently the Pople¹⁰ approach, which circumvents many of the shortcomings encountered in Ramsey's method, is most commonly adopted for calculations on molecules of medium and larger sizes. An account of the relative merits and of difficulties often found in the application of Ramsey's and Pople's nuclear shielding models is presented elsewhere.⁷

In either case the total nuclear shielding is represented by the summation of diamagnetic terms, which are positive in sign, and negative paramagnetic contributions.

The nitrogen shielding of ammonia has continued to attract the attention of workers in the field of *ab initio* molecular orbital (MO) calculations.¹¹⁻¹⁴ Conventional coupled Hartree-Fock calculations, incorporating large Gaussian basis sets,¹¹ yield an averaged value for the paramagnetic contribution to the nitrogen shielding of ammonia of -82.9 ppm. This is in reasonable agreement with the experimentally determined result of -89.7 ppm.¹⁵

Similar calculations, using an individual gauge for localized orbitals, provide satisfactory shielding data even when relatively small basis sets are used.¹² In the case of ammonia the calculated average value of the total nitrogen shielding is 265.4 ppm, which compares favourably with the measured result of 264.5 ppm.¹⁶ The comparable value produced by calculations utilizing a large Gaussian basis set is 266.1 ppm.¹¹

The method of individual gauge for localized orbitals has also been applied to the nitrogen shielding of N_2 , HCN, N_2O and FNO.⁹⁷ For these multiply bonded molecules, large basis sets, of about triple zeta quality together with polarization functions, are found to be necessary. The results obtained are presumed to be close to the Hartree-Fock limit. Even with the large basis sets employed, the calculated shieldings and anisotropies are only in fair agreement with the available experimental data. In general it appears that the paramagnetic shielding contributions are overestimated

by the calculations. This could be due to the absence of a consideration of electron-correlation effects. However, accurate experimental data also appear to be lacking. Some gas-phase nitrogen shielding measurements extrapolated to 0 K, are required in order to more thoroughly examine the calculated results.⁹⁷

The importance of including configuration interaction (CI) in sum-over-states (SOS) shielding calculations is stressed by a comparison of various *ab initio* nitrogen shielding results for ammonia obtained with the 4-31G basis set.^{13,14} In the absence of CI the nitrogen shielding is calculated to be 277.8 ppm, whereas the inclusion of CI yields a value of 244.1 ppm, which compares favourably with the 244.2 ppm obtained from finite perturbation (FP) calculations¹⁷ while not being too close to the experimental result. Some comparable SOS-CI calculations of nitrogen shielding using a 6-31G basis set have been reported for ammonia, the ammonium ion, molecular nitrogen, the cyanide ion, hydrogen cyanide and hydrogen isocyanide.¹⁰⁰ The overall shielding trends are reasonably reproduced, but some significant deviations from the experimental results are noted.

A minimal-basis-set *ab initio* calculation on ammonia yields 310.9 ppm for the nitrogen shielding.¹⁸ Calculations employing the same basis set have been performed for formamide and the nitrogen shielding so obtained compared with the data produced by a larger set containing a split basis for the valence shell and by the 4-31G basis set.¹⁹ It is found that the calculated nitrogen shielding result depends sensitively both upon the basis set and the molecular geometry chosen. The split basis set is found to be a reasonable compromise between accuracy and computational feasibility for molecules of this size. In addition the split basis set is necessary to reproduce the nitrogen shielding decrease found in passing from formamide to *N*-methylformamide.¹⁹ More recently the shieldings of the various nuclei in cytosine have been estimated by means of this basis set.²⁰ In general, the results obtained are fairly encouraging in that they reproduce qualitatively the observed shielding trends as a function of the molecular position of the nitrogen atom, its possible intermolecular interactions and variations in molecular conformation.

It is anticipated that more quantitatively satisfactory results will be produced for molecules of this size when sufficient computing power is available to permit the use of larger basis sets, such as the 4-31G set.

Semi-empirical MO calculations are most commonly encountered in theoretical analyses of the various electronic factors contributing to nitrogen nuclear shielding. Such investigations are usually based upon Pople's shielding model,¹⁰ whereby chemical-shift trends for nitrogen nuclei in different environments arise almost entirely from variations in the local paramagnetic shielding contribution,^{7,8} the corresponding local diamagnetic term being effectively constant.¹

Since a description of excited electronic states enters the expression for the local paramagnetic term^{1,7} it is of some importance that semi-empirical nuclear shielding calculations incorporate a parameter set that adequately describes these states. The most satisfactory appear to be the CNDO/S and INDO/S sets.

An indication of the utility of CNDO/S parametrized nitrogen shielding calculations is afforded by a study of $(\text{CH}_3)_2\text{CNSO}$.²¹ The calculated results show an increase in nitrogen shielding of about 25 ppm on passing from the planar *cis* to the distorted *cis* form. This contrasts with a predicted decrease of about 70 ppm in passing to the *trans* structure. Comparison with the experimental nitrogen chemical shifts indicates that the most probable structure for $(\text{CH}_3)_2\text{CNSO}$, both in diethyl ether and as a neat liquid, is the distorted *cis* form with both the methyl carbons rotated out of the CNSO plane.

Semi-empirical shielding calculations usually only involve the estimation of one-centre integrals. The inclusion of some two-centre integrals in CNDO/S parametrized nitrogen SOS shielding calculations can lead to a more satisfactory agreement with experimental data, as shown in Table 1.²² Some FP nitrogen shielding calculations, using INDO parameters, suggest that non-local terms make only small contributions to shielding variations.¹⁰⁸

Whereas the CNDO/S scheme ignores one-centre exchange integrals, these are included in INDO/S calculations. As noted previously,¹ INDO/S parametrized calculations of nitrogen nuclear shielding are usually satisfactory. During the period under review such calculations have been particularly successful in predicting the relative chemical shifts of different nitrogen nuclei in a given molecule.²³⁻²⁷

Since Pople's SOS model relies upon a satisfactory description of excited electronic states, the shielding results obtained reflect this dependence. When comparing semiempirically predicted chemical-shift differences, for a series of molecules, with experiment, often the agreement is not too satisfactory. This lack of close alignment between the two sets of results is often due to the variability of the accuracy of the semiempirical description of the excited electronic states. Such variability is effectively removed when comparing the shielding differences of a number of nuclei of the same type in a given molecule. This point has been demonstrated by INDO/S parameterized calculations of nitrogen shielding in various N-heterocyclic systems.²³⁻²⁷

As shown in Fig. 1, INDO/S-SOS calculations provide a very satisfactory account of relative nitrogen shielding trends in some azopyridines. Such calculations may be confidently used to assign ¹⁵N signals in those cases where experimental support, such as ¹⁴N linewidths or ²J(¹⁵N-¹H) splittings, is lacking.

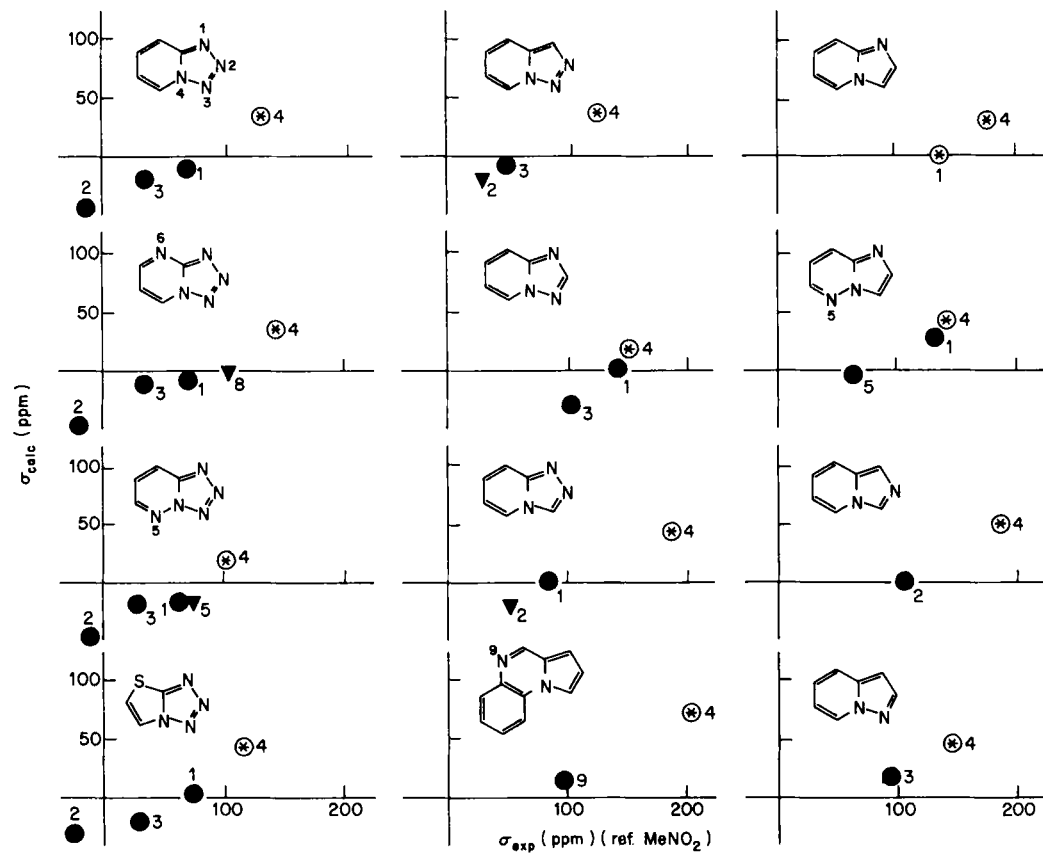


FIG. 1

The questions of considering the possible effects of solute-solvent interactions on nuclear shielding may be resolved *via* specific effects such as hydrogen bonding and non-specific effects. The latter appear to be satisfactorily accounted for by the solvaton model.²⁸

Minimum-basis-set *ab initio* calculations have been used to investigate the effects of hydrogen bonding on the nitrogen shielding of imidazole¹⁸ and formamide.¹⁹ The experimental trends are qualitatively reproduced. In the case of imidazole, and some other N-heterocycles, however, as shown in Table 2, INDO/S-SOS calculations provide a more accurate prediction of nitrogen shielding changes upon hydrogen-bond formation.²⁹ The rather poorer agreement between the *ab initio* and experimental data for hydrogen-bonded imadazole most probably arises from the necessity of having to use a minimum basis set in the calculation. For the present it seems that semiempirical MO calculations of nitrogen shielding in monocyclic N-heterocycles and larger systems, must suffice.

The majority of users of Pople's shielding model rely upon the average excitation energy (AEE) approximation. By this means the local paramagnetic shielding term, $\sigma_A^p(\text{loc})$, for nucleus A becomes

$$\sigma_A^p(\text{loc}) = -\frac{\mu_0 \hbar^2 e^2}{8\pi m^2} \frac{1}{\Delta E} \langle r^{-3} \rangle_{2p} \sum_B Q_{AB} \quad (1)$$

where the summation over nucleus B includes A.

$$\begin{aligned} Q_{AB} = & \frac{4}{3} \delta_{AB} (Px_A x_B + Py_A y_B + Pz_A z_B) \\ & - \frac{2}{3} (Px_A x_B Py_A y_B + Px_A x_B Pz_A z_B + Py_A y_B Pz_A z_B) \\ & + \frac{2}{3} (Px_A y_B Px_B y_A + Px_A z_B Px_B z_A + Py_A z_B Py_B z_A) \end{aligned} \quad (2)$$

where δ_{AB} is the Kronecker delta, the P s are the elements of the charge density-bond order matrix, ΔE is the AEE and $\langle r^{-3} \rangle_{2p}$ is the mean inverse cube of the radius of the 2p orbitals on the atom containing nucleus A.

From equations (1) and (2) it follows that if ΔE and $\langle r^{-3} \rangle_{2p}$ either remain constant for a given series of molecules or vary in a compensatory fashion then a change in nitrogen chemical shift may depend linearly upon variations in bond orders and charge densities. Under such circumstances, a relationship between nitrogen chemical shift and activation energy for rotation about a bond involving the nitrogen atom might be anticipated.

From a consideration of the nitrogen chemical shifts of a series of ureas and thioureas it appears that a linear relationship exists between the shifts and N-C bond orders for the sterically uncrowded molecules whereas in the presence of steric crowding such a relationship is no longer applicable.³⁰

Some simple amides are reported to behave in a similar fashion.³¹ It is thus probable in these cases that variations in nitrogen chemical shift will provide a reasonable correlation with N-C bond rotational energy. However, it is important to bear in mind that a change in solvent can influence both

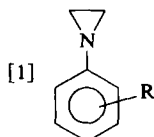
the rotational energy and the nitrogen shielding, as demonstrated for some *N,N*-dimethylformamides³² and unsymmetrically *N*-substituted amides.³³ Thus care is required in the interpretation of nitrogen chemical shifts in terms of restricted *N*-C bond rotation as mentioned for some vinylogous amides,³⁴ some *N,N*-di-*t*-butylamines³⁵ and for *N*-P bond rotation in some trivalent phosphorus derivatives.³⁶ A review on isomerization processes around *N*-X bonds, as studied by NMR, has recently appeared.¹⁰⁶

Shielding calculations employing the AEE approximation have been successfully used to demonstrate the π -electron conjugation effects, between the vinyl group and pyrrole ring, on the nitrogen chemical shifts of some *N*-vinylpyrroles.³⁷ The compounds considered represent extreme cases of *N*-C bond restricted rotation effects on nitrogen shielding.

Ring-current calculations have been performed on some porphyrins and metallo-porphyrins. It is reported that the effects of ring currents are small from the point of view of nitrogen shieldings. It seems that the influence is likely to be of the order of 6 ppm per unit net charge on the nitrogen atoms concerned.¹⁰⁷

From equations (1) and (2) it is possible to construct arguments that lead to the claim that nitrogen shielding variations may be construed in the light of a dominant change in charge density and/or electronic excitation energy. Discussions implying that nitrogen chemical shifts may be interpreted in terms of charge density variations have been presented for 2,4,6-trimethylpyridine and its anions,³⁸ some amines and amides³⁹ and some nitrobenzenes.⁴⁰ In another study the nitrogen residual π charges, after making allowance for ring currents, of porphyrin and some of its derivatives provide an account of relative nitrogen shieldings.⁴¹

The presence of the ΔE factor in equation (1) arises from the use of second-order perturbation theory in the development of the expression for the local paramagnetic shielding term.^{7,10} If it were possible to calculate this shielding term exactly then the approximations implicit in perturbation theory would be absent. Consequently ΔE enters equation (1) as an artefact of quantum mechanics rather than as a parameter bearing any direct relationship to experimentally observable electronic transitions. Hence attempts to interpret nitrogen shielding variations, such as those reported for some aryl azides,⁴² some azabenzenes,⁴³ and some fluoronitrogen cations⁹⁹ in terms of a change in observable electronic transitions are best treated with some scepticism. Similarly, a lack of correlation between the lone-pair ionization potentials of some substituted *N*-phenylaziridines [1] and their nitrogen chemical shifts is not altogether surprising.⁴⁴



Discussions based on the use of the AEE approximation have been widely used in the interpretation of the effects of protonation and hydrogen bonding on nitrogen chemical shifts. In the period under review such reports have related to the nitrogen chemical shifts of some polycyclic polyamines,⁴⁵ a series of simple amides,⁴⁶ some nucleic acid bases⁴⁷ and a series of compounds containing the >C=N- group.⁴⁸ Such interpretations are covered in greater detail, together with those relating to other solvent influences on nitrogen shielding in Section V.A.

Other applications of AEE shielding calculations include an account of the ^{15}N shieldings of some octasubstituted cyclotetraphosphazines,⁴⁹ and an attempt to explain the increase in nitrogen shielding of ammonia upon complexation to platinum and its sensitivity to a variation in *trans* ligands.⁵⁰

The sensitivity of nitrogen shielding to changes in environment may be useful as a probe of intermolecular forces and intramolecular force fields. Thus, in principle, a study of nitrogen shieldings can provide information on the intramolecular potential of a given molecule as well as the intermolecular potential between two molecules and on the structure of fluids and solutions. Such investigations require an understanding of temperature isotope and solvent effects on nitrogen shielding.⁵¹

The present state of the theory describing such phenomena makes it more readily applicable to the gaseous rather than the condensed phases.⁵¹ Thus considerable interest is attached to the study of the nitrogen shielding of fairly simple molecules in the gas phase. For example the ^{15}N shielding of gaseous nitrogen⁵² and ammonia⁵³ has been reported as a function of temperature and density, while that of hydrogen cyanide has been studied as a function of temperature.⁵⁴ Usually the temperature coefficient for the nuclear shielding in an isolated molecule is negative, an exception being that of ^{15}N in NH_3 .⁵³ Some CNDO/S-SOS shielding calculations⁹⁵ demonstrate that, with respect to the equilibrium geometry, an extension of the N-H bonds yields a shielding decrease, whereas a decrease in the HNH bond angle produces a shielding increase. Taken together, these two variations are able to account for the observed small, positive, temperature coefficient for the ^{15}N shielding in isolated NH_3 .

Normally, intermolecular interactions lead to nuclear deshielding. Such is found to be the case following an analysis of the temperature-dependent nitrogen shielding data for nitrous oxide,⁵⁵ gaseous nitrogen⁵² and ammonia.⁵³ However, the opposite appears to be true for gaseous hydrogen cyanide,⁵⁴ which is supported by some *ab initio* calculations of nitrogen shielding in monomeric and dimeric hydrogen cyanide.¹⁰⁴

This observation leads to the concept of two classes of nitrogen nuclear environments capable of hydrogen bonding. In one class the lone-pair electrons are directly involved in the hydrogen bondings, and a π -electron system is available for low-energy $n \rightarrow \pi^*$ transitions to be considered as

possible contributions to the paramagnetic shielding term. The effective removal of the lone pair from the nitrogen atom eliminates the $n \rightarrow \pi^*$ contribution such that the paramagnetic term is reduced in magnitude and an increase in the total nuclear shielding occurs. Examples of this category are cyanides, imines, azines and pyridine-type nitrogen nuclei in azoles.

The second class of nitrogen environments comprises those where the nitrogen lone-pair electrons may not be directly involved in hydrogen bonding and/or there is no suitable π system available for $n \rightarrow \pi^*$ contributions to be worthy of consideration. In such cases hydrogen-bond formation could lead to an increase in the $\langle r^{-3} \rangle_{2p}$ term in equation (1) and thus to an overall shielding decrease. Behaviour of this kind is expected for alkylamines in general, amides, isonitriles and pyrrole-type nitrogen nuclei in azoles.

Gas-phase nitrogen NMR studies on nitrous oxide, ammonia, nitrogen and hydrogen cyanide have lead to the production of a nitrogen shielding scale based upon $^{15}\text{NH}_3$.⁵⁶ In relating the data for the isolated molecule at 300 K to liquid-phase shielding results taken at some other temperature, intermolecular effects produce the requirement of significant corrections of either sign. For example the ^{15}N shielding correction required for ammonia is about -20 ppm while that for hydrogen cyanide is around $+12$ ppm. From this, and other observations, it is clear that considerable care is required in the interpretation of rather small liquid-phase nitrogen shielding variations.

B. Calculations of nitrogen spin-spin couplings

Electron-coupled nuclear spin-spin interactions are normally discussed in the framework developed by Ramsey.⁵⁷ The appearance of his seminal paper on spin-spin couplings three years after that on the theory of nuclear shielding⁹ reflects the later discovery of spin-spin splittings of chemically shifted signals in NMR spectroscopy.

The total spin-spin coupling interaction between a pair of nuclei is expressed, at the non-relativistic level, as a sum of contact, orbital and dipolar terms.^{7,57,58} The mathematical expressions for these coupling contributions are not repeated here but can be found elsewhere.^{7,57-59} The coupling interactions may be determined by the use of sum-over-states (SOS) perturbation,⁶⁰ finite perturbation (FP)⁶¹ or self-consistent perturbation (SCP)⁶² techniques. The computational aspects of evaluating the expressions arising from these perturbation procedures have recently been reviewed.⁵⁹

In addition to the choice of perturbation technique, a further distinguishing feature of the theoretical procedure adopted is the level of approximation employed in the calculation of the requisite eigenvalues and eigenvectors. Large-basis-set *ab initio* calculations have become more readily applicable to spin-spin coupling interactions in recent years.⁵⁹ However, their

application is of necessity mainly restricted to small molecules. Semiempirical MO calculations are still the workhouse for molecules of a chemically reasonable size. For calculations of spin-spin couplings the INDO set of parameters seems to be the most satisfactory at the semiempirical level.

The contact contribution to spin-spin couplings, in semi-empirical MO calculations, depends upon the product of the s-electron densities at the coupled nuclei, but is independent of p-, d- etc. electron distributions. The opposite is the case for the orbital and dipolar spin-spin coupling interactions.

Thus couplings involving protons are predicted to be solely dependent upon the contact interaction. Some *ab initio* calculations for ammonia have demonstrated that this is not always the correct interpretation and that the non-contact terms also contribute to $^1J(^{15}\text{N}-^1\text{H})$.⁶³

Other *ab initio* calculations of couplings involving nitrogen have been considered on the basis of the contact term alone. Coupled Hartree-Fock and FP calculations, including CI, of the contact interaction have been reported for ammonia⁶⁴ and for $^1J(^{15}\text{N}-^1\text{H})$; $^2J(^{15}\text{N}-^1\text{H})$ and $^1J(^{15}\text{N}-^{13}\text{C})$ of aminomethane.⁵⁴ Other *ab initio* MO calculations of contact interactions have appeared for $^1J(^{15}\text{N}-^{13}\text{C})$ of the cyanide ion⁶⁶ and hydrogen cyanide,⁹⁶ and $^1J(^{15}\text{N}-^{15}\text{N})$ of hydrazine.⁵⁷

In general the results are in reasonable agreement with experiment. The calculated values of -15.37 Hz and -23.93 Hz for $^1J(^{15}\text{N}-^{13}\text{C})$ in the isolated cyanide ion have the correct sign but appear to be too large in magnitude for this very pH-dependent coupling.⁶⁸

The spin-unrestricted multiconfiguration SCF calculation for hydrogen cyanide⁹⁶ overcomes the problem of unrestricted Hartree-Fock instabilities. The contact contribution to $^1J(^{15}\text{N}-^{13}\text{C})$ is calculated to be -14.1 Hz together with -5.2 Hz from the orbital interaction, the total calculated value of the coupling is -19.3 Hz, which is in satisfactory agreement with the experimental value of -18.6 Hz with any contribution from the dipolar term being ignored. However, it must be stressed that the coupling results obtained are very basis-set- and correlation-dependent. The results quoted above are for a large-basis-set calculation and include a 13.4 Hz contribution to the contact interaction from correlation effects.

Similar calculations of $^2J(^{15}\text{N}-^1\text{H})$ for hydrogen cyanide⁹⁶ produce a value of -4.8 Hz for the contact contribution and -4.6 Hz due to the orbital term, thus strongly suggesting that the, as yet unmeasured, sign of this coupling is negative.

Some SOS calculations, including CI, have been reported for the cyanide ion, hydrogen cyanide and hydrogen isocyanide.¹⁰⁰ A 6-31G basis set is used in the calculations. Satisfactory agreement with experiment is obtained for the various N-C and N-H couplings. The dominance of the non-contact contributions to $^1J(\text{N}-\text{C})$ of the cyanides supports earlier semi-empirical

calculations,⁷⁵ whereas the corresponding coupling in hydrogen isocyanide appears to be controlled by a large and negative contact interaction.¹⁰⁰

The recent *ab initio* calculations⁶⁷ confirm earlier INDO predictions of the sign of $^1J(^{15}\text{N}-^{15}\text{N})$ for hydrazine and its analogues^{60,70} and the dependence of the coupling magnitude on molecular conformation.

In principle, *ab initio* calculations are able to provide a more intimate account of the electron-coupled processes determining spin-spin interactions than semi-empirical theories. *Ab initio* results reveal that the orbital contribution to $^1J(^{15}\text{N}-^{13}\text{C})$ in hydrogen cyanide, methyl cyanide and methyl isocyanide can be of either sign and variable in magnitude.⁷¹ Further *ab initio* calculations, including all three coupling mechanisms, are eagerly awaited for spin-spin interactions involving nitrogen.

The molecular interpretation of N-C couplings continues to attract considerable interest. The sign of $^1J(^{15}\text{N}-^{13}\text{C})$ for both hydrogen cyanide and the cyanide ion has been unambiguously shown to be negative.^{68,72,73}

The results of some early INDO parametrized FP calculations are in agreement with the observed sign of $^1J(^{15}\text{N}-^{13}\text{C})$ for hydrogen cyanide but not for that of the cyanide ion.⁷⁴ The choice of an isolated species as the model for calculations on the cyanide ion leaves something to be desired—especially when the strong pH dependence of $^1J(^{15}\text{N}-^{13}\text{C})$ for this ion is considered.⁶⁸ However, some more recent SCP calculations incorporating INDO parameters correctly predict a negative $^1J(^{15}\text{N}-^{13}\text{C})$ for various cyanides and isocyanides.⁷⁵ In these calculations⁷⁵ the orbital and dipolar contributions dominate that from the contact term in the case of the cyanides. The major coupling contribution is predicted to arise from the dipolar term which has yet to yield to satisfactory *ab initio* calculations on the cyanide ion.¹⁰⁰

Calculations of $^1J(^{15}\text{N}-^{13}\text{C})$, and its anisotropy, have appeared for acetonitrile. It appears that relativistically parametrized semi-empirical calculations show no significant improvement over the results obtained from INDO calculations.¹⁰³

It has been demonstrated that single-bond N-C couplings are usually dominated by the contact interaction,^{76,102} whereas the non-contact mechanisms normally control the couplings across multiple N-C bonds.⁷⁵ This is consistent with the view that only s-electron density contributes to the contact interaction, whereas p-, d- etc. electrons produce the non-contact coupling contributions.

Some *ab initio* SCPT calculations, using a restricted basis set, of the effects of hydration on the contact contributions to N-C couplings of imidazole¹⁸ and *N*-methylformamide¹⁹ have appeared. The calculated values of $^1J(^{15}\text{N}-^{13}\text{C})$ are systematically larger than the measured data and not always of the correct sign.¹⁸ Perhaps the use of a more extensive basis set and/or the inclusion of the non-contact contributions would provide a

more reliable comparison with the measured couplings. A coupling variation of only a few hertz is predicted owing to hydration, which is in reasonable agreement with the experimental results.

The solvaton model²⁸ has been used, together with INDO parametrized SOS and FP coupling calculations, to study solvent effects on $^1J(^{15}\text{N}-^{13}\text{C})$ for some cyanides and isocyanides.⁷⁷ The magnitude of $^1J(^{15}\text{N}-^{13}\text{C})$ is predicted to increase by up to 2 Hz as the dielectric constant ϵ of the medium increases from 1 to 80. Although changes occur in all three coupling mechanisms, as ϵ varies, the total coupling variation is controlled by changes in the contact term.

A greater sensitivity to changes in ϵ is noted for the couplings of the isocyanides than for those of the cyanides. This is in agreement with the generally accepted view that the N-C bonding in isocyanides is more polar than that in cyanides. Consequently a more polar medium is expected to decrease the N-C bond order in isocyanides to a greater extent than in cyanides. Such a bond order decrease implies a higher p-electron density on each of the coupled atoms which serves to increase the nuclear shielding, resulting in a lower s-electron density and a diminution of the positive contact term. Overall the effect is of an increase in the negative value of $^1J(^{15}\text{N}-^{13}\text{C})$ as ϵ increases.

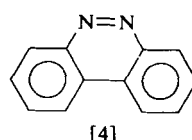
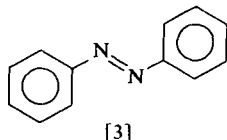
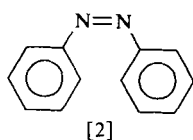
Similar calculations have been reported for some single-bond $^1J(^{15}\text{N}-^{13}\text{C})$ values.⁷⁸ Compared with the triple-bond couplings, the less-polarizable nature of N-C single bonds results in $^1J(^{15}\text{N}-^{13}\text{C})$ being less sensitive to a change of solvent, the predicted changes being not more than 0.6 Hz as ϵ varies from 1 to 80. Again, changes in the contact interaction are mainly responsible for the variation in $^1J(^{15}\text{N}-^{13}\text{C})$, as a function of ϵ , even when the non-contact terms dominate the total coupling interaction.

The effect of a lone pair of electrons, with s-character, on the contact contribution to spin-spin coupling has been further investigated.¹⁻⁹⁸ It is well known^{58,79} that the presence of such a lone pair, on one of the atoms containing the coupled nuclei, results in a contact contribution to the coupling which is opposite in sign to that produced by s-bonding electrons. In the case of $^1J(^{15}\text{N}-^{13}\text{C})$ the s-bonding electrons make a negative contribution to the contact term;⁷⁶ thus the s-lone-pair contribution is a positive one. For pyridine-type nitrogen atoms the two effects are largely cancelling so that the resulting contact term is small and the orbital interaction often dominates $^1J(^{15}\text{N}-^{13}\text{C})$.^{76,79} In the case of pyrrole-type nitrogen atoms the transfer of the lone pair to a p-type orbital results in a dominating, negative contact interaction.⁷⁶

Similar effects are found as a result of SCP-INDO calculations of some N-C couplings of the neutral and dicationic species of 4-aminoazobenzene.⁸⁰ Such calculations have assisted in determining that in weak acid solution 4-aminoazobenzene exists in two monocationic forms, in one of

which a proton is attached to the β -azonitrogen and in the other the amino nitrogen is protonated. In contrast with this, a dicationic form is produced in strong acid solutions. This is protonated at the amino and the α -azo nitrogen nuclei, but not at the β -azo nitrogen.

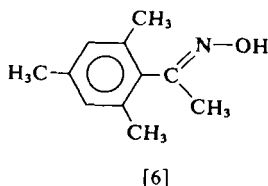
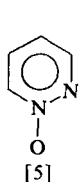
The s-lone-pair effect on N-C couplings has also been demonstrated as a result of SCP-INDO calculations on *cis* [2] and *trans*-azobenzenes [3], and benzo[*c*]cinnoline [4]:⁸¹



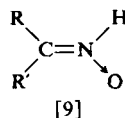
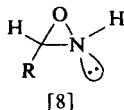
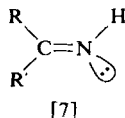
A similar outcome has been obtained as a result of calculations on pyridine, the pyridinium ion^{82,83} and pyridine *N*-oxide.⁸³

Calculated values of $^1J(^{15}\text{N}-^{13}\text{C})$ have been shown to be rather sensitive to the choice of semi-empirical input parameters by means of some SCP-INDO calculations.⁸⁴ Such work points to the caution required when comparing the results of calculated spin-spin couplings obtained by different techniques.

Other calculations of N-C couplings include those on pyridazine-*N*-oxide [5],⁸⁵ *E*-1-(2,4,6-trimethylphenyl)ethanone oxime [6],⁸⁶ some *N,N*-dimethylanilines and nitrobenzenes,⁸⁷ imidazole, several methylated imi-

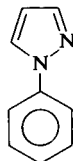


dazoles and some protonated species,⁸⁸ some conjugated N-heterocycles containing between one and four condensed six-membered rings,⁸⁹ and those on some ketimines [7], oxazaridines [8], and nitrones [9].⁹⁰



Since the magnetogyric ratio of ^{15}N is negative, while that of ^{13}C is positive, it follows that the s-lone-pair contribution to the contact interaction of $^1J(^{15}\text{N}-^{15}\text{N})$ is opposite to that of $^1J(^{15}\text{N}-^{13}\text{C})$. Hence the presence of s-lone pairs on coupled nitrogen nuclei is expected to lead to large negative

values of $^1J(^{15}\text{N}-^{15}\text{N})$.^{67,70} An example of this influence is provided by [10], for which FP-INDO calculations predict $^1J(^{15}\text{N}-^{15}\text{N})$ to be -12.78 Hz, which compares favourably with -12.91 Hz measured in a $^{15}\text{N}\{-^1\text{H}\}$ SPT experiment.⁹¹ From a restricted-basis-set *ab initio* calculation of the contact interaction, $^2J(^{15}\text{N}-^{15}\text{N})$ in imidazole is predicted to be negative in sign.¹⁸



[10]

In the case of $^1J(^{31}\text{P}-^{15}\text{N})$ the sign of the s-lone-pair contribution to the contact interaction will be the same as it is for $^1J(^{15}\text{N}-^{13}\text{C})$, since the magnetogyric ratio of ^{31}P is positive. Consequently the presence of lone pairs with s-character is expected to produce a positive contact contribution to $^1J(^{31}\text{P}-^{15}\text{N})$. As shown in Table 3, this spin-spin coupling interaction is controlled by the contact term for the cases studied.⁹² The removal of the phosphorus lone-pair electrons in passing from tri- to pentavalent phosphorus is reflected in a change from positive to negative in the sign of the contact contribution.

Within the series of pentavalent phosphorus compounds considered in Table 3, the s-character of the nitrogen lone-pair electrons plays an important role. As the nitrogen bonding environment becomes less pyramidal, and thus more planar, the lone-pair electrons assume a greater p-character. This change serves to diminish the positive s-lone-pair contribution to $^1J(^{31}\text{P}-^{15}\text{N})$; thus the coupling becomes more negative.⁹²

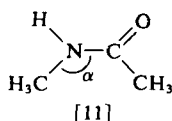
Some CNDO/2 parametrized SOS calculations, within the AEE approximation, of $^1J(^{31}\text{P}-^{15}\text{N})$ for some octasubstituted cyclotetraphosphines show the dominance of the contact contribution to the couplings considered.⁴⁹ Comparable calculations of $^1J(^{31}\text{P}-^{15}\text{N})$ for some cyclotriphosphazenes reveal the importance of non-contact contributions.¹⁰⁵

A number of calculations of N-H couplings have appeared during the period under review. These include some restricted-basis-set *ab initio* SCP calculations on imidazole¹⁸ and *N*-methylformamide.¹⁹ The $^1J(^{15}\text{N}-^1\text{H})$ and $^3J(^{15}\text{N}-^1\text{H})$ results are in reasonable agreement with experiment. In contrast, the $^2J(^{15}\text{N}-^1\text{H})$ calculated data^{18,19,96} are found to be very basis-set-dependent. The couplings considered are predicted to be relatively insensitive to hydration effects. Some SOS-CI calculations of N-H couplings, using 6-31G basis sets, provide reasonable agreement with experiment.^{100,101}

The solvaton model, together with FP-INDO calculations, has been used to study possible solvation effects on $^1J(^{15}\text{N}-^1\text{H})$ of aniline and 4-nitroaniline.⁹³ As the dielectric constant of the medium increases, the value of

$^1J(^{15}\text{N}-^1\text{H})$ is predicted to become more negative. This is consistent with a change from sp^3 to sp^2 character for the nitrogen atom of the amino group and is in reasonable accord with experiment. For $^1J(^{15}\text{N}-^1\text{H})$ the s-lone-pair contribution to the contact term is a positive one; so passing from sp^3 to sp^2 hybridization at the nitrogen atom increases the p-character of the lone pair and thus gives a more negative $^1J(^{15}\text{N}-^1\text{H})$ interaction.

Some SCP-INDO calculations of $^1J(^{15}\text{N}-^1\text{H})$ of *cis*-N-methylacetamide [11] as a function of the angle α ,⁹⁴ shows that the coupling becomes less negative as α increases. Thus a small value of α is invoked to account for a large negative $^1J(^{15}\text{N}-^1\text{H})$.



Since the calculations have not permitted the $\text{CH}_3\hat{\text{C}}\text{N}$ or $\text{N}\hat{\text{C}}\text{O}$ angles to vary, they are not too relevant to a consideration of a change in hybridization at the nitrogen atom. Thus the s-lone-pair effect may not be invoked on the basis of these calculations, to account for the predicted changes in $^1J(^{15}\text{N}-^1\text{H})$.

Other semiempirical MO calculations on $^{15}\text{N}-^1\text{H}$ couplings include those on some conjugated N-heterocycles,⁸⁹ pyridazine-*N*-oxide,⁸⁵ pyridine and the pyridinium ion⁸² and some ^2J and ^3J couplings in a variety of ketimines, oxaziridines and nitrones.⁹⁰

In general the calculations of $^2J(^{15}\text{N}-^1\text{H})$ are the least satisfactory of the N-H couplings considered. This is in line with the poor performance of semiempirical calculations in reproducing other ^2J data. Most probably this is due to the absence of a calculated correlation contribution to the contact interaction as well as the neglect of the non-contact terms for couplings involving protons. In large-basis-set *ab initio* calculations all of these contributions can be significant for geminal proton couplings.⁵⁹

III. CALIBRATION OF SPECTRA

This problem has already been covered in detail,^{1,4} and only some important points are raised here. First of all, there is the question of the sign convention used in reporting the positions of nitrogen resonance signals relative to the reference signal employed. With rapid advances in the theory, techniques and amount of experimental data available in the field of NMR (including nitrogen NMR, which covers ^{15}N and ^{14}N nuclei), it is highly advisable to use terms and notations that have rigorous physical significance; such a term is the nuclear screening (shielding), either absolute (referred to a bare

nucleus) or relative (referred to any shielding selected as a reference). The use of the shieldings for characterizing resonance signals in molecules and ions under various experimental conditions imposes more responsibility on the investigator, who is then compelled to consider all random and systematic errors inherent in the experimental technique employed from the point of view of relationships between observed resonance frequencies and the shieldings. This is especially important in the growing field of applications of nitrogen NMR to the observation of molecular interactions. Thus we are quite firm about using relative shielding constants, or simply "shieldings" for the characterization of nitrogen resonance positions. A simple consequence of this is the use of the positive sign for the direction of increasing shielding, which corresponds to an increase in external magnetic field at a constant resonance frequency, or to a decrease in resonance frequency at a constant external field. We deliberately refrain from the use of the term "chemical shift", which is employed mostly, but not exclusively, with the sign convention that assigns the positive sign to the deshielding direction. The term "shielding", referred to nitrogen or any other nucleus, is simple enough, leaves no doubt about the signs, is consistent with the physical theory of NMR, and at least draws one's attention to systematic errors in the determination thereof. It can be recommended for general usage in NMR, with the possible exceptions of ^1H and ^{13}C chemical shifts measured against internal SiMe_4 as reference, which is as bad as almost any other internal standard from the point of view of molecular interaction effects on its resonance. In the latter case, no sign convention or terminology would be of much help in bringing the chemical shifts to a common, rigorous scale of nuclear screenings.

So far, all attempts at estimating absolute shieldings for nitrogen nuclei in various molecular environments have relied on theoretical calculations (Section V.A), and in practical NMR spectroscopy one has to resort to some arbitrary standard. Then, one should consider the merits and demerits of employing internal standards (reference substances dissolved in the sample involved) and external standards (those placed in a separate container, e.g. a small tube or capillary inside a sample tube). The vast amount of nitrogen shielding data that have been accumulated within the past ten years (see the tables in the present volume, and those elsewhere^{1,4,109,110}) indicate clearly that internal standards are generally unreliable in nitrogen NMR when their nitrogen resonance signals are used as actual references for calibration of nitrogen shieldings. The latter are quite sensitive to molecular interactions, and for any given substance in a variety of popular solvents they can span a range of more than 10 ppm, even if only aprotic solvents are considered (Section V.H), and this includes obviously the shieldings of the internal standards themselves. The position of the nitrogen resonance of an internal standard can also be affected by solute-standard

interactions. Internal standards also exert other adverse effects, since they contaminate the sample under examination and disturb chemical equilibria, molecular interactions, etc. The use of internal standards has, however, a distinct advantage, since it eliminates bulk-susceptibility effects, which usually complicate the external referencing technique. This can be quite important when one has to deal with paramagnetic substances, whether as such, as contaminants in the sample involved or as relaxation reagents added to the sample in order to shorten the long relaxation times of ^{15}N nuclei. There are essentially two cases where this advantage can be exploited while the disadvantages are minimized. First, if a sufficiently dilute solution of a sample in a nitrogenous solvent is examined, the solvent signal can be used as a reference, and the corresponding reference shielding can be assumed to be equal to that of the neat standard; needless to say, the latter should be calibrated precisely against any commonly accepted primary reference in order to take full advantage of the method. Examples of this technique can be found in Table 16, notes (c) and (d). One should note, however, that the presence of a large solvent peak in a spectrum that is obtained by accumulation of pulse-excited spectra (the PFT technique, which is now used always in ^{15}N -NMR, and often in ^{14}N -NMR) can result in well-known difficulties concerned with the dynamic range of analog-to-digital converters and the computer word-length (see e.g. ref. 111, p. 196). This situation does not occur if ^{15}N -labelled molecules are examined in a non-enriched solvent. The second case where the internal referencing method can be used to its advantage includes situations where one deals with sufficiently low concentrations of both the sample and the internal reference employed so that the sample-reference interactions are minimized. In this case the reference shielding can be assumed to be that of a dilute solution of the standard, and calibrated against a primary reference substance.

It is obvious that the methods based on internal standards, as described above, have only very limited utility in the calibration of nitrogen shieldings. There is, however, a way to circumvent, at least partially, the difficulties concerned with internal referencing of nitrogen shieldings. The method relies on the use of proton shieldings of an internal reference, for example SiMe_4 (TMS). If a minute amount of TMS is added to a primary reference substance used in the calibration of nitrogen shieldings (e.g. neat liquid nitromethane) then the nitrogen shielding of the latter is hardly affected. One should then measure the resonance frequency of ^{15}N or (^{14}N) of the nitromethane sample and that of ^1H in TMS at exactly the same magnetic field. This can be accomplished if the two measurements are carried out with the same probe, using either a ^1H -TMS lock whose frequency is monitored or an external (e.g. deuterium) lock with an independent measurement of ^1H frequency. The same procedure is then repeated with the sample examined

together with some internal TMS standard. Assuming that any change in the ^1H TMS frequency between the two measurements comes exclusively from a change in the external magnetic field B_0 , one can simply correct the ^{15}N nitromethane frequency to which the ^{15}N sample frequency should be referred in the calculation of the nitrogen shielding:

$$\sigma_{\text{sample}}^{15\text{N}} = \frac{\nu_{\text{nitromethane, corrected}}^{15\text{N}} - \nu_{\text{sample}}^{15\text{N}}}{\nu_{\text{nitromethane, corrected}}^{15\text{N}}}$$

where

$$\nu_{\text{nitromethane, corrected}}^{15\text{N}} = \nu_{\text{nitromethane, neat}}^{15\text{N}} \frac{\nu_{\text{TMS in sample}}^{1\text{H}}}{\nu_{\text{TMS in nitromethane}}^{1\text{H}}}$$

and σ denotes the shielding referred to that in neat liquid nitromethane, while the ν s represent the corresponding resonance frequencies. This recalculation of the nitromethane frequency is based on the simple fact that the frequency ratio of nitromethane versus TMS does not depend on B_0 , at least at the same temperature and composition of the reference sample, which in this case is almost neat nitromethane containing a trace of TMS. The method was claimed recently (Table 70, note (e) and reference therein) to constitute a solution to the problem of internal referencing of nitrogen shieldings. An analogous procedure was employed for ^{15}N -labelled compounds (Table 24, note (a) and reference therein), which differed from that described above in using a double-resonance technique (^{15}N decoupling of ^1H spectra) for the measurement of nitrogen resonance frequencies.

The method is actually quite old (ref. 3, pp. 45 and 171), and has never gained popularity. It does not really require any nitrogenous reference, since any frequency within the nitrogen NMR spectral range can be used as a reference provided that it is assigned to correspond to a given ^1H frequency of TMS or any other proton standard. It puts stringent requirements on measuring nitrogen and proton frequencies at exactly the same conditions, possibly without changing sample tubes, probes, etc.; even then, some difficulties may arise from different spectral regimes in ^{15}N and ^1H measurements, which can, for example, change appreciably with the sample temperature and external field at the sample site. From this point of view, optimum conditions are maintained in double-resonance measurements for ^{15}N -labelled substances (^{15}N -decoupled proton spectra) or in time-consuming two-dimensional spectroscopy. However, the method has a serious flaw, which is common to all internal referencing procedures in general. The proton shielding in TMS (or any other proton standard) is also susceptible to medium effects which are transmitted to nitrogen shielding calibrations simply as errors. The well-known work of Bacon and Maciel¹¹² reports a range of 0.6 ppm for solvent effects on the proton

shielding in TMS, for example

Solvent	¹ H shielding in SiMe ₄ (in ppm, referred to neat SiMe ₄)
pyridine	+0.34
benzene	+0.30
toluene	+0.26
acetone	+0.03
cyclohexane	-0.04
CH ₂ Cl ₂	-0.08
CHCl ₃	-0.14
CCl ₄	-0.16
CS ₂	-0.23

Since the values are obtained for quite concentrated solutions of TMS, 20% v/v, the actual range is probably at least twice that reported, and other proton standards fare no better. Therefore the uncertainty inherent in the method discussed is larger than 1 ppm, which is appreciably less than that concerned with direct internal referencing in nitrogen NMR spectra, but is comparable to that involved in most external referencing procedures without correcting for bulk-susceptibility effects. It seems that it pays better to put some effort into refining the external referencing technique towards either reliable corrections for bulk-susceptibility effects or the use of concentric spherical sample/reference containers (these eliminate the latter effects) than to rely on any internal reference procedure.

Most of the nitrogen NMR work that has been done recently employs external references for the calibration of nitrogen shieldings. The external referencing technique has an obvious advantage over the internal reference procedures since no contamination of the sample with the standard is involved. Another important asset is concerned with the fact that precisely defined standards can be used, e.g. neat nitromethane or 0.5 M aqueous NaNO₃. The price to pay for this is the appearance of bulk-magnetic-susceptibility effects. The relevant equations that relate true (intrinsic) differences in the shieldings between two samples with apparent (observed) differences are given in Table 4. The equations, as well as the values of bulk susceptibility in Table 5 are consistent with the SI system of units, and they differ from those reported within the CGS system.^{1,4} The SI system has already been used,¹¹⁰ but the numerical values of susceptibilities quoted there are slightly different from those in Table 5, because of different origins. The data in Table 5 are based on Landolt-Börnstein, *Zahlenwerten und Funktionen*, 6th ed., Band II, Teil 10, Springer-Verlag, Berlin, 1967, with a few exceptions; they are recalculated from originally reported molar

susceptibilities into volume susceptibilities, using the corresponding densities at 30°C (ref. 1, Table 5 therein, and reference 80 therein).

It is evident from the master equation in Table 5 that the susceptibility effects vanish in the case of spherical samples. Thus a set of concentric spherical sample/reference containers should allow one to measure directly true differences in shieldings between the sample and the reference. This technique has already been employed on a large scale in the field of ^{14}N NMR (e.g. Table 6, and refs. 1,4), where sample spinning is not required because the relevant signal widths are usually greater than 10 Hz, and may reach a kilohertz. Non-spinning concentric spherical samples do not show any signal splitting of the annular (outer) sample, which is not the case for coaxial cylindrical samples.

In ^{15}N NMR the most practical solution in the external referencing procedure is the use of coaxial cylindrical sample/reference tubes. Sample spinning is necessary here, for two essential reasons. First, all efforts should be made in order to reduce field inhomogeneity broadening of ^{15}N signals, since the difference between the observed signal width, $(\pi T_2^*)^{-1}$, and $(\pi T_1)^{-1}$, where T_1 is the spin-lattice relaxation time, is one of the major factors that adversely affect the signal-to-noise ratio in accumulated, pulse-excited ^{15}N spectra. The second reason is the additional signal splitting and broadening for the sample contained in the outer compartment (the annulus). However, the latter effect can be exploited profitably for direct measurements of bulk-magnetic-susceptibility differences between the sample and the standard employed. Since bulk-susceptibility effects are the same for any nuclei involved, the corresponding proton spectrum may be used for the measurement. A routine procedure would involve measurement of an externally referenced ^{15}N spectrum in a system of coaxial tubes (spinning), followed by a measurement of the proton spectrum of the same, but non-spinning system, not necessarily in the same probe. Since the (proton) signal splitting for the substance in the annulus depends on the difference in the susceptibility between the substances in the two compartments, and on some geometrical factors, a calibration of the magnitude of the splitting in terms of susceptibility differences can be carried out simply by using liquids of known susceptibility (Table 5). If neat liquid nitromethane is employed as an external standard, there should be no confusion about the sign of the measured difference in the susceptibilities, since liquid nitromethane has almost the lowest negative susceptibility among those quoted in Table 5. The measured difference in susceptibilities should then be used in correcting the observed nitrogen shielding according to the master equation in Table 4. The corrections depend significantly on the orientation of the direction of the external field B_0 relative to the sample-tube axis. With minor exceptions, including spectrometers designed especially for solid-state NMR, the directions are parallel in superconduct-

ing magnet systems, and perpendicular in electromagnet systems. The corrections do not depend on whether the reference substance is in the inner or outer tube.

For systems where the field B_0 is *parallel* to the sample-tube axis the master equation from Table 4 becomes

$$(\sigma_{\text{sample}} - \sigma_{\text{ref}})_{\text{true}} = (\sigma_{\text{sample}} - \sigma_{\text{ref}})_{\text{observed}} - \frac{1}{3}(\chi_{\text{ref}} - \chi_{\text{sample}})$$

If nitromethane is used as a reference, the largest correction expected (if brominated solvents are excluded) amounts to -1.6 ppm.

For cases where the field B_0 is *perpendicular* to the sample-tube axis the equation from Table 4 becomes

$$(\sigma_{\text{sample}} - \sigma_{\text{ref}})_{\text{true}} = (\sigma_{\text{sample}} - \sigma_{\text{ref}})_{\text{observed}} + \frac{1}{6}(\chi_{\text{ref}} - \chi_{\text{sample}})$$

and the analogous maximum correction amounts to $+0.8$ ppm.

Attention is drawn to the fact that in the case of the field parallel to the sample tube, the correction is twice as large in magnitude, and opposite in sign, relative to that for the field perpendicular to the sample tube. This may result in apparent differences of up to 2.5 ppm for the same sample run under the two conditions. A good example of this can be found in Table 74, notes (b) and (c), and in Table 75, where a large number of nitrogen shieldings in polypeptides are compared. Actually, such differences can be used for finding true (intrinsic) shieldings, which should lie exactly at $\frac{1}{3}$ of the difference, in passing from the perpendicular to the parallel field arrangement; this is true only if other conditions are the same in both cases.

The magnitude of the corrections, or systematic errors, resulting from bulk-susceptibility effects in the external referencing technique can be much larger than those expected from the data in Table 5. This may happen when paramagnetic substances are present in the sample or the standard employed, even in trace amounts. Paramagnetism adds large positive increments to the susceptibilities quoted in Table 5, and its origin can be concerned with the presence of paramagnetic impurities or with the addition of the so called relaxation reagents, such as chromium(III) *tris*acetylacetonate, $\text{Cr}(\text{acac})_3$. It has already been shown (ref. 1, p. 145 and ref. 4) that intrinsic changes in nitrogen shieldings induced by such reagents are often small, but much larger apparent changes in the shieldings can come from the bulk-susceptibility effects resulting from the presence of these reagents. An example can be found in Table 117, notes (a) and (b), where the addition of $\text{Cr}(\text{acac})_3$ to solutions of azo compounds is shown to change the nitrogen shieldings (externally referenced) by about 1.5 ppm.

Additional effects can, and do, occur in the external referencing technique when one recalculates shieldings, obtained relative to a given reference, to any other reference, since the conversion constant does not always come from the same source. There is a great deal of confusion in this matter, since numerous authors do not realize the consequences of such recalculations. Possible situations and consequences thereof are collected in Table 4. The four schemes, I-IV, are based on various combinations of apparent and true values of shieldings referred to an actual reference (reference II), which will be called simply "shieldings", and the shielding of reference II referred to a primary standard (e.g. nitromethane), which will be called "the conversion constant", since it should be added algebraically to the former in order to obtain shieldings referred to the primary standard. Scheme I is trivial, since both the shielding and the conversion constant have true values, and no corrections are needed upon conversion. Scheme II is often used in the present work; it involves an apparent value of the shielding while a true value of the conversion constant is available. A conversion according to scheme II requires a correction (or otherwise includes an error due to the bulk-susceptibility difference between the actual reference and the sample examined. Scheme II can be employed deliberately in order to eliminate or minimize bulk-susceptibility effects. For example, if the sample is an aqueous solution, one can select an aqueous reference, say, aqueous NaNO_3 , provided that a true conversion constant is available for the latter relative to neat nitromethane. Since the output of the conversion includes bulk-susceptibility effects resulting from the bulk-susceptibility difference between the two aqueous solutions, they can be small or even negligible. Scheme III includes rare cases where true shieldings are measured relative to an actual reference, but only an apparent value of the conversion constant is available; scheme III introduces bulk-susceptibility effects resulting from the susceptibility difference between the two standards involved, the actual and the primary reference. Scheme IV includes apparent shieldings and apparent conversion constants, and is frequently employed in conversion. If both the apparent values originate from measurements where the relationship between the field direction and that of the sample-tube axis is uniform (either parallel or perpendicular in both cases), conversion according to scheme IV_a or IV_b is involved; the output is equivalent, provided that there are no errors coming from other sources, to a direct measurement relative to the primary standard given under experimental conditions, i.e. it includes bulk-susceptibility effects that come from the susceptibility difference between the primary standard and the sample examined.

Much confusion arises, however, when one tries to carry out a conversion using apparent values of the shielding and the conversion constant where one of the values comes from measurements made with the field perpendicular to the sample-tube axis, while the other value results from measur-

ments where the field is parallel to the sample tube axis. This corresponds to schemes IV_c and IV_d (Table 4) and includes errors that depend on the values of the three susceptibilities involved, those of the sample and the two references; seldom, however, do the readers, and the authors, realize that schemes IV_c or IV_d are actually involved, and such recalculations should be considered simply as erroneous. Unfortunately, they occur frequently, and examples can be found in the following Tables (corresponding notes are given in parentheses): 12 (f), (m); 14 (k); 15 (b); 18 (f); 34 (c); 50 (c); 53 (a); 70 (c); 72 (b); 104 (a), (h); 112 (c), (e); 118 (d); 119 (c); 120 (a)–(h); 122. In all such cases, we have tried to recover the original values and, if necessary, to convert them to the neat-nitromethane scale according to schemes II, IV_a or IV_b (Table 4), where applicable. Confusion of this kind stems largely from the suggestion¹⁰⁹ that nitrogen shieldings referred to neat nitromethane be recalculated to a fictitious "liquid NH₃" standard, taken at +380.2 ppm from neat nitromethane (on the shielding scale). The latter value, as well as some author conversion constants published (ref. 109, pp. 32, 33, and ref. 4 therein) come from measurements where the magnetic field was perpendicular to the sample-tube axis. Since quite a lot of nitrogen NMR work has recently been done with superconducting magnet systems, where the field is parallel to the axis of the sample tube, a number of authors have tried to perform such recalculations to the NH₃ scale using the conversion constants mentioned above, thus falling, quite unconsciously, into the consequences of scheme IV_d in Table 4. All this does not necessarily mean that errors (or corrections required) inherent in schemes IV_c and IV_d are always larger than those concerned with the other conversion procedures, II–IV_b, but the former can lead to quite appreciable deviations of the apparent shieldings involved as compared with true shieldings; they increase the spread of apparent shieldings for any given sample composition; finally, their origin can be easily confused with that concerning schemes IV_a and IV_b. Let us consider some contrived, but practical examples of external referencing consequences under experimental conditions corresponding to the schemes in Table 4 (susceptibilities taken from Table 5).

Example A

Sample: neat N-methylpiperidine (susceptibility = -7.779 ppm).

Actual reference: saturated aqueous NH₄Cl (susceptibility = -9.664 ppm).

Conversion to: neat nitromethane (susceptibility = -4.863 ppm).

Scheme involved:	I	II _a	II _b	III _a	III _b	IV _a	IV _b	IV _c	IV _d
Correction required (in ppm):	0	-0.31	+0.63	+0.80	-1.60	+0.49	-0.97	-1.91	+1.43

Example B

Sample: dilute solution in CHCl_3 (susceptibility of $\text{CHCl}_3 = -9.173$ ppm).

Actual reference: aqueous 1 M HNO_3 (susceptibility = -8.985 ppm).

Conversion to: neat nitromethane (susceptibility = -4.683 ppm).

Scheme involved:	I	II _a	II _b	III _a	III _b	IV _a	IV _b	IV _c	IV _d
Correction required (in ppm):	0	+0.03	-0.06	+0.69	-1.37	+0.72	-1.44	-1.34	+0.62

In these two examples, references are chosen that are characterized by large differences in the susceptibility. Example A shows an adverse effect of situations where schemes IV_c and IV_d are relevant. Example B illustrates the advantage of the procedure under scheme II in eliminating bulk-susceptibility effects by the use of an auxiliary reference whose susceptibility is close to that of the sample involved.

The discussion above is concerned with liquid samples and references. In the case of gaseous samples, one can usually assume that the magnetic susceptibility of the gas is not significantly different from zero; in consequence, the largest effects due to magnetic susceptibility are expected when aqueous external standards are employed (Table 5); they are twice as large as the maximum effects for liquid samples. However, the use of neat liquid nitromethane, which has a very low (negative) susceptibility (Table 5), as a primary standard brings the magnitude of the necessary corrections within the range of those for liquid samples. For example, if we take the shielding of gaseous N_2 (extrapolated to zero pressure, Table 124, note (a), and reference therein), $+74.70 \pm 0.05$ ppm from neat liquid nitromethane at 300 K, measured under conditions where the field is perpendicular to the sample tube, the corrected ("true") value becomes $+73.9$ ppm.

Since the magnitude and the sign of bulk-susceptibility effects depend on the direction of B_0 relative to the axis of the sample tube, it is necessary to specify the resonance frequency of the nitrogen NMR measurements involved. Those in excess of 18 MHz for ^{15}N indicate that a superconducting magnet is used, and this means almost invariably that the field is parallel to the sample tube. Those below 10.2 MHz usually mean that an electromagnet is employed and the field is perpendicular to the sample tube. Some authors forget about that, and either do not specify the frequency at all, or do not indicate which is applicable to a given measurement when the two arrangements are employed. Examples can be found in the following Tables (corresponding notes in parentheses): 23; 35 (i); 85 (e); 86 (c), (k); 87 (c); 93 (e); 95 (h); 104 (g); 114 (c); 121 (e) and references therein.

There is still another situation from the point of view of the direction of B_0 relative to the axis of rotation of a sample. This occurs in the spectra of solid samples where the axis of rotation is tilted at the magic angle ($54^\circ 44'$) relative to the field. One could try to derive the corresponding equation for bulk-susceptibility effects, but since such samples cannot usually be considered as elongated cylinders, it is advisable to calibrate susceptibility effects experimentally, using liquid samples and references whose relative shieldings and magnetic susceptibilities are known.

As far as the choice of standards is concerned for the calibration of both ^{14}N - and ^{15}N -NMR shieldings, there is a general recommendation^{1,4,109,110} that *neat liquid nitromethane*, MeNO_2 , should be used as an external reference. It has a high nitrogen concentration per unit volume (18.42 M at 30°C). A mixture of CD_3NO_2 and $\text{CH}_3^{15}\text{NO}_2$ provides not only a good external standard, but also a convenient external deuterium lock for the magnetic field, in the case of ^{15}N -NMR spectroscopy. The ^{14}N resonance signal of MeNO_2 has a relatively small linewidth, so that the standard can be used in both ^{14}N - and ^{15}N -NMR. Our experience indicates that its nitrogen shielding does not change upon annealing in a glass container, even in high-precision measurements (± 0.02 ppm). Recent measurements of temperature effects on nitrogen shieldings (Table 9) indicate that nitro derivatives of hydrocarbons as well as the NO_3^- ion in *neutral* aqueous solutions (KNO_3) do not show any significant temperature coefficient of their nitrogen shieldings.

Neat nitromethane is gaining ground as the universal external reference for both ^{14}N and ^{15}N measurements of nitrogen shieldings, as can be inferred from the following comparison:

Standard	Percentage of papers under review where the standard specified was employed
neat nitromethane	40%
NH_4^+ ion with various gegenions, in various solutions	15%
NO_3^- ion with various gegenions, in various solutions (HNO_3 excluded)	10%
HNO_3 , aqueous, various concentrations	10%
liquid NH_3	10%
occasionally used references: formamide, dimethyl- formamide, aqueous KNO_2 , aniline, aqueous NH_3 , nitrobenzene, acetamide, CN^- ion	15%

There is little to recommend as far as the other standards are concerned. A possible exception is aqueous NaNO_3 (or KNO_3), provided that no acid is added, and that its concentration is specified (Table 6). Its nitrogen shielding is practically insensitive to temperature effects (Table 9); it can

be used as an auxiliary standard for aqueous solutions, which are characterized by high (negative) values of magnetic susceptibility (Table 5). Since the true values of the nitrogen shielding in NaNO_3 solutions are available (Table 6), the shieldings referred to NaNO_3 can be easily converted to the nitromethane scale by making use of scheme II (Table 4), which in this case allows one to eliminate or minimize bulk-susceptibility effects. However, there are drawbacks. First, the maximum concentration per unit volume does not exceed 8 M. Secondly, the nitrogen shieldings in neutral aqueous NaNO_3 or KNO_3 can be easily confused with those in the NO_3^- ion in acidified NaNO_3 , NH_4NO_3 or HNO_3 . What is true for the former becomes quite untrue for the latter standards. The NO_3^- shielding increases appreciably with decreasing pH of the solution (Table 6). The shielding in HNO_3 encompasses a range from +3.5 to +42.5 ppm relative to neat nitromethane, depending on HNO_3 concentration. It is thus pointless to speak of a " HNO_3 standard" without any specification of the concentration (Table 72, note (a), and reference therein). The NO_3^- shielding in NH_4NO_3 (Table 6) shows significant effects arising from the composition of its solution. A number of values (referred to neat nitromethane), ranging from -2.6 to +5.1 ppm, have been reported for reference samples containing acidified aqueous NaNO_3 , as is shown in the following Tables (corresponding notes in parentheses): 12 (h), (k); 18 (c); 25 (a)-(c); 27 (a), (h) 30 (c), (h); 34 (d); 37 (b); 42 (c); 44 (a); 47 (e); 54 (c); 55 (a); 106 (e), (f) (h); 108 (g), (i); and references therein. A part of this spread of values can be explained in terms of bulk-susceptibility effects, including those of relaxation reagents added, but sample composition is certainly responsible for another part of the divergence.

The shielding in the NH_4^+ ion is also an unreliable standard for the calibration of nitrogen shieldings. It depends appreciably on the sample composition, and is susceptible to gegenion effects (Table 6) in solution and in the solid state (Table 30). The range of such effects can exceed 10 ppm, and this can lead to much confusion. For example, in some instance aqueous NH_4Cl is reported as a reference but the data indicate that the standard is probably NH_4NO_3 , where the NH_4^+ shielding is larger by ca 10 ppm; see the following Tables (corresponding notes in parentheses) 18 (a); 35 (h); 47 (f); 55 (b); 98 (g); 99 (d); 101 (g); 108 (k), (l); 118 (f) 127 (d); and references therein.

Liquid NH_3 can hardly be considered as a practical standard, and has rarely been employed as such. Its nitrogen shielding is quite sensitive to temperature effects,⁵³ +0.068 ppm/deg within the temperature range 300-360 K; the latter value is much higher than any other of the values reported in Table 9. This alone can disqualify liquid NH_3 as a standard in nitrogen NMR, in contrast with the opinion expressed in ref. 109 (p. 30 therein) which is based on old data. Additional chaos has been introduced into the

published values of nitrogen shieldings by the recommendation¹⁰⁹ that nitrogen shieldings referred to neat nitromethane, or other standards, should be recalculated to a liquid NH_3 reference whose shielding relative to neat nitromethane is given as +380.23 ppm; the latter value, as well as some other conversion constants reported, is actually obtained from measurements where the external magnetic field is perpendicular to the sample-tube axis. Consequences of such recalculations from the point of view of bulk-susceptibility effects involved have already been considered in the present section, in the discussion of external referencing procedures.

It is evident from the data in Tables 6 and 9 that aqueous solutions and, generally, samples where extensive hydrogen bonding takes place, are unreliable references for nitrogen shieldings, since such references display significant effects of sample composition (concentration, additives, gegenions, etc.) or significant temperature effects, or both.

Table 6 presents the nitrogen shieldings, referred to neat liquid nitromethane, of various substances that have been employed as references in the literature. Attention is drawn to the distinction between the true values, which do not contain bulk-susceptibility effects, and the apparent values obtained under various experimental conditions of the direction of the external field. An indiscriminate use of any apparent value, without regard to actual experimental conditions, can lead to significant errors. Our general policy in the recalculation of literature data to the nitromethane scale of nitrogen shieldings is to use any original conversion constant available (this corresponds to schemes IV_a and IV_b in Table 4) or, lacking that, the relevant true values from Table 6 (this corresponds to scheme II in Table 4). If none of these are available, apparent conversion constants obtained under analogous experimental conditions are employed in order to conform with schemes IV_a or IV_b, Table 4. The data that are referred originally to neat nitromethane usually bear a comment "uncorrected for bulk-susceptibility effects", which means that the errors involved, or the corrections required, are those resulting from the master equation in Table 4, for a given arrangement of the direction of the magnetic field relative to the sample tube. We do not endeavour to introduce any bulk-susceptibility corrections into the literature data that are not originally reported, since such procedures are liable to errors resulting from the lack of detailed knowledge of experimental conditions concerned, and especially of the presence, or absence, of any paramagnetic impurities or additives.

There is still another factor that can introduce some apparent discrepancy in the value of nitrogen shielding, even of that calculated from any given spectrum. This results from the fact that

$$(\sigma_{\text{sample}} - \sigma_{\text{ref}}) = \frac{\nu_{\text{ref}} - \nu_{\text{sample}}}{\nu_{\text{bare nucleus}}}$$

where the σ s are the nuclear shielding constants, and the ν s are the corresponding resonance frequencies at a constant value of B_0 . If anything else is used for the denominator, for example the frequency of the reference, an error arises in the absolute value of the relative shielding $|\sigma_{\text{sample}} - \sigma_{\text{ref}}|$, which is

$$\text{error } |\sigma_{\text{sample}} - \sigma_{\text{ref}}| = |\sigma_{\text{sample}} - \sigma_{\text{ref}}| \sigma_{\text{ref}}^0$$

where σ_{ref}^0 is the absolute shielding constant (i.e. referred to a bare nucleus, with its proper sign) in the reference. There are reasons to believe⁵⁶ (Section II) that

$$\sigma_{\text{neat nitromethane}}^0 \approx -130 \text{ ppm},$$

and, in consequence of the above value, that

$$\nu_{\text{bare nitrogen nucleus}} = \nu_{\text{neat nitromethane}} \times (1 + 130 \times 10^{-6})$$

The latter value should be used in the denominator of the equation for $\sigma_{\text{sample}} - \sigma_{\text{ref}}$. Since the nitrogen signal of nitromethane does not lie too far from that of a bare nitrogen nucleus, and since it occurs almost in the centre of the nitrogen shielding range for diamagnetic molecules and ions (Table 10), the errors are small when one uses $\nu_{\text{nitromethane}}$ instead of $\nu_{\text{bare nucleus}}$. This is not necessarily true for other references. Let us consider the simple case of a nitrogen NMR spectrum measured for a system of coaxial tubes, with liquid NH_3 in the inner tube, and saturated aqueous NaNO_2 in the outer tube. From the data in Table 6, one can deduce the absolute shieldings (those referred to a bare nitrogen nucleus) for NH_3 and NaNO_2 , *ca.* +250 ppm and *ca.* -360 ppm respectively. Let us assume that the bulk-susceptibility corrections required have been applied, and that we want to calculate the relative shielding of NH_3 versus NaNO_2 . If we employ ν_{NaNO_2} in the denominator of the relevant equation, we obtain a value of the shielding that is too small, by 0.22 ppm; if we use ν_{NH_3} instead, we obtain a value that is too large by 0.15 ppm. Thus the two calculations, based on the same spectrum, yield two apparent values which differ from each other by about 0.4 ppm. Such significant errors appear when large differences in nitrogen shieldings are considered and the differences of the relevant resonance frequencies are divided by a frequency that is significantly remote from that for a bare nitrogen nucleus. Since it is fairly easy to obtain a crude estimate of $\nu_{\text{bare nucleus}}$ the use of the latter value is strongly recommended. From this point of view alone, one should treat with suspicion any precision better than 0.1 ppm, reported for large differences in nitrogen shieldings, even if the corresponding resonance signals originate from the same sample, and are thus free from bulk-susceptibility effects.

IV. EXPERIMENTAL TECHNIQUES

Some of the properties of the naturally occurring nitrogen nuclei, ^{14}N and ^{15}N are given below.

Isotope	^{14}N	^{15}N
Natural abundance	99.64%	0.36%
Spin number I	1	$\frac{1}{2}$
Quadrupole moment eQ (in $e \times m^2$)	$+7.1 \times 10^{-30}$	0
Magnetic moment (in nuclear magnetons)	+0.40357	-0.28304
Gyromagnetic ratio, $\gamma/2\pi$ (in $\text{T}^{-1} \text{s}^{-1}$)	$+3.076 \times 10^6$	-4.315×10^6
Resonance frequency at magnetic field B_0 specified (corresponding proton resonance frequency in parentheses)		
1.409 T (60 MHz)	4.334 MHz	6.080 MHz
1.879 T (80 MHz)	5.779 MHz	8.106 MHz
2.114 T (90 MHz)	6.502 MHz	9.120 MHz
2.349 T (100 MHz)	7.224 MHz	10.133 MHz
4.228 T (180 MHz)	13.00 MHz	18.24 MHz
4.698 T (200 MHz)	14.45 MHz	20.27 MHz
5.872 T (250 MHz)	18.06 MHz	25.33 MHz
6.342 T (270 MHz)	19.50 MHz	27.36 MHz
7.047 T (300 MHz)	21.67 MHz	30.40 MHz
8.456 T (360 MHz)	26.01 MHz	36.49 MHz
9.396 T (400 MHz)	28.90 MHz	40.53 MHz
11.745 T (500 MHz)	36.12 MHz	50.67 MHz
14.094 T (600 MHz)	43.34 MHz	60.80 MHz

As a rule of thumb, ^{15}N frequencies are about $\frac{1}{10}$ of those for protons, and ^{14}N frequencies are about $\frac{3}{4}$ of those for ^{15}N .

A general problem in nitrogen NMR, both ^{14}N and ^{15}N , is concerned with the low intensity of nitrogen resonance signals, the broad range of relaxation rates and some adverse effects of the negative nuclear Overhauser effect (NOE) in the case of ^{15}N nuclei. The low intensity results from the small magnetic moments of ^{14}N and ^{15}N ; the latter has quite a low natural abundance, which additionally deteriorates the sensitivity. Since ^{14}N has a non-zero quadrupole moment, the quadrupolar relaxation rates concerned cover a range corresponding to signal widths from about 1 Hz to some kilohertz. It is usually impossible to optimize the intensity over such a range of relaxation rates and compromises have to be devised. On the other hand, ^{15}N NMR is often plagued by very small relaxation rates, since the corresponding longitudinal relaxation times T_1 can vary from those of the order

of 0.1 s to about 1000 s. A combination of long T_1 s with relatively short T_2^* values (where $\pi T_2^* = \Delta\nu_{1/2}^{-1}$, and $\Delta\nu_{1/2}$ is the observed half-height width of the resonance signal involved, including field-inhomogeneity effects, and those of, e.g., proton decoupling) results in further losses in the signal-to-noise (S/N) ratio available upon pulse excitation of ^{15}N spectra and the accumulation of the resulting free-induction decays (FIDs). One should note that it is the combination considered that is responsible for the deterioration of the S/N ratio rather than long T_1 values alone. The latter either induce saturation effects or require long waiting periods between consecutive exciting pulses, but they would produce, taken alone, very narrow ^{15}N signals, which would compensate for the losses in the S/N ratio resulting from saturation or long intervals between the pulses. The large range of relaxation rates in ^{15}N NMR also requires compromises from the point of view of optimizing intensities. Another important factor that often operates in ^{15}N NMR is concerned with the negative ^{15}N NOE on proton decoupling. The latter can often totally cancel ("null") the ^{15}N resonances involved.

In ^{15}N NMR, where the resonance signals are generally narrow, and the spectral widths range from a few kilohertz to about 50 kHz, the pulse excitation technique, with the subsequent accumulation of FIDs and the Fourier-transformation thereof, is invariably employed. In this case it has an obvious advantage in sensitivity per unit time over CW excitation of the spectra. In ^{14}N NMR, where the signal widths can reach the kilohertz range, and the corresponding spectral widths constitute about $\frac{3}{4}$ of those for ^{15}N , the advantage is less obvious, and both techniques are commonly employed.

A. Pulsed Fourier-transform technique (PFT)

Since this technique is currently used in all ^{15}N NMR spectral measurements, we consider it mainly from the point of view of ^{15}N spectra, with some comments concerning ^{14}N NMR. The general principles of the PFT method can be found elsewhere,¹¹¹ as well as some of its applications in the field of ^{15}N NMR.^{1,3,109,110} While it is difficult or even impossible to provide advice about optimum spectrometer settings in individual cases, one can try and draft some useful guidelines across the chaos of possible combinations of PFT parameters in ^{15}N NMR spectroscopy.

The large range of nitrogen shieldings has direct consequences on the selection of the *spectral width* SW, the *pulse frequency* ν_{pulse} and the maximum *pulse width* PW. We shall consider two general cases from the point of view of nitrogen shielding range. The *full* range, at least for diamagnetic samples, covers slightly more than 1000 ppm (Table 10), from about -600 ppm to +400 ppm referred to neat nitromethane. However, about a half of the full range is represented by various nitroso groups, $-\text{N}=\text{O}$, and azo-bridges, $-\text{N}=\text{N}-$. Since in some cases we can exclude such moieties from consider-

ation, we therefore may define a *limited* range of nitrogen shieldings of about 500 ppm, from -100 ppm to $+400$ ppm referred to neat nitromethane.

Another distinction arises from the detection procedure employed. If we use the *single-detection* method (one detector only), the pulse frequency must be outside the spectral range concerned, preferably close to either of its edges. In this case, the spectral-width setting includes the entire range of nitrogen shieldings considered, plus any offset frequency difference. If the *quadrature detection* system is employed, one using two detectors with a 90° mutual phase shift, the pulse frequency should fall on the midpoint of the spectral range examined, and the spectral width concerned amounts to a half of the range.

Let us consider the actual location of the pulse frequency ν_{pulse} in ^{15}N (or ^{14}N) spectra, in terms of the resonance frequency of the neat nitromethane standard at a given value of B_0 . The following values of ν_{pulse} should be recommended for the combinations shown.

ν_{pulse} values	For full range of nitrogen shieldings, -600 to $+400$ ppm	For limited range of nitrogen shieldings, -100 to $+400$ ppm
For single detection	Slightly higher than $1.000600\nu_{\text{MeNO}_2}$ or slightly lower than $0.999600\nu_{\text{MeNO}_2}$	Slightly higher than $1.000100\nu_{\text{MeNO}_2}$ or slightly lower than $0.999600\nu_{\text{MeNO}_2}$
For quadrature detection	$1.000100\nu_{\text{MeNO}_2}$	$0.999850\nu_{\text{MeNO}_2}$

Quadrature detection systems, provided that they are of good design, are recommended for use in ^{15}N NMR, since they halve the usually large spectral widths, with all the consequences thereof, including a theoretical gain in the S/N ratio of $\sqrt{2}$, as compared with the single detection method.

In nitrogen NMR the spectral widths (frequency differences between the pulse and the limit of the range where nitrogen resonance signals can appear) are considerably larger, at a given value of B_0 , than those encountered in ^{13}C NMR, not to speak of ^1H NMR. The SW setting in a spectrometer has direct and usually automatic consequences in determining the sampling rate of the FID involved. In order to reproduce the offset frequencies of the signals (referred to that of a pulse), the rate is set equal to the so-called Nyquist frequency, 2 SW ; thus large spectral widths require twice as large sampling rates. The time interval between consecutive samplings, or the *dwell time*, DW , is then equal to $(2\text{ SW})^{-1}$. The total time devoted to the sampling of a given FID, the *acquisition time*, AQ , determines the *digital resolution* available, equal to the reciprocal of the latter, $(\text{AQ})^{-1}$. The digital

resolution should not exceed that resulting from the signal width, $(\pi T_2^*)^{-1}$, and for most practical purposes in ^{15}N NMR it can be set to about 1 Hz, which corresponds to $AQ = 1$ s. The value of AQ cannot be set directly in most spectrometer systems, but it can be adjusted indirectly as

$$AQ = M/2 SW$$

where M is the number of memory locations in a computer that are assigned to collecting and accumulating the FIDs. Thus, for a given AQ , the increasing SW requires an increase in memory storage M . Let us consider some typical examples in ^{15}N NMR.

^{15}N resonance frequency and detection system employed	Spectral width, SW , for nitrogen shielding range specified (in parentheses, memory storage M required to yield $AQ = 1$ s for that SW value; M expressed in multiples of $k = 1024$)	
	Full range of nitrogen shieldings, -600 to +400 ppm	Limited range of nitrogen shieldings, -100 to +400 ppm
10.13 MHz (corresponding to proton frequency of 100 MHz)		
Single detection	ca. 11 kHz (22 k)	ca. 6 kHz (12 k)
Quadrature detection	ca. 6 kHz (12 k)	ca. 3 kHz (6 k)
50.67 MHz (corresponding to proton frequency of 500 MHz)		
Single detection	ca. 51 kHz (102 k)	ca. 26 kHz (52 k)
Quadrature detection	ca. 26 kHz (52 k)	ca. 13 kHz (26 k)

It is evident from the examples shown above that large memory storages are required, particularly at high magnetic fields when the full range of nitrogen shieldings has to be taken into account. These can be reduced proportionally, for example, if AQ is set to 0.5 s (this causes the digital resolution to deteriorate to 2 Hz), the M values above should be halved. In the case of proton-decoupled spectra there is a significant contribution of the decoupling process to the ^{15}N signal width, which can be of the order of a few Hz, and therefore a resolution of 2 Hz is acceptable.

In PFT ^{14}N NMR the digital resolution required is usually concerned with the ^{14}N signal width of the standard employed, neat nitromethane,

and should be set to something like 10 Hz ($AQ = 0.1$ s). Since the spectral widths for ^{14}N amount to about $\frac{3}{4}$ of those for ^{15}N at the same field, the M values for ^{14}N are about 0.075 of those for ^{15}N quoted above.

After setting the spectral width and the acquisition time, one must consider filtering out the frequency components that are outside the spectral width, in order to eliminate the folding over of the relevant noise components into the spectral range (ref. 111, p. 147). Usually, the spectrometer system sets the *filter bandwidth*, FW, to something like

$$\text{FW} = 1.25 \text{ SW}$$

after SW has been set, but attention is drawn to the type of filter employed, if there is any choice. For ^{15}N spectra, which contain rather sharp signals, the Butterworth type, or any with sharp cut-off characteristics, can be used. However, for ^{14}N spectra, where the ^{14}N signals can be quite broad, it is better to employ filters with less-steep characteristics at the bandwidth limits, for example the Bessel type, in order to avoid distortions in the lineshape. Needless to say, any precise determination of nitrogen shieldings from broad resonances of ^{14}N have to rely on lineshape-fitting procedures.

Given a spectral width, SW, one should also consider the maximum acceptable pulse duration, in order to provide a possibly uniform excitation within the spectral width involved. The following relations (which can be derived from the data in ref. 111, p. 102, and references therein) hold:

Pulse width, PW	Excitation power at $\pm$ SW limits, referred to that at the pulse frequency
$\text{PW} = (4 \text{ SW})^{-1}$	98.4%
$\text{PW} = (2 \text{ SW})^{-1}$	82.0%
$\text{PW} = (\text{SW})^{-1}$	ca.0%

Thus, in any setting of PW, which is discussed later in the present section, one should bear in mind that PW should not exceed $(4 \text{ SW})^{-1}$. For example, if the spectral width $\text{SW} = 51$ kHz (^{15}N spectrum, 50.67 MHz, single detection, full range of nitrogen shieldings), PW should not be larger than 5 μs ; for $\text{SW} = 3$ kHz (^{15}N spectrum, 10.13 MHz, quadrature detection, limited range of nitrogen shieldings), PW should not exceed 83 μs .

The pulse width, PW, expressed in time units is important from the point of view of its maximum limit discussed above. For further considerations, PW should be expressed in terms of the *pulse angle* or "*flip angle*" α , which is the angle by which the magnetization vector of the nuclei involved is tilted from the z -axis upon the action of the pulse. The calibration of PW in terms of the flip angle should be made experimentally for the nucleus

concerned (^{15}N or ^{14}N) and the spectrometer system employed. This can be done simply by recording a signal intensity as a function of an increase in pulse width; the second nulling point corresponds to $\alpha = 360^\circ$, and should be used in interpolations for other values of the flip angle (see ref. 111, p. 185).

In the case where a single pulse, and the resulting single FID, provide a spectrum with an adequate S/N ratio (this will almost never be the case for nitrogen nuclei), an optimum intensity is obtained by setting $\alpha = 90^\circ$. Because of the low sensitivity of nitrogen NMR measurements, one has almost always to accumulate the FIDs, obtained in a long sequence of pulses, spaced at time intervals t_p (*pulse repetition times*). In this situation, the S/N ratio alone is not important as such from the point of view of sensitivity, but the S/N ratio obtained within a given period of time becomes significant. Compromises therefore have to be found between the desired increase of the spectrum accumulation rate (by decreasing t_p) and the requirement that t_p be long enough to include the acquisition time, AQ , required and provide a sufficient relaxation of the nuclear spins involved before starting the next pulse/FID cycle.

There is still another important factor that affects the optimum settings of the flip angle α and the pulse repetition time t_p . If proton-coupled ^{15}N spectra are measured, the spin-spin splittings of the ^{15}N signals involved reduce the S/N ratio considerably. Therefore proton-decoupling procedures are often employed, and these not only collapse the multiplet patterns, but also give rise to NOE enhancements. The latter can yield desirable or unwanted results, which should be taken into account when one looks for optimum conditions of ^{15}N measurements. There is no such problem in ^{14}N NMR, since the quadrupolar relaxation rates of ^{14}N are usually fast enough to effectively decouple ^{14}N from neighbouring protons.

The theory and general problems concerning NOE have been adequately dealt with.¹¹³ We shall limit ourselves here only to raising some important points relevant to ^{15}N NMR. In the so-called extreme narrowing limit, where molecules rotate rapidly compared with the ^{15}N resonance frequencies involved, if the ^{15}N nuclei are decoupled continuously from protons, the ^{15}N signal intensities I obey the following equation:

$$\frac{I(\text{with NOE})}{I(\text{without NOE})} = 1 + 4.93 \frac{(T_1^{\text{dd}})^{-1}}{(T_1^{\text{dd}})^{-1} + \sum (T_1^{\text{other}})^{-1}} \quad (3)$$

nuclear Overhauser
enhancement factor (NOEF)

where I without NOE is that resulting from a simple collapse of the multiplet pattern of a ^{15}N signal; T_1 are the spin-lattice relaxation times of ^{15}N representing various relaxation mechanisms (dd = dipole-dipole). Thus the

NOEF can vary from 0 to -4.93 , depending on the contribution of the dipole-dipole relaxation rate $(T_1^{\text{dd}})^{-1}$ to the total relaxation rate $(T_1)^{-1} = (T_1^{\text{dd}})^{-1} + \sum (T_1^{\text{other}})^{-1}$; the corresponding relative intensity can change from $+1$ to -3.93 , which means in the latter case an inverted signal of about a fourfold magnitude relative to that without NOE. It is evident from equation (3) that the *magnitude* of the ^{15}N signal with NOE is reduced (relative to that without NOE) when the NOEF attains values between zero and -2 ; the signal is cancelled totally (nulled) if $\text{NOEF} = -1$. On the other hand, if the NOEF is between -2 and -4.93 , a net gain in the magnitude of the ^{15}N signal is obtained, which can reach 3.93 *I* without NOE. An unfavourable NOE can be suppressed by either the so-called inverse-gated decoupling technique, which is considered later in the present section, or by the use of paramagnetic relaxation reagents, which contribute significantly to $\sum (T_1^{\text{other}})^{-1}$. Even more serious problems may occur with the NOE if the molecules do not move very fast relative to the ^{15}N resonance frequency employed (ref. 110, p. 18). If they move very slowly then the maximum negative $\text{NOEF} = -0.12$; this means a small reduction in the signal magnitude. However, the maximum negative value of NOEF changes quickly as a function of molecular rotation rate, from -4.93 to -0.12 , when the latter is comparable to the resonance frequency. For ^{15}N , proton-decoupled spectra taken at about 50 MHz, this occurs within the 10^{10} – 10^9 Hz range of reciprocal correlation times for molecular rotations. At about 10 MHz the range involved is 10^9 – 10^8 Hz. In these intermediate regions NOEF can easily attain values that result in signal nulling, and the question of NOE suppression becomes even more important.

It is important to note, from the point of view of NOE suppression by the inverse-gated decoupling method mentioned, that the NOE grows and decays (upon turning the decoupler on or off, respectively) at a rate equal to $(T_1)^{-1}$, where T_1 is the total resultant spin-lattice relaxation time for ^{15}N , i.e. $(T_1)^{-1} = (T_1^{\text{dd}})^{-1} + \sum (T_1^{\text{other}})^{-1}$, as in equation (3).

Let us turn back now to the problem of optimizing the *S/N* ratio in PFT ^{15}N spectra. First, we consider a typical timing scheme for a PFT spectral measurement (Scheme 1). Since AQ is set according to the digital resolution required, we can adjust PW (and the corresponding flip angle α) or RD or both. There are quite evident indications from the general theory of PFT spectra (ref. 111, p. 179) that for any value of AQ+RD the optimum condition is attained when one sets PW to correspond to a flip-angle α value equal to the *Ernst angle* α_E ,

$$\cos \alpha_E = E_a E_d \quad (4)$$

$$E_a = \exp(-\text{AQ}/T_1) \quad (5)$$

$$E_d = \exp(-\text{RD}/T_1) \quad (6)$$

SCHEME 1

Frequency channel	Repeated timing sequence	Decoupling effect on ^{15}N spectrum			
^{15}N , irradiate and observe	<table><tr><td>PW</td><td>AQ</td><td>RD</td></tr></table>	PW	AQ	RD	
PW	AQ	RD			
^1H decoupling					
(a) none	<table><tr><td>off</td></tr></table>	off	None (proton-coupled spectrum, no NOE)		
off					
(b) continuous	<table><tr><td>on</td></tr></table>	on	Proton-decoupled spectrum with NOE		
on					
(c) gated	<table><tr><td>off</td><td>on</td></tr></table>	off	on	Proton-coupled spectrum with partly retained NOE	
off	on				
(d) inverse-gated	<table><tr><td>on</td><td>off</td></tr></table>	on	off	Proton-decoupled spectrum with partly quenched NOE	
on	off				

PW = pulse width
AQ = acquisition time of free induction decay (FID)
RD = relaxation delay

where T_1 is the spin-lattice relaxation time for ^{15}N . Moreover, RD should be set to zero, thus rendering $E_d = 1$, in all cases that do not require RD for special purposes, for example, in the gated and inverse-gated decoupling procedures; if $\text{RD} = 0$ then $\cos \alpha_E = E_a$. The latter setting is recommended for ^{15}N PFT spectra which are measured without proton-decoupling or with a continuous decoupling (Scheme 1, cases (a) and (b)). This optimization requires only the knowledge of T_1 or at least a reasonable estimate thereof, and does not throw one into the chaos of published or recommended combinations of the flip angles α and the pulse repetition times $t_p = \text{AQ} + \text{RD}$ for ^{15}N PFT spectra (such as those reported in ref. 109, p. 20, and ref. 110, pp. 40, 41). However, T_1 measurements are fairly routine in most modern spectrometer systems, and the resulting accumulation of T_1 data, such as that presented in ref. 110, p. 21, together with those for NOEF values, should provide a more sound basis for any estimates of optimum conditions of ^{15}N PFT measurements in individual cases.

Before proceeding to more complicated cases, which include more refined ^1H irradiation procedures in ^{15}N spectral measurements, as well as comparisons of ^{15}N signal intensities, we consider some general equations for

the S/N ratio in ^{15}N PFT measurements. We shall consider only relative S/N ratios, referred to as *standard S/N ratio* which we define as follows.

Volume concentration of ^{15}N , temperature, spectrometer system, resonance frequency, and other conditions unless indicated otherwise:	Same as for the sample examined
T_2^* :	0.3 s (this corresponds to signal half-height width of about 1 Hz)
Acquisition time, AQ:	1 s (this corresponds to digital resolution of 1 Hz)
Pulse width, PW:	Corresponding to flip angle $\alpha = 90^\circ$
Relaxation delay, RD:	Zero
^{15}N relaxation:	Imaginary mechanism is assumed which restores the magnetization, without signal broadening, before commencing the next pulse
Total time of measurement:	Same as for the sample examined
NOE and polarization transfer:	None

The conditions include an imaginary relaxation mechanism, but the standard S/N ratio can be obtained experimentally, by setting a long relaxation delay RD (relative to T_1) while only the acquisition periods, AQ, are counted as the total time of measurement, provided that all of the remaining conditions are fulfilled.

There is still another condition that we assume to hold in all cases considered, including that of the standard S/N ratio. It is assumed that the free induction decay, FID, accumulated, prior to its Fourier-transformation, is multiplied by the weighting function $\exp(-t/T_2^*)$, where t is the time elapsed from the beginning of the FID acquisition. This optimizes the S/N ratio in the spectrum obtained from a given FID, and is frequently referred to as the use of a "matched filter". The procedure also doubles the signal width that would be obtained without any filtering at this stage. In spectrometer systems this can be performed simply by setting a parameter, which may be called the *line broadening*, LB, equal to $(\pi T_2^*)^{-1}$, the experimental signal width.

For ^{15}N PFT spectra obtained under the conditions of Scheme 1 one can derive a general equation for the (relative) S/N ratio, on the basis of the general theory of PFT spectra;¹¹¹

$$\frac{S/N}{(S/N)_{\text{standard}}} = \left(\frac{T_2^*}{0.3} \right)^{1/2} \frac{1 + \eta \text{ NOEF}}{(AQ + RD)^{1/2}} \frac{(1 - E_a E_d) \sin \alpha}{1 - E_a E_d \cos \alpha} \quad (7)$$

where η is the fraction of the NOEF retained in the spectrum considered, α is the flip angle (not necessarily the Ernst angle), E_a and E_d are defined in equations (5) and (6) respectively, AQ is the acquisition time, and RD

is the relaxation delay (Scheme 1). The fraction of NOEF retained may be independent of the other parameters in equation (7);

$$\eta = 0 \quad \text{for no decoupling (Scheme 1, case (a))}$$

$$\eta = 1 \quad \text{for continuous decoupling (Scheme 1, case (b))}$$

or can be related to AQ, RD and T_1 (via E_a and E_d):

$$\eta = \frac{E_d(1 - E_a)}{1 - E_a E_d} \quad (8)$$

$$E_d = \frac{\eta}{1 + E_a(\eta - 1)} \quad (9)$$

for *inverse-gated decoupling* (Scheme 1, case (d)), and

$$\eta = \frac{1 - E_d}{1 - E_a E_d} \quad (10)$$

$$E_d = \frac{1 - \eta}{1 - \eta E_a} \quad (11)$$

for *gated decoupling* (Scheme 1, case (c)).

Equation (7) should be used in S/N calculations in cases where, in addition to NOEF and T_1 , AQ, RD, and α are also given, for example, from an optimizing procedure performed for some other ^{15}N resonance signal in the spectrum considered. If we want to optimize S/N , then the Ernst angle α_E (equation 4), should be used for α , and this reduces equation (7) to the form

$$\frac{S/N}{(S/N)_{\text{standard}}} = \left(\frac{T_2^*}{0.3} \right)^{1/2} \frac{1 + \eta \text{ NOEF}}{(AQ + RD)^{1/2}} \left(\frac{1 - E_a E_d}{1 + E_a E_d} \right)^{1/2} \quad (12)$$

Equations (7), (8), (10) and (12) are simple enough to be fitted even into a programmable pocket calculator system. The use of equation (12) in optimizing S/N is fairly simple. If we know T_2^* , and make a reasonable guess about the parameters characteristic of the ^{15}N nucleus in question (NOEF, T_1), then the only parameter to be varied in search of a maximum S/N is the relaxation delay RD, since AQ is set to meet the digital resolution requirements (and consequently E_a is also set), and η is either set (0 or 1, for no decoupling and continuous decoupling respectively) or is simply related to RD (via E_d equations (8) and (10), for inverse gated decoupling, and gated decoupling respectively).

Since long T_1 values (relative to T_2^*) adversely affect the S/N ratio, it is common practice to use *relaxation reagents* in ^{15}N NMR measurements; the most popular is $\text{Cr}(\text{acac})_3$. The latter increases the total relaxation rate

$(T_1)^{-1} = (T_1^{\text{dd}})^{-1} + \sum (T_1^{\text{other}})^{-1}$, equation (3), by adding a substantial increment to $\sum (T_1^{\text{other}})^{-1}$, and this results also in quenching the NOEF. If one knows the NOEF and T_1 for a sample without a relaxation reagent, and T_1 for the sample with some amount of the latter, then it is fairly simple to calculate the modified value of the NOEF in the presence of the reagent:

NOEF (with relaxation reagent)

$$= \text{NOEF (without relaxation reagent)} \frac{T_1 \text{ (with reagent)}}{T_1 \text{ (without reagent)}} \quad (13)$$

The quenching of NOEF effected by the relaxation reagent does not mean that the inverse-gated decoupling technique becomes unnecessary. If a given sample contains a number of non-equivalent ^{15}N nuclei, some of which have large negative NOEFs (for example, those in the NH , NH_2 , and NH_3^+ moieties), the relaxation reagent can cause such NOEFs to assume values that result in signal nulling. In such cases, the inverse-gated decoupling (Scheme 1, case (d)) should be used, and the relaxation delay RD should be first adjusted to optimize S/N for the ^{15}N nuclei with large negative NOEFs; then the flip angle α should be modified so as to correspond to the Ernst angle, equation (4), calculated on the basis of the slowly relaxing nuclei in the sample. In this way, we make certain that all of the NOEFs are sufficiently reduced, independently of the further optimization of the flip angle.

In general, for proton-decoupled ^{15}N spectra, the inverse-gated decoupling technique is recommended in order to get rid of at least a large part of the NOE. The only exceptions should be when one is interested only in the ^{15}N signals of moieties where the nitrogen atoms are bonded directly to protons (NH , NH_2 , etc.). Such moieties are usually characterized by large negative NOEFs, and one can take advantage of the latter from the point of view of the S/N ratio, and use the continuous decoupling method, with $\text{RD} = 0$, and the flip angle set to the Ernst angle. However, in the latter case, there is strong competition from polarization-transfer techniques which usually work best for such NH -type moieties and provide larger gains in sensitivity. The consideration above applies only to cases where the NH -type moieties do not exchange their protons with the surroundings. The exchange can reduce or virtually eliminate the NOE, with all the consequences thereof.

Polarization-transfer methods can be used profitably for ^{15}N measurements in numerous cases. Such methods transfer the corresponding proton polarization obtained when B_0 is applied into ^{15}N polarization, at least for some periods of time of the polarization-transfer experiment involved. The maximum gain in the S/N ratio relative to the standard S/N ratio is of the order of 9.86, on the basis of the polarization-transfer process alone; it is augmented by the fact that polarization-transfer methods in this case

allow one to optimize measurements on the basis of the T_1 values of protons rather than of the ^{15}N nuclei; the former are usually much shorter than those for ^{15}N . However, such methods suffer from a general drawback as far as the ^{15}N spectra of liquids and solutions are concerned, since the polarization transfer from ^1H to ^{15}N is then governed by the scalar couplings J between ^1H to ^{15}N , and the experiments have to be adjusted to some specific J values, with various consequences of a mismatch, which can even lead to signal nulling. The polarization transfer methods are usually arranged such as to virtually eliminate the "natural" ^{15}N signal intensities (i.e. those obtained owing to the ^{15}N polarization in B_0) and this eliminates all NOE enhancements that would be observed otherwise.

The *cross-polarization* technique of polarization transfer (CP) has already been used widely in solid-state NMR, and a number of applications thereof to solid-state ^{15}N NMR have appeared recently (Section IV.G). The method is based on the Hartmann-Hahn condition

$$\gamma(^1\text{H})B_1(^1\text{H}) = \gamma(^{15}\text{N})B_1(^{15}\text{N}) \quad (14)$$

where B_1 are the respective radiofrequency field vectors in the corresponding rotating frame coordinates. This is equivalent to a requirement that the precession rates of ^1H and ^{15}N in their respective coordinates be equal in order to induce polarization transfer from ^1H to ^{15}N . First, a 90° ^1H pulse is applied in order to bring the ^1H magnetization to the (x', y') plane in the rotating frame, for example, to the x' axis. The next step involves turning on the radiofrequency field along the x' axis, which corresponds to a 90° phase shift of B_1 relative to that of the pulse, simultaneously with a B_1 field in the ^{15}N frequency region, adjusted to match the Hartmann-Hahn condition, equation (14). During the latter step, polarization transfer takes place from ^1H to ^{15}N , and direct dipole-dipole interactions (direct couplings D) in the solid state are responsible for the transfer. Thus, a tolerance of the order of such interactions is acceptable in fulfilling the Hartmann-Hahn condition. After a time τ , adjusted to obtain optimum transfer, the ^{15}N field is turned off, and the free induction decay is collected while the ^1H field can be left on for decoupling purposes. Analogous techniques can be employed for liquid samples, but then the corresponding scalar couplings J are responsible for the transfer of polarization, hence the name *J-cross polarization* (JCP) method. In the latter case, the conditions are more stringent, since the scalar interactions are much smaller, and it is difficult to maintain the Hartmann-Hahn condition over a larger range of both J s and nitrogen shieldings. The function that relates the amount of polarization transfer to the contact time τ includes terms of the type $\sin^2(A\tau J)$ where A is a constant and J is the coupling responsible for the transfer; thus τ should be optimized on the basis of a given J . This, and the difficulties in

covering the large range of nitrogen shieldings of about 1000 ppm, limits the utility of the JCP method in ^{15}N NMR, and only a few works have appeared recently where the method is employed,¹¹⁴⁻¹¹⁶ in spite of some modifications thereof¹¹⁶ which can be termed adiabatic JCP.

Another method of polarization transfer that has a limited utility in ^{15}N NMR is the *selective population-transfer* (SPT) or *selective spin-inversion* (SPI) technique. It can be explained simply on the basis of an AX-type spectrum, where $A = ^{15}\text{N}$ and $X = ^1\text{H}$, which consists of two doublets, one in the ^{15}N frequency range, and the other in the proton spectrum. If we reverse the magnetization along the z axis of one of the components of the ^1H doublet, the population of the energy levels concerned are reversed, and this results in a transfer of the proton polarization to the energy-level pairs that are responsible for the ^{15}N transitions. The inversion of the magnetization is performed using a selective (long enough in order not to excite the other component) 180° pulse applied to one of the ^1H doublet components, followed by a ^{15}N exciting pulse, and the acquisition of the resulting ^{15}N FID. We do not consider the method in detail, since the details concerned are essentially the same as those in the more general INEPT method, which is given special attention in the present section. The limitation of the SPT method lies in the requirement of an *a priori* knowledge of the position of the proton transition to be irradiated, and the latter is usually a weak ^{15}N satellite signal in the proton spectrum involved. The method can be employed for the determination of the signs of couplings in ^1H - ^{15}N systems.^{91,117,118}

The *INEPT* (*insensitive nuclei enhancement by polarization transfer*) method is based essentially on the same principles as the SPT method, but the magnetization inversion of a half of the doublet components in the proton spectrum is effected non-specifically (thus comprising the entire range of the proton spectrum involved, without knowledge of the positions of the components) using a more refined pulse sequence (Scheme 2).

Let us consider a doublet pattern in a proton spectrum where the spacing of the doublet results from ^{15}N - ^1H spin-spin coupling and is equal to $|J(\text{N-H})|$

$$\begin{array}{ccccc} H_A & | \leftarrow J(\text{N-H}) \rightarrow | & H_B & & \\ \nu_A & & \nu_B & & \leftarrow \nu \end{array}$$

where ν_A and ν_B are the corresponding frequencies relative to that of the proton-exciting pulse and, obviously, $\nu_A - \nu_B = |J(\text{N-H})|$. We also assume that the angles of the magnetization vectors within the (x', y') plane of the rotating-frame coordinates, corresponding to the pulse frequency, are referred to the $+y'$ direction. Let us follow the angles of the vectors corresponding to H_A and H_B under conditions of the INEPT sequence (Scheme 2):

SCHEME 2
INEPT method of polarization transfer from ^1H to ^{15}N

Frequency channel	Repeated timing sequence							
^{15}N		PW	τ	PW	DE	AQ		
		$180^\circ_{x'}$		$90^\circ_{x'}$				
^1H	PW	τ	PW	τ	PW	DE	DCPL	RD
	$90^\circ_{x'}$		$180^\circ_{x'}$		$90^\circ_{y'}$			

PW = pulse width (with flip angle and axis specified)
 τ = delay in spin-inversion sequence
 DE = refocusing delay
 AQ = acquisition of FID
 DCPL = decoupler status during AQ (on or off)
 RD = relaxation delay for protons

If one selects $\tau = (4J(\text{N-H}))^{-1}$ then the angles for H_A and H_B become $+90^\circ$ and -90° respectively, independently of the actual frequencies ν_A and ν_B . Thus the respective magnetization vectors are brought to the $+x'$ and $-x'$ axes of the rotating frame. The $90^\circ_{y'}$ ^1H pulse turns them into the $+z$ and $-z$ axes respectively (parallel and antiparallel to B_0), thus effecting the spin

	H_A	H_B
After $90^\circ_{x'}$ ^1H pulse	0°	0°
After first delay τ	$360^\circ \times \nu_A \tau$	$360^\circ \times \nu_B \tau$
After $180^\circ_{x'}$ ^1H pulse	$-360^\circ \times \nu_A \tau$	$-360^\circ \times \nu_B \tau$
After simultaneous 180° ^{15}N pulse (this inverts ^{15}N spins)	$-360^\circ \times \nu_B \tau$	$-360^\circ \times \nu_A \tau$
After second delay τ	$-360^\circ \times \nu_B \tau$ $-360^\circ \times \nu_B \tau$ $+360^\circ \times \nu_A \tau$ $\underbrace{\hspace{1.5cm}}$ $360^\circ \times \tau J(\text{N-H}) $	$-360^\circ \times \nu_A \tau$ $-360^\circ \times \nu_A \tau$ $+360^\circ \times \nu_B \tau$ $\underbrace{\hspace{1.5cm}}$ $-360^\circ \times \tau J(\text{N-H}) $

inversion of a half of the doublet, and polarization transfer into the corresponding ^{15}N transitions. The simultaneous 90° ^{15}N pulse brings the enhanced ^{15}N magnetization into the respective (x' , y') plane, and allows one to collect the ^{15}N FID. If there is no delay ($\text{DE} = 0$, Scheme 2) before

the FID acquisition, the resulting spectrum is proton-coupled, intensity-enhanced, but the ^{15}N multiplet components show phase differences (180° if the ^{15}N signal is a doublet). Any attempt at proton decoupling at this stage (i.e. during the immediate acquisition) would simply null all the polarization transfer enhancement. If we introduce some delay (refocusing delay, DE, Scheme 2) before starting the acquisition, AQ, which allows the ^{15}N multiplet components to converge, then the resulting spectrum will show phase-coherent multiplet patterns (*refocused INEPT*). If the proton decoupler is turned on during the acquisition, AQ, in this case, enhanced and proton-decoupled spectra are obtained (*decoupled, refocused INEPT*). The refocusing delay, DE, is also adjusted on the basis of the $J(\text{N-H})$ concerned, but the number of protons coupled with the ^{15}N nucleus, where the coupling involves the same $J(\text{N-H})$ must be taken into account. After the end of the FID acquisition, a relaxation delay RD is introduced before repeating the sequence, in order to allow the proton magnetization to relax.

Thus the INEPT method can provide polarization-transfer enhancement in both proton-coupled and decoupled ^{15}N spectra. The enhancement, however, depends critically on the adjustment of essentially three parameters: the magnitude of the coupling $J(\text{N-H})$ that is responsible for the polarization transfer (this determines τ and, partly, DE, Scheme 2), the expected multiplet pattern of ^{15}N (this determines DE for a given $J(\text{N-H})$), and the expected T_1 value of the protons (this determines RD). Before proceeding to a more detailed discussion of the intensity gains obtainable in INEPT ^{15}N measurements, we present an equation for the S/N ratio in ^{15}N INEPT spectra referred to the standard S/N ratio; the equation is approximate, and can be inferred from the general principles of INEPT:

$$\begin{aligned} \frac{(S/N)_{\text{INEPT}}}{(S/N)_{\text{standard}}} &= \left(\frac{T_2^*}{0.3} \right)^{1/2} \exp\left(-\frac{4\tau}{T_1} \right) \exp\left(-\frac{2 \text{ DE}}{T_2^*} \right) \\ &\times \frac{1 - \exp(-\text{RD}/T_1)}{(\text{AQ} + \text{RD} + 2\tau + \text{DE})^{1/2}} \\ &\times \sin(360^\circ \times J(\text{N-H})\tau) A \times 9.86 \end{aligned} \quad (15)$$

where T_1 is the spin-lattice relaxation time for the protons (it is assumed here to be equal to T_2), T_2^* represents the ^{15}N signal width, $(\pi T_2^*)^{-1}$; τ , DE and RD are the corresponding delay times according to Scheme 2, AQ is the FID acquisition time; finally, A is the refocusing term, which is the average of the A_n terms,

$$A_n = \sin(360^\circ \times nJ(\text{N-H}) \text{ DE}) \quad (16)$$

for the corresponding multiplet pattern of ^{15}N upon proton-decoupling:

^{15}N pattern	Values of n	Value of A
N(H)	1	A_1
N(H)_2	2	A_2
N(H)_3	1, 3	$\frac{1}{2}(A_1 + A_3)$
N(H)_4	2, 4	$\frac{1}{2}(A_2 + A_4)$

where the ^{15}N multiplet patterns are given in terms of the number of protons (not necessarily of those bound directly to the nitrogen atom involved) coupled to the ^{15}N nucleus with the same value of J . Equations (15) and (16) yield the following *optimum values* of the delay times τ and DE (Scheme 2) for a given value of J :

$$\left. \begin{aligned} \tau &= (4J(\text{N-H}))^{-1} \\ \text{DE} &= (4J(\text{N-H}))^{-1} \quad \text{for N(H) pattern} \\ \text{DE} &= (8J(\text{N-H}))^{-1} \quad \text{for N(H)}_2 \text{ pattern} \\ \text{DE} &= (10J(\text{N-H}))^{-1} \quad \text{for N(H)}_3 \text{ pattern} \\ \text{DE} &= (12J(\text{N-H}))^{-1} \quad \text{for N(H)}_4 \text{ pattern} \end{aligned} \right\} \text{maximum signal}$$

One should also consider the consequences of adjusting DE for a given pattern on other patterns:

DE	N(H)	Value of A for pattern specified		
		N(H)_2	N(H)_3	N(H)_4
$(4J(\text{N-H}))^{-1}$	1	0	0	0
$(8J(\text{N-H}))^{-1}$	0.71	1	0.71	0.50
$(10J(\text{N-H}))^{-1}$	0.59	0.95	0.77	0.77
$(12J(\text{N-H}))^{-1}$	0.50	0.87	0.75	0.87
proton-decoupled				

Thus, setting $\text{DE} = (4J(\text{N-H}))^{-1}$ optimizes ^{15}N (H)-type signals, but results in signal nulling of the other patterns; it is therefore safer, unless one is interested in ^{15}N (H) signals only, to set DE for the ^{15}N (H)₂ or ^{15}N (H)₃ pattern in order to get a reasonable coverage of all four pattern types.

In INEPT routines of spectrometer systems, it is usually sufficient to specify $J(\text{H-N})$ and the multiplet pattern, and this automatically sets τ and DE; if one knows or assumes the value of T_1 for the protons concerned, it is possible to optimize the relaxation delay RD (Scheme 2) using equation (15).

Since it is obvious from the considerations above that an INEPT ^{15}N measurement must be set to some specific value of $J(\text{N-H})$, one should consider also the consequences of such a setting for ^{15}N signals with $J(\text{N-H})$ values other than that assumed. The simplest way is to use equation (15), but there are rather simple rules as far as signal nulling is concerned:

Assumed parameters $J^{\text{assumed}}(\text{N-H})$	Values of $J(\text{N-H})$ that result in signal nulling ($k = 0, 1, 2, 3, \dots$) for actual patterns specified
N(H) pattern	$2kJ^{\text{assumed}}(\text{N-H})$ for N(H), $kJ^{\text{assumed}}(\text{N-H})$ for other patterns
N(H) ₂ pattern	$2kJ^{\text{assumed}}(\text{N-H})$ for all patterns

Additional nulling points occur when the actual pattern is N(H)₄ and when the assumed pattern is N(H)₃ or N(H)₄; these can be evaluated from equation (15).

The simplest case in the use of the INEPT method for ^{15}N spectra involves moieties such as NH, NH₂, NH₃⁺, etc. In most cases, $^1J(^{15}\text{N-H}) = -90 \pm 10$ Hz (Table 130, and ref. 1, Table 145 therein), and thus setting the procedure to $J(\text{N-H}) = 90$ and the N(H)₂ pattern should give significantly enhanced signals for such moieties, even if one does not know in advance the actual values of $J(\text{N-H})$ and the actual patterns involved. In the latter case, the nearest nulling points occur at $J(\text{N-H}) = 0$ and $J(\text{N-H}) = 180$ Hz, far enough from the range of the couplings concerned. However, the ^{15}N nuclei in such moieties are usually characterized by rather short T_1 times and favourable NOEFs, and thus the net gain in sensitivity over conventional measurements with continuous proton decoupling is not as formidable as in the cases of slowly relaxing ^{15}N nuclei, with unfavourable NOEFs. The latter situations usually require that the INEPT procedure be set to long-range $J(\text{N-H})$ values whose absolute magnitudes range from nearly zero to about 20 Hz. In such cases, one should set $J(\text{N-H})$ as close to the actual value as possible, but one should remember that, according to equation (15), even at the limits $\pm 0.5J^{\text{assumed}}(\text{N-H})$, the INEPT enhancement drops to one half of its maximum value for the case concerned, and this still provides a substantial gain in signal intensity obtained within a given period of time. The use of long-range $^{15}\text{N-H}$ couplings in the INEPT method has still another advantage; it relieves the method from proton exchange effects in groups like NH and NH₂, which can destroy the polarization transfer through the couplings across one bond, $^1J(\text{N-H})$. It is true that smaller $J(\text{N-H})$ values require longer delays τ and DE (Scheme 2), but even if $J(\text{N-H}) = 5$ Hz, the sum $\tau + \tau + \text{DE}$ does not exceed 0.15 s, which is not much compared with the acquisition time required for obtaining a reasonable digital resolution, $\text{AQ} = 0.5\text{--}1$ s. The opinion expressed in ref. 110, p.

34, that the INEPT method is less appropriate when one has to employ long-range ^{15}N - ^1H couplings seems to be quite erroneous; actually, recent applications of the method to ^{15}N NMR employed long-range couplings¹¹⁹⁻¹²⁵ as well as one-bond couplings.^{118,126-132} In rare cases where the quadrupole relaxation rates of ^{14}N are slow enough, and $J(^{14}\text{N}-^1\text{H})$ splittings appear in the corresponding spectra, the INEPT procedure can be employed for obtaining polarization-transfer-enhanced ^{14}N spectra.¹³³

The question arises as to whether it is possible to find a single value of $J(\text{N-H})$ that could be used for setting an INEPT procedure in order to provide a good coverage of most of the actual values of ^{15}N - ^1H couplings; needless to say, such a value should lie within the range of long-range $J(\text{N-H})$ values. In principle, setting the INEPT sequence to $J(\text{N-H}) = 10$ Hz should adequately cover a range of $J(\text{N-H})$ from 5 Hz to 15 Hz; if the $\text{N}(\text{H})_2$ pattern is assumed there will be nulling points at 0, 20, 40, 60, 80, 100, 120 Hz, etc., for $\text{N}(\text{H})$, $\text{N}(\text{H})_2$ and $\text{N}(\text{H})_3$ patterns, and, from the point of view of $^1J(\text{N-H})$, a range of 90 ± 5 Hz should be covered. However, the latter is too small and, moreover, the long delays τ and DE (compared with those set directly to correspond to $^1J(\text{N-H})$) make the enhancement sensitive to pulse and timing imperfections. The setting of DE to an $\text{N}(\text{H})_2$ pattern also reduces the maximum enhancement available for the other patterns. One can check, using equation (15), that $J(\text{N-H})$ values other than 10 Hz do not improve the situation; nevertheless, three INEPT experiments, set to $J(\text{N-H}) = 5, 10$, and 90 Hz, respectively, should cover a good deal of the possible values of $J(\text{N-H})$, both long-range type and those across one bond, when one does not have enough information about $J(\text{N-H})$ values in the sample examined.

There is another simple application of the INEPT method: that based on a detailed knowledge of $J(\text{N-H})$ data. The latter can be measured for the compound examined, or any related model compound, either at a high concentration of the latter or using ^{15}N enrichment. The $J(\text{N-H})$ values obtained may be employed then for setting the INEPT sequence in the case of dilute solutions of the compound concerned.

Equations (7), (8), (10), (12) and (15) allow one to directly compare the S/N ratios that can be obtained in ^{15}N NMR measurements using various techniques. Let us consider an example of a ^{15}N nucleus in pyridine, where the ^{15}N relaxation is fairly slow, and the NOE is unfavourable (Case Study I); this is a typical situation for ^{15}N nuclei in aromatic heterocycles. It is evident from Case Study I that the use of the Ernst angle as the flip angle, with the relaxation delay $\text{RD} = 0$, has an advantage over any other combination of values of α and RD , even if one of them is set and the other is optimized. There is also a clear indication of a considerable gain in the S/N ratio available upon inverse-gated decoupling of protons in order to quench unfavourable NOEFs. Here the gain is about twofold when

CASE STUDY I

Pyridine (neat liquid); $T_1(^{15}\text{N}) = 85\text{ s}$, $T_1(^1\text{H}) = 12\text{ s}$, $T_2^*(^{15}\text{N}) = 0.3\text{ s}$, $\text{NOEF}(^{15}\text{N}) = -0.4$.

General settings: $\text{AQ} = 1\text{ s}$, $\text{LB} = 1\text{ Hz}$.

Spectrum	$(S/N)/(S/N)_{\text{standard}}$
1. Normal PFT spectrum with continuous decoupling. Parameter set: $\alpha = 90^\circ$. Parameter optimized: $\text{RD} = 106\text{ s}$	0.04153
2. Normal PFT spectrum with continuous decoupling; Ernst angle used. Parameter set: $\text{RD} = 0$. Parameter optimized: $\alpha = 8.8^\circ$	0.04600
3. Normal PFT spectrum with inverse-gated decoupling. Parameters optimized: $\alpha = 49.4^\circ$, $\text{RD} = 35.6\text{ s}$, $\eta = 0.025$	0.07550
4. Decoupled, refocused INEPT spectrum, set to $^2J(\text{N-H}) = -10.93\text{ Hz}$ and N(H)_2 -type pattern. Parameter optimized: $\text{RD} = 16.5\text{ s}$	1.6238

Note: relaxation data from refs. 110, 113.

the relaxation delay RD is optimized (the flip angle α and the fraction of NOEF retained, η , are optimized automatically, for a given RD , from equation (12)). Finally, the advantage of the INEPT method is shown to amount to about a 20-fold increase in the S/N ratio in this case over the conventional PFT method with inverse-gated decoupling. In this case the INEPT sequence is adjusted to the exact value of $^2J(\text{N-H})$; one can calculate, however, that a mismatch of about 5 Hz in this situation would only halve the gain in S/N .

Now, we turn to the effects exerted by relaxation reagents on the S/N ratio, and we use the same model compound, pyridine (Case Study II). In this case, the use of the relaxation reagent results in a considerable increase in the S/N ratio compared with those in Case Study I. This is valid provided that the reagent reduces T_1 without significantly affecting T_2^* or, in other words, the ^{15}N signal width.

The situations shown in Case Studies I and II for pyridine are typical for the ^{15}N nuclei in nitrogen atoms that bear lone-pair electrons and are not bound directly to hydrogen atoms. Such ^{15}N nuclei are characterized usually by fairly long T_1 values and unfavourable NOEFs (about -1). Moieties like NH and NH_2 are often characterized by rather short T_1 values of their ^{15}N nuclei, and usually by large negative NOEFs , provided that the protons are not exchanged with the environment. Such large negative NOEFs , particularly if combined with short T_1 data, constitute an asset in conventional PFT measurements with continuous decoupling; if, however, one has to take account of other types of ^{15}N nuclei in a given sample,

CASE STUDY II

Pyridine (neat liquid + 0.05 M Cr(acac)₃); $T_1(^{15}\text{N}) = 3.9$ s, $T_2^*(^{15}\text{N}) = 0.3$ s, $T_1(^1\text{H}) = 0.3$ s,
 $\text{NOEF}(^{15}\text{N})_{\text{calculated}} = -0.018$.

General settings: AQ = 1 s, LB = 1 Hz.

Spectrum	$(S/N)/(S/N)_{\text{standard}}$
1. Normal PFT spectrum with continuous decoupling. Parameter set: $\alpha = 90^\circ$. Parameter optimized: RD = 3.9 s	0.3173
2. Normal PFT spectrum with continuous decoupling; Ernst angle used. Parameter set: RD = 0, Parameter optimized: $\alpha = 39.3^\circ$	0.3507
3. Normal PFT spectrum with inverse-gated decoupling. Parameters optimized: $\alpha = 47.7^\circ$, RD = 0.55 s, $\eta = 0.60$	0.3519
4. Decoupled, refocused INEPT spectrum, set to $^2J(\text{N}-\text{H}) = -10.93$ Hz and $\text{N}(\text{H})_2$ type pattern. Parameter optimized: RD = 0.8 s	4.6238

Note: relaxation data from ref. 1.

using the inverse-gated decoupling technique or relaxation reagents, the large negative NOEFs of the NH-type moieties can be brought accidentally to the unfavourable range around the nulling condition, $\text{NOEF} = -1$. In such cases it is important to choose a strategy that will result in reducing the large negative NOEFs to about zero. Examples of such strategies are shown in Case Studies III and IV. There is still another type of ^{15}N nucleus from the point of view of relaxation and NOE properties. This is characterized by very long T_1 values, and essentially negligible NOEFs; this occurs when the relaxation rates of ^{15}N are governed mostly by mechanisms other than the dipole-dipole interaction mechanism. This situation takes place in the case of nitro groups, NO_2 , bound to large hydrocarbon moieties as well as in some amino groups, NR_3 , where the Rs are alkyl or aryl groups, particularly if the latter prevent any significant interactions of the lone-pair electrons of the nitrogen atoms with the environment. In such cases, the optimum strategy seems to involve simply setting the flip angle to correspond to the Ernst angle for a given (known or assumed) T_1 , and RD = 0; this also includes situations where relaxation reagents are used in order to shorten the long T_1 . However, it is better to assume a small value of NOEF, say -0.05 , and to adjust an optimum inverse-gated-decoupling sequence, since the latter can be useful in eliminating the unfavourable NOEFs of other ^{15}N nuclei.

Needless to say, the distinction between the three types of ^{15}N nuclei is quite approximate, but allows one to consider the consequences of various

compromises that have to be made from the point of view of obtaining the ^{15}N spectra of samples with a variety of nitrogenous moieties. Let us consider first a contrived example shown in Case Study III, which is concerned with a ^{15}N spectrum containing three signals, representing the three kinds of ^{15}N nuclei.

CASE STUDY III

Contrived example, three different ^{15}N signals, no relaxation reagent used.

General settings and parameters: $AQ = 1\text{ s}$, $LB = 1\text{ Hz}$, $T_2^* = 0.3\text{ s}$.

1- ^{15}N : $T_1 = 10\text{ s}$, $\text{NOEF} = -4.93$.

2- ^{15}N : $T_1 = 50\text{ s}$, $\text{NOEF} = -1.00$.

3- ^{15}N : $T_1 = 150\text{ s}$, $\text{NOEF} = -0.05$.

Spectrum	$(S/N)/(S/N)_{\text{standard}}$
1. PFT spectrum with continuous decoupling, optimized for 1-N. $\alpha = 25.2^\circ$, $\text{RD} = 0$	(-) 0.8784 for 1-N 0.0000 for 2-N (nulled) 0.0266 for 3-N
2. PFT spectrum with inverse-gated decoupling, optimized for 2-N. $\alpha = 70.7^\circ$, $\text{RD} = 54.3\text{ s}$, $\eta(2\text{-N}) = 0.01$. Resulting values: $\eta(1\text{-N}) = 0.0004$, $\eta(3\text{-N}) = 0.015$	0.1263 for 1-N 0.0944 for 2-N 0.0507 for 3-N
3. PFT spectrum with inverse-gated decoupling, optimized for 3-N. $\alpha = 39.1^\circ$, $\text{RD} = 29.2\text{ s}$, $\eta(3\text{-N}) = 0.03$. Resulting values: $\eta(1\text{-N}) = 0.005$, $\eta(2\text{-N}) = 0.024$	0.132 for 1-N 0.0838 for 2-N 0.0576 for 3-N

We recall that for continuous-decoupling experiments RD is set to zero, and α is set to the corresponding Ernst angle (for 1-N in this case); equation (12) is used for 1-N, and equation (7) for 2-N and 3-N. For the inverse-gated decoupling procedures RD is optimized for either 2-N or 3-N, and the other parameters follow automatically from equation (12) (and equation (10)) for the signal being optimized; the α and RD values thus obtained are then used in equation (7) (and equation (10)) to calculate S/N and η values for the other signals.

Spectrum 1 in Case Study III shows clearly that the largest intensities (S/N ratios) for 1-N nuclei (these represent NH-type moieties) are obtained when one makes use of the favourable NOEFs; but this can either null (owing to unfavourable NOEFs) or significantly reduce (owing to saturation effects) the 2-N and 3-N signals, which represent slowly relaxing ^{15}N nuclei. Thus the conditions of spectrum 1 can be recommended, with any modifications in the flip angle value that may result from a more detailed knowledge of T_1 , for cases where one is interested in NH-type moieties

only; however, the use of the INEPT technique set to $J(\text{N-H}) \approx 90$ Hz should give still larger intensities, comparable to that in Case Study I, spectrum 4.

If one is interested in the slowly relaxing nuclei 2-N and 3-N one has to sacrifice the NOE enhancement of 1-N, but then efforts should be made in order to quench all the NOEFs, including those of 1-N nuclei, using the inverse-gated decoupling sequence. Fortunately, it is evident from spectra 2 and 3 in Case Study III that the optimization of the sequence for either 2-N or 3-N type nuclei reduces the NOEF for 1-N to negligibly small values. This happens owing to the simple fact that large negative NOEFs are usually accompanied by rather short T_1 values and small negative NOEFs correspond to long T_1 values; we recall that T_1 is also responsible for the relaxation of the NOE concerned. Thus the strategy in the case of PFT ^{15}N spectra when one does not use any relaxation reagent, and one is interested in various nitrogenous moieties that can be present in the sample examined, is fairly simple; one should adjust the measurement to slowly relaxing nuclei. The data from Case Study III indicate that inverse-gated decoupling should be employed, and the following set of parameters can be recommended:

$$\text{RD (in seconds)} / \alpha (\text{degrees}) = \frac{3}{4}$$

within the limits $\text{RD} = 55$ s, $\alpha = 70^\circ$ and $\text{RD} = 30$ s, $\alpha = 40^\circ$, for the acquisition time $\text{AQ} = 1$ s. For other AQ values, one can simply calculate other relevant sets, using equations (7) and (12) and the data from Case Study III (except AQ).

From this point of view, let us consider the parameter sets recommended in ref. 109 (p. 20, Table 2.2 therein); the values suggested there imply that for general purposes, RD should be set to about 10 s, and the flip angle α to about 30° . Using these values under the conditions of Case Study III yields the following S/N values: 0.0836 for 1-N, 0.0581 for 2-N and 0.0543 for 3-N; except for 3-N, where the values are comparable, the latter results are evidently inferior to those obtained in Case Study III, particularly for 2-N type nuclei.

Since the S/N ratios available in PFT measurements of ^{15}N are often not large enough to obtain usable signals in a reasonable time, particularly for slowly relaxing ^{15}N nuclei, paramagnetic relaxation reagents, such as $\text{Cr}(\text{acac})_3$, are often employed in order to enhance the signals concerned (Case Study II). However, if the sample examined contains 1-N type nuclei (Case Study III), the relaxation reagent can reduce the NOEFs concerned to still significant values, but they occur in the nulling range, $\text{NOEF} \approx -1$. Thus the strategy in such cases should be different from that used when no relaxation reagent is employed. The inverse-gated decoupling technique is still recommended here, but it should be adjusted to quenching the residual

NOEFs of 1-N type nuclei, or, in other words, the relaxation delay RD should be optimized from this point of view. Then, in order to improve the intensities of 2-N and 3-N type signals, one should retain the RD, and adjust the flip angle as the Ernst angle calculated on the basis of the T_1 expected, and the sum of RD+AQ, according to equation (4). This is considered in Case Study IV, which is a modification of Case Study III. It is assumed that $\text{Cr}(\text{acac})_3$ is used as a relaxation reagent for the ^{15}N nuclei from Case Study III, and that the reagent reduces the corresponding T_1 and NOEF values (equation (13)) by a factor of $\frac{1}{15}$. The latter factor can vary significantly from compound to compound, and certainly depends on the concentration of the reagent used, but we simply assume its value as being close to that observed experimentally for pyridine (Case Studies I and II).

CASE STUDY IV

Contrived example, three different ^{15}N signals, 0.05 M $\text{Cr}(\text{acac})_3$ used as relaxation reagent.

General settings and parameters: AQ = 1 s, LB = 1 Hz, $T_2^* = 0.3$ s.

1- ^{15}N : $T_1 = 0.7$ s, NOEF = -0.35.

2- ^{15}N : $T_1 = 3$ s, NOEF = -0.06.

3- ^{15}N : $T_1 = 10$ s, NOEF = 0.00.

Spectrum	$(S/N)/(S/N)_{\text{standard}}$
1. PFT spectrum with inverse-gated decoupling, RD optimized for 1-N, then flip angle optimized for 2-N. $\alpha = 56.5^\circ$, RD = 0.78 s, η (1-N) = 0.27	0.5448 for 1-N 0.3906 for 2-N 0.1894 for 3-N
2. PFT spectrum, with inverse-gated decoupling, RD optimized for 1-N, then flip angle optimized for 3-N. $\alpha = 33.2^\circ$, RD = 0.78 s, η (1-N) = 0.27	0.3663 for 1-N 0.3314 for 2-N 0.2233 for 3-N

Thus the results obtained in Case Study IV suggest the following set of parameters to be used when relaxation reagents are employed: inverse-gated decoupling, a relaxation delay RD of about 0.8 s, and a flip angle of 55° - 35° , if AQ = 1 s. These can be accepted as trial values when one does not have any detailed information about the actual relaxation times in the presence of the reagent. If such information is available, it is fairly simple to use the same strategy as in Case Study IV, and equations (7) and (12), in order to adjust the parameters concerned.

So far, we have considered two methods of eliminating the adverse consequences of long T_1 times (relative to T_2^*) for ^{15}N nuclei. *Polarization-transfer techniques* allow one to take advantage, of the shorter T_1 times for the corresponding ^1H nuclei, in addition to the signal enhancement due to

the polarization transfer from ^1H to ^{15}N . The use of paramagnetic *relaxation reagents* results in a reduction of T_1 , but such effects are sometimes selective, since the reagents can be considered as Lewis acids, which are prone to bind with basic nitrogenous moieties. Evidence of that may be found in Table 7 of ref. 1, which shows the intrinsic changes in nitrogen shieldings effected by such reagents; the changes are often small, but they become significant for such nuclei as ^{15}N in pyridine. In addition, the reagents can give rise to quite considerable apparent changes in nitrogen shieldings owing to bulk-susceptibility effects (Section III). The most popular relaxation reagent in ^{15}N NMR is certainly $\text{Cr}(\text{acac})_3$, but some other chelates may be employed (ref. 1, p. 22); for aqueous solutions some Gd complexes are recommended. Recently, a Gd complex with diethylenetriaminepenta-acetic acid, $\text{Gd}(\text{DTPA})^{2-}$, has been suggested as a "non-specific" relaxation reagent for aqueous solutions, and a Gd complex with triethylenetetraaminehexacetic acid, $\text{Gd}(\text{TTHA})^{3-}$, as a "specific" reagent.¹³⁴ However, the latter investigations include only three model compounds, imidazole, pyrrolidine and pyridine; thus the question of specificity or non-specificity of the reagents seems to be open. The effectiveness of relaxation reagents in increasing the S/N ratio within a given time of spectrum accumulation is limited to situations where the reagents reduce T_1 without any significant shortening of T_2^* (equations (7) and (12)). There is still another method of shortening T_1 ; this relies on the use of *viscous solvents*. The viscosity has to be adjusted such as to reduce T_1 without signal broadening, as in the case of relaxation reagents; this requires that the extreme narrowing condition be fulfilled. Calculations show¹³⁵ that at the ^{15}N resonance frequency of 9.04 MHz (magnetic field of 2.11 T) the maximum viscosity acceptable on theoretical grounds is about 6.6 poise. However, experiments indicate¹³⁵ that much higher viscosities may be employed. This is attributed to appreciable differences between macro- and microviscous effects. Therefore glycerol (viscosity of ca. 8 poise) is suggested for water-soluble molecules, and toluene saturated with polystyrene (viscosity of ca. 50–80 poise) for compounds that are soluble in organic solvents.

As far as ^{14}N PFT spectra are concerned, the problems are quite different from those concerning ^{15}N spectra. Usually, the relaxation of ^{14}N nuclei is governed by the quadrupole relaxation interaction, so that $(T_Q)^{-1} = (T_1)^{-1} = (T_2^*)^{-1}$; the corresponding signal widths can vary from a few hertz to a few kilohertz, or, in other words, $T_1 = T_2^* = T_Q$ can be found within a range of 0.1–0.0001 s. There is no problem with saturation effects, such as those in ^{15}N NMR where $T_1(^{15}\text{N})$ is usually much longer than T_2^* ; the effective NOE in the case of ^{14}N is essentially zero, because of the dominant contribution of $(T_Q)^{-1}$ in the overall relaxation rate. However, there is an acute problem due to diverse values of $T_1 = T_2^* = T_Q$ that can be found in ^{14}N spectra. Equations (7) and (12) indicate that, for a given value of $T_1 = T_2^*$, one can

obtain the maximum value of about 1 for the S/N ratio (referred to $(S/N)_{\text{standard}}$) if the flip angle α is set to about 90° while the acquisition time AQ is set to (πT_2^*) , the reciprocal signal width. This setting will result in reduced S/N ratios for signals characterized by other widths. For example the ^{14}N signal of nitromethane is characterized by a half-height width of *ca.* 10 Hz ($T_1 \approx 0.03$ s); the optimum setting would then be $\alpha \approx 90^\circ$, $AQ = 0.1$ s, $RD = 0$ (Scheme 1, and the corresponding S/N value would be about 1. The same setting used in the case of a ^{14}N signal with $T_1 = 0.0003$ s (signal width of about 1000 Hz) will give $S/N = 0.1$; the latter includes, of course, the reduction in the S/N ratio that results from the larger width, but it also includes the enhancement due to the use of a matched filter, $LB = 1000$ Hz compared with $LB = 10$ Hz for nitromethane. If the latter line-broadening factor is employed for the broad signal, the S/N ratio drops to 0.01. Thus, if the measurement is adjusted to a maximum S/N ratio for the sharp ^{14}N resonance signal of the standard, nitromethane, the S/N ratios for broader signals decrease proportionally to their respective widths. If AQ and LB are chosen to match a broad signal, the resonance of the standard is also broadened, and can show additional disturbances in its lineshape, those resulting from the FID truncation at some still significant value. Therefore, if precise values of ^{14}N shieldings are required, it is better to adjust the parameters to the resonance of the standard, since high-precision results in ^{14}N NMR can be obtained only by lineshape fitting procedures; one should then avoid any disturbances in the respective lineshapes that cannot be included simply into the corresponding lineshape equations. One should also remember that the problem of sensitivity is less severe for ^{14}N spectra, compared with ^{15}N , since the standard S/N ratio for the former is some 250 times higher than for the latter at the ^{15}N natural abundance. Thus, if a ^{14}N signal with a width of 1000 Hz yields $S/N = 0.01$ (in terms of $(S/N)_{\text{standard}}$) this corresponds to an S/N value of 2.5 for ^{15}N (Case Studies I-IV) at its natural abundance level; such values for ^{15}N are available only upon polarization transfer from protons.

It should be mentioned that recently an application of PFT ^{14}N spectra to NMR "imaging" has been reported;¹³⁶ this involves the determination of the spatial distribution of nitrogen within a sample consisting of a sample tube filled with water, with two ampoules immersed, one containing saturated aqueous NH_4Cl , and the other containing aqueous 4 M acetylcholine bromide. This case is concerned with rather sharp signals; further investigations in this field should be interesting.

B. Continuous-wave (CW) method

Continuous-wave excitation in nitrogen NMR is occasionally employed, but only for ^{14}N NMR spectra, for which, the advantage of PFT over CW

excitation can be negligible, particularly if broad resonance signals are involved (see e.g. ref. 111, p. 109). IN CW ^{14}N NMR rather fast sweep rates can be used, without producing any significant transient effects on the lineshape concerned: combined with the use of high-intensity radio-frequency fields B_1 , this can improve the sensitivity available in CW ^{14}N NMR. In most cases of ^{14}N nuclei, $T_Q = T_1 = T_2^*$, and the following requirement should be fulfilled in order to avoid transient effects in CW ^{14}N spectra:

$$\frac{\text{SW}}{t} < (2\pi T_Q^2)^{-1} \quad (17)$$

where SW is the spectral width, t is the time of the sweep, SW/t is the sweep rate. Usually, the sharpest signal in a ^{14}N spectrum is that of nitromethane ($T_Q \approx 0.03$ s) used as a standard. Thus equation (17) shows that sweep rates as fast as about 100 Hz/s can be employed, which correspond to sweep times of 25–250 s, depending on the external magnetic field, for the whole range of nitrogen shieldings. Sweep times of 25 s were actually used in the ^{14}N measurements reported in Table 6, notes (a) and (e).

The problem of spectral resolution in ^{14}N NMR spectra is more severe than in ^{15}N spectra, because of the large signal widths of ^{14}N . However, this is concerned with signals of comparable widths and with relatively small differences in the nitrogen shieldings involved. If the widths are appreciably different, it is fairly easy to resolve signals, even if they are characterized by exactly the same nitrogen shielding, using lineshape fitting procedures. This is particularly true when the differential saturation technique is employed (see ref. 1, pp. 23, 24, for a discussion and the corresponding lineshape equations) where audiofrequency modulation sidebands are generated in addition to the central band and advantage is taken of the different saturation levels in the sidebands compared with the central band. The technique is quite simple and yields, in addition to precise values of ^{14}N shieldings, the corresponding relaxation rates and relative numbers of ^{14}N nuclei.

C. Double-resonance methods, including two-dimensional techniques

Simple double-resonance measurements of nitrogen shieldings, those based on the observation of proton spectra under conditions of ^{15}N decoupling, are now employed only rarely,^{137–142} since their practical use is limited to ^{15}N -enriched samples or to rare instances where ^{14}N – ^1H couplings are resolvable in the proton spectra (the latter obviously involve ^{14}N decoupling).

Double-resonance experiments at the natural abundance level of ^{15}N can be performed using ^1H – ^{15}N *double-resonance difference spectroscopy*, which usually employs the PFT technique and a subtraction of ^{15}N -decoupled

proton spectra from the corresponding non-decoupled proton spectra. The subtraction is performed at the stage of free-induction decays. The method is also known as AISEFT (abundant isotope signal elimination by Fourier transformation) since the transformation of the accumulated differences in the FIDs should give essentially only the ^{15}N -coupled proton signals (ref. 4, p. 147, and references therein). The method has recently been used in determining ^{15}N shieldings in tRNA of *Escherichia coli*¹⁴³ and ^1H - ^{15}N spin-spin couplings in partially oriented phthalonitrile.¹⁴⁴

More refined techniques use ^1H - ^{15}N *two-dimensional* PFT spectroscopy (2D spectroscopy) in order to provide contour maps which allow one to trace ^{15}N - ^1H coupling relations between the corresponding ^1H and ^{15}N spectra even in large and complicated molecules of biological interest.^{131,145} Such techniques are important from the point of view of ^{15}N signal assignments. They suffer, however, from the low sensitivity of ^{15}N NMR at the natural abundance of ^{15}N . The latter difficulty can be overcome, at least to a significant degree, by including polarization transfer from protons to ^{15}N into 2D spectroscopy procedures (ref. 1, p. 127, and references therein). Recently, still more powerful techniques in the field of two-dimensional ^1H - ^{15}N spectroscopy have appeared; they make use of *multiple quantum coherence*, which, in theory, can provide ^{15}N signal enhancements larger by an order of magnitude relative to that obtained by polarization transfer.¹⁴⁶ Such pulse sequences have to be adjusted to a given value of $J(\text{N-H})$ as well as to a given multiplet pattern (for example, NH), as is the case in INEPT sequences (Section IV.A). The simplest sequence is given in Scheme 3; various modifications thereof are available,¹⁴⁶ and they can offer more convenience from the point of view of data presentation.

At present it is difficult to tell whether sensitivity gains (in terms of the S/N ratio available for a given time of measurement) inherent in the multiple quantum coherence technique come close to the theoretical enhancement factor of about 100 relative to conventional PFT ^{15}N spectra. Nevertheless, recent applications of the technique¹⁴⁶⁻¹⁴⁸ show that reasonable S/N ratios are obtained within an hour or so for two-dimensional ^1H - ^{15}N spectra of ca. 0.1 M solutions of large molecules, such as those of polypeptides and nucleotides.

The same technique can be applied to ^{14}N - ^1H NMR^{149,150} in those instances where ^{14}N - ^1H couplings are resolvable. It has been claimed¹⁴⁹ that the use of multiple quantum coherence can improve the resolution in ^{14}N NMR, owing to the scaling of shielding differences and spin-spin couplings according to the number of quanta involved while the signal widths remain constant or even decrease, but so far there have been no convincing proofs of that.

Two-dimensional techniques can also be employed in order to separate dipolar and quadrupolar splittings in ^{14}N spectra of single crystals.¹⁵¹

SCHEME 3
Multiple quantum coherence technique in two-dimensional ^1H - ^{15}N NMR

Frequency channel	Repeated timing sequence											
^1H	<table border="1"> <tr> <td>PW</td> <td colspan="4"></td> <td>AQ</td> </tr> </table>						PW					AQ
PW					AQ							
	$\alpha^\circ_{x'}$											
^{15}N	<table border="1"> <tr> <td></td> <td>Δ</td> <td>PW</td> <td>t</td> <td>PW</td> <td></td> </tr> </table>							Δ	PW	t	PW	
	Δ	PW	t	PW								
	90°_f			$90^\circ_{x'}$								

PW = pulse width (with flip angle and axis specified)
 α = flip angle (below 90°) set in order to optimize intensity and unwanted signal suppression
 f = phase cycled in sequence: x' , y' , $-x'$, $-y'$
 Δ = delay set to $(2J(\text{N-H}))^{-1}$ for NH-type multiplet pattern
 t = evolution period changed in increments in order to map out the two-dimensional contour
AQ = acquisition time of ^1H transverse magnetization that is converted from multiple quantum coherence

Finally, we briefly mention applications of ^{14}N ENDOR (electron-nuclear double resonance), which are not exactly within the scope of the present work.¹⁵²⁻¹⁶⁰

D. Measurements of relaxation times

As far as ^{15}N relaxation is concerned, standard methods of measurement can be employed (ref. 109, pp. 158-164; ref. 111, pp. 323-344). However, there are problems with the low sensitivity of ^{15}N measurements at the natural abundance of the isotope. This problem has been discussed recently,¹²⁷ and use of the INEPT technique (Section IV.A) has been recommended in order to significantly shorten measurement times. The time savings are not so large as in the case of ^{15}N shielding measurements, but they seem to be large enough in order to facilitate the relaxation experiments. This method was actually employed¹²⁸ in a study of linear peptides.

Fairly routine methods are also employed in ^{14}N relaxation measurements (ref. 1, pp. 113-115, 128-131; ref. 4, pp. 233-237).

E. Quantitative nitrogen NMR

In ^{14}N NMR spectroscopy, when one employs lineshape fitting procedures, particularly those concerned with the differential saturation technique (Section IV.C, and ref. 1, p. 23), the procedures should automatically

give the relative numbers of ^{14}N nuclei corresponding to different ^{14}N signals. However, large errors can be expected when the S/N ratio is poor, or when there is a considerable overlap of ^{14}N signals that are characterized by comparable half-height widths. Nonetheless, the fact that the procedures yield reasonable estimates of the errors involved in the counting of the nuclei makes the latter process generally sound. Since for ^{14}N nuclei, at least in most cases, $T_0 = T_1 = T_2^*$, any saturation effects that may appear in ^{14}N spectra can be easily accounted for in lineshape equations; moreover, such effects can be profitably exploited from the point of view of the precision of the results obtained, including the count of ^{14}N nuclei.

The situation is quite different in ^{15}N NMR. There are so many factors affecting the intensities of ^{15}N resonance signals (Section IV.A) that the intensities hardly bear any close relationship to the corresponding numbers of ^{15}N nuclei; this is illustrated in Case Studies III and IV (Section IV.A). As far as simple PFT measurements are concerned, the only remedy would be to increase the relaxation delays (Scheme 1) in order to minimize both saturation and NOE effects, using the inverse-gated decoupling procedure. Calculations according to equations (7) and (12) show that for the ^{15}N nuclei in Case Study III the following parameters should secure the proportionality between the signal intensities and the respective numbers of ^{15}N nuclei, with deviations not larger than 1%:

$$\text{flip angle } \alpha = 89^\circ$$

$$\text{relaxation delay RD} = 600 \text{ s}$$

$$\frac{S/N}{(S/N)_{\text{standard}}} = 0.0400 \pm 0.005 \text{ for 1-N, 2-N, and 3-N}$$

The calculation is valid for T_1 values that do not significantly exceed 150 s; the intensities obtained are about 60% of the maximum intensity available for the ^{15}N nuclei with the longest T_1 (150 s in this case). The latter intensity is already poor enough (*ca.* 0.06, see Case Study III) to make such an experiment feasible only for rather high volume concentrations of ^{15}N , and long accumulation times.

Analogous calculations performed for Case Study IV indicate that the proportionality can be reached for $\alpha = 89^\circ$, $\text{RD} = 40 \text{ s}$ (using the inverse-gated decoupling technique, as in the preceding example), and that the S/N value is then 0.154 ± 0.002 . However, it is more difficult to predict the effects of a relaxation reagent on the respective T_1 s; the latter can be significantly different from those given in Case Study IV, since relaxation reagents may exhibit appreciable selectivity of their effects, particularly when steric effects are involved. In general, one can expect that the proportionality should hold when the gated decoupling method is employed and the relaxation delay RD is about four times the longest T_1 expected.

Polarization-transfer methods are quite selective from the point of view of the $J(\text{N-H})$ values that are responsible for the transfer, and one cannot rely on the signal intensities thus obtained as a measure of relative numbers of ^{15}N nuclei.

F. Liquid-crystal-phase measurements

^{14}N NMR spectra taken in anisotropic liquid media are employed in order to observe quadrupolar splittings. The latter may provide information about molecular motions and conformations, including large molecules of biological interest. The ^{14}N spectra of liquid-crystalline phases of phospholipids that contain choline moieties¹⁶¹⁻¹⁶⁵ indicate the degree of orientation of the choline headgroups in model and biological membranes, within a broad range of temperatures which include phase transition regions. The quadrupolar splittings can be used as a convenient measure of relative ^{14}N quadrupole coupling constants, as was shown for N_2O ,¹⁶⁶ and the azide ion, N_3^- ;¹⁶⁷ in the latter case, disodium chromglycate (DSCG) was used as a nematic phase, and it seems to be a convenient medium for studies on ordered ions, since the ions do not significantly affect the nematic structure of the orienting medium. The ^{14}N spectrum of nitromethane, in poly- γ -benzyl-L-glutamate (PBLG)/ CH_2Cl_2 as an orienting medium, in combination with the corresponding proton and deuterium spectra as well as the measurements of the respective relaxation times, afford a value of 1679 ± 139 kHz for the quadrupole coupling constant of ^{14}N in nitromethane;¹⁶⁸ PBLG is a weakly orienting medium suitable for ^{14}N NMR studies since it yields the corresponding quadrupolar splittings, which are not too large (ref. 1, p. 27, and references therein). The ^{14}N quadrupolar splittings obtained in the ^{14}N spectra of a hexagonal liquid-crystal phase of dodecyltrimethylammonium chloride and hexadecyltrimethylammonium chloride,¹⁶⁹ and the absence of the splittings of their cubic liquid-crystalline phases, are helpful in a determination of two modes of motion of the ammonium moieties involved.

As far as ^{15}N NMR spectra, in orienting media, are concerned, they constitute a source of information on direct spin-spin couplings in addition to scalar couplings. The former can be employed in establishing molecular geometries, as in the case of benzonitrile;¹⁷⁰ additional data can be found in ref. 1, p. 27. One can also use the corresponding ^{15}N satellites in the proton spectra; this was done for pyrimidine and pyrazine¹⁷¹ using the AISEFT technique (Section IV.C) in order to suppress the proton signals of the ^{14}N -containing molecules.

The direct ^{15}N - ^1H couplings observed in the ^{15}N spectra of partially oriented *p*-nitro- and *p*-bromoaniline molecules¹⁷² indicate that the NH_2 moiety is non-planar and that the non-planarity is reduced with the increasing electron-withdrawing effect of the *para*-substituent.

G. Solid-state nitrogen NMR

High-resolution ^{15}N NMR spectra of solids can be obtained using a combination of *cross-polarization and magic-angle sample spinning* (CP-MASS technique), and a short account of the methods concerned has been presented.¹⁷³ Such techniques have been employed widely for obtaining nitrogen shieldings in a variety of solid compounds: silatranes, Table 20, note (b); ammonium salts, Table 30, notes (a) and (b); ureas and amides, Table 43, note (e), Table 50, notes (a) and (1); amino acids, Table 56, note (f), Table 59, note (b); gramicidin-S, Table 70, note (a); amino-acid residues in some proteins and free amino acids produced by bacteria cells, Table 72, notes (c), (d), (e) and (f); polypeptides, Table 73, Table 74, note (a); thiocyanate ion, Table 79, note (c); DNA of fd bacteriophage, Table 103, note (a); imino and immonium moieties, Table 109; nitrate ion, Table 114, note (r); imidazole, Table 85, note (f). The CP-MASS technique was used in the determination of nitrogen utilization in the synthesis of storage proteins in soybeans,¹⁷⁴⁻¹⁷⁶ where the nitrogen sources are ^{15}N -labelled asparagine, glutamine, glycine, and ammonium nitrate. Analogous studies were carried out¹⁷⁷ on the metabolism of ^{15}N -labelled nitrate ions in *Neurospora crassa*. It is shown that ^{15}N CP-MASS spectra can reveal discrete resonance signals for various nitrogen sites in DNA and protein structures, such as those in *Escherichia coli* cells infected with fd bacteriophage.¹⁷⁸ The spectra are particularly useful in studies on viruses, since there is a clear distinction between the nitrogen shielding ranges of DNA and coat protein structures of a virus. The mobility of amino-acid residues in the coat protein of a virus can also be examined using ^{15}N CP-MASS spectra, as is indicated by a study¹⁷⁹ of fd bacteriophage labelled with ^{15}N . The α -helix and β -sheet structures of solid polypeptides can be differentiated on the basis of nitrogen shieldings obtained from ^{15}N CP-MASS spectra,¹⁸⁰ Table 73, but the resolution is inferior to that available in the corresponding ^{13}C CP-MASS spectra, and often the signals due to a minor component cannot be resolved from the large peak of the corresponding major component. Pyridine sorbed on alumina and mordenite shows separate ^{15}N signals, corresponding to various binding sites, in the ^{15}N CP-MASS spectra,¹⁸¹ Table 96. Various groups of nitrogenous moieties can be identified with the aid of ^{15}N CP-MASS spectra in a mixture of solids formed in the reaction of HCN with NH_3 .¹⁸²

A variation of the cross-polarization technique (CP) can be used for the selective enhancement of ^{15}N resonance signals in solids. The method is called *double cross-polarization*, and involves polarization transfer from protons to ^{13}C , and then from ^{13}C to ^{15}N .¹⁸³ This technique enhances the signals of ^{15}N nuclei that are coupled to ^{13}C ; it may be helpful in the detection of doubly labelled moieties, for example ^{15}N - ^{13}C . Applications of this to an estimation of incorporation and turnover rates of such double labels have been reported in the case of soybean cultures.^{174,184,185} The

method seems to be quite attractive, since it enables one to follow the fate of a given pair of bonded atoms in metabolic pathways.

If the magic-angle spinning rates are not large enough to average out dipolar and anisotropy splittings in the ^{15}N spectra of solids, high-resolution spectra are still obtained, but spinning sidebands appear which may be exploited in determinations of nitrogen shielding tensors; the technique is usually abbreviated as MASSs (*magic-angle spinning sidebands*). CP-MASSs spectra of ^{15}N in histidine and imidazole,¹⁸⁶ Table 53, are employed in order to detect various tautomeric and protonated forms of imidazole moieties in lyophilized powders of the compounds concerned, prepared from aqueous solutions characterized by various pH values. The same technique was used in a study on the protonation of imino-moieties in bacteriorhodopsin,¹⁸⁷ Table 109.

It is possible to separate dipolar and shielding anisotropy effects in CP-MASSs spectra of ^{15}N by the application of two-dimensional methods, as was shown for polycrystalline glycylglycine hydrochloride monohydrate.¹⁸⁸ In some cases of inorganic solids, for example NH_4NO_3 ,¹⁸⁹ ^{15}N MASSs spectra may be obtained without cross-polarization and dipolar decoupling. CP-MASSs spectra of ^{15}N in NH-type moieties of DNA structures can provide information about N-H dipolar couplings and therefore N-H bond lengths.¹⁹⁰

Techniques that do not use magic-angle spinning are also frequently employed in solid-state nitrogen NMR. *Single-crystal* ^{15}N spectra can afford information about nitrogen shielding tensors, as in the case of histidine hydrochloride monohydrate,¹⁹¹ Table 59, and *single-crystal* ^{14}N spectra allow one to follow quadrupole splittings as a function of the orientation of the crystal relative to the magnetic field in order to estimate electric field gradients and electron distribution in molecules and ions. The latter method was applied to single crystals of Li_3N ,¹⁹² and the ionic structure of the nitride is confirmed, in contrast with some earlier NMR data for polycrystalline samples. *Multiple quantum coherence* methods in the case of ^{14}N spectra¹⁹³ of solid samples should give appreciable enhancements as well as effective reduction in the ratio of signal widths to signal splitting; however, large quadrupole splittings, in excess of 300 kHz, may require the use of very strong radiofrequency fields. A method of double-quantum cross-polarization, via dipolar order, has been suggested¹⁹³ which reduces the requirements and can be applied for quadrupole splittings larger than 1 MHz.

Powder-pattern ^{15}N spectra of solid $^{15}\text{N}_2$ at temperatures below 4.2 K were employed in order to monitor orientational ordering processes in this molecular solid, and a method of stimulated echoes was proposed¹⁹⁴⁻¹⁹⁶ for the detection of slow rotational motions in such systems. The same method was applied to solid mixtures of N_2 with Ar.¹⁹⁷ *Powder-pattern* ^{15}N spectra

of the peptide backbone of the coat protein in fd bacteriophage¹⁹⁸ indicate that any rapid motions that may take place in the polypeptide chain must have small amplitudes. *Powder-pattern* ^{14}N spectra yield quadrupole splittings, which can be informative about molecular motions and conformations. They are employed in studies of tetraalkylammonium salts,¹⁹⁹ and choline moieties in phospholipids.^{165,200,201}

Finally, we mention briefly that ^{14}N - ^{13}C dipolar couplings can be observed in CP-MASS and single-crystal spectra of ^{13}C nuclei;²⁰²⁻²⁰⁸ such couplings are not averaged out by the magic-angle spinning since the ^{14}N quadrupole moment tilts the axis of quantization of ^{14}N relative to the direction of the external magnetic field.²⁰²

H. Chemically induced dynamic nuclear polarization (CIDNP)

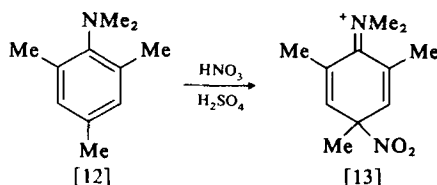
The application of Kaptein's rules to ^{15}N -CIDNP spectra leads to the following equation:²⁰⁹

$$\Gamma_{\text{net}}[^{15}\text{N}_{(i)}] = -\mu\epsilon \Delta g a^{15}\text{N}_{(i)} \quad (18)$$

where Γ is the sign of the net polarization of $^{15}\text{N}_{(i)}$ in radical 1 of the radical pair r_1r_2 considered; μ is + for triplet precursors or F-pairs, and - for singlet precursors of the radical pair; ϵ is + for recombination/disproportionation products, and - for escape products; Δg is the sign of the difference $g_1 - g_2$ in the corresponding g -factors; $a^{15}\text{N}_{(i)}$ is the sign of the corresponding hyperfine coupling constant.

Such rules are employed in a consideration of the ^{15}N -CIDNP spectra of aryldiazonium ions which undergo a decomposition in weakly alkaline aqueous solutions (Table 8). The rules are helpful in the determination of the mechanism of a homolytic decomposition of the ions, as shown in Table 8. They allow one to exclude any significant role for a symmetrical azobenzene radical in the decomposition,²⁰⁹ contrary to some earlier reports.

CIDNP enhancements observed in the ^{15}N spectra of nitration products of *N,N*-dimethylaniline²¹⁰ suggest that at least a part of the *N,N*-dimethyl-*p*-nitroaniline formed comes from a reaction that includes a radical pair as an intermediate, possibly $\text{ArH}^+ \cdot \cdot \text{NO}_2$. In the following reaction,



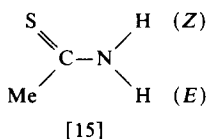
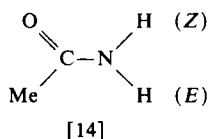
the cation [13] formed gives rise to an enhanced absorption ^{15}N signal if the ion is obtained using H^{15}NO_3 , and exchange starts with H^{14}NO_3 .²¹¹ If

H^{14}NO_3 is used first, and then H^{15}NO_3 , the emission signal is observed at the initial stage of the exchange. These observations can be rationalized, according to Kaptein's rules, in terms of participation of the radical pair $\text{ArMe}^+ \cdot \cdot \text{NO}_2$ in the exchange of the NO_2 moieties. The initial enhancements of absorption signals of ^{15}N in *N*-nitro and *C*-nitro moieties observed during the acid-catalysed rearrangement of 2,6-dibromo-*N*-nitroaniline²¹² into (mainly) 4-nitro-2,6-dibromoaniline can be explained, using Kaptein's rules, as a result of an intramolecular rearrangement which involves the radical pair $\text{ArNH}_2^+ \cdot \cdot \text{NO}_2$.

One should remember, however, that it is difficult to estimate the actual contribution of CIDNP-indicated mechanisms to overall reaction pathways, because of the large magnitude of CIDNP effects on signal intensities, including those of ^{15}N .

I. Dynamic nitrogen NMR

Signal collapse and broadening effects due to spin exchange can, in principle, be exploited in nitrogen NMR in order to obtain the respective rates, but there are numerous difficulties in both ^{15}N and ^{14}N NMR that limit the application of dynamic effects to rather rough estimates of the rates of exchange under conditions where the signals collapse. In ^{15}N PFT spectra (Section IV.A), apart from the problem of achieving adequate *S/N* ratios, the effects of rather long and diversified T_1 values and of NOE factors on proton decoupling, etc., preclude the use of any rigorous lineshape fitting procedure. In ^{14}N spectra there is a problem with an adequate resolution of the relevant resonance signals in the slow-exchange limit, and the necessity to take into account the diverse and temperature-dependent relaxation rates of quadrupolar ^{14}N nuclei. So far, only a few examples in the field of ^{15}N NMR have been reported as far as the use of dynamic effects is concerned²¹³ (ref. 1, pp. 47, 52, 71, 80; ref. 110, pp. 332–334), but a large number of these are concerned with the collapse of NH-type multiplets due to proton exchange at NH-type sites. The latter case is favourable, since one has to deal with a collapsing multiplet pattern only. Under conditions of ^{15}N labelling and the use of high magnetic fields, one can reach an adequate *S/N* ratio, and employ lineshape fitting procedures; a recent work in this field²¹⁴ indicates that in acetamide [14] and thioacetamide [15] (^{15}N -labelled)

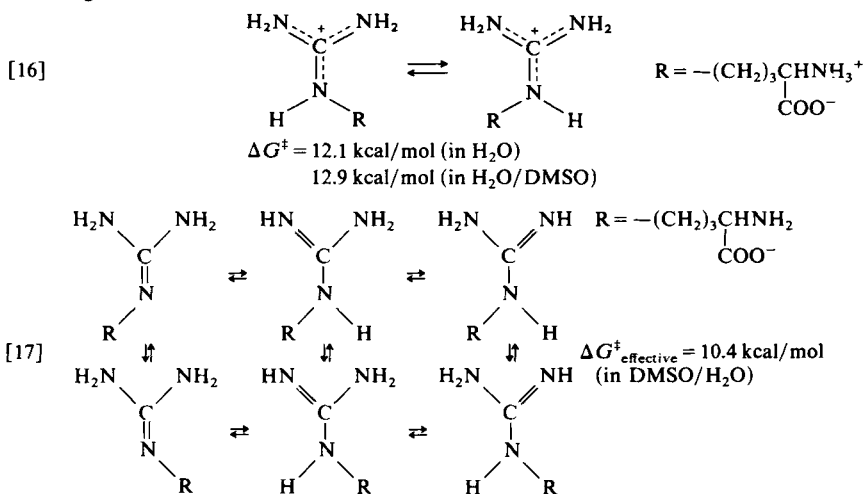


in aqueous solutions, the *Z* protons exchange much faster than the *E*

protons (the corresponding rate ratios are estimated as 6 ± 1 for acetamide, and 3 ± 1 for thioacetamide).

Analogous measurements for base- and acid-catalysed proton exchange in urea, thiourea, acetamide and thioacetamide²¹⁵ yield the corresponding rates; the base-catalysed exchange in the thio-derivatives is much faster than in the amide structures, but this is reversed in the case of acid-catalysed exchange.

In some favourable cases, where T_1 values and NOE (if any) are about the same for the exchanging ^{15}N spins, dynamic effects in ^{15}N NMR lineshapes can be analysed rigorously, but this again requires reasonable S/N ratios, and this usually entails high concentrations, high magnetic fields and ^{15}N -labelling. Such procedures are applied in a study of the barriers to isomerization in the guanidino [17] or guanidinium [16] moieties in L-arginine:²¹⁶



In the case above, ^1H dynamic NMR would be virtually useless, because of the tautomerization as well as intermolecular exchange of protons.

Analogous measurements for base- and acid-catalysed proton exchange in urea, thiourea, acetamide and thioacetamide yield the corresponding rates; the base-catalysed exchange in the thio-derivatives is much faster than in the amide structures, but this is reversed in the case of acid-catalysed exchange.

V. GENERAL CONSIDERATIONS OF NITROGEN SHIELDINGS

General accounts of nitrogen shieldings may be found, as far as data up to 1980 are concerned, in refs. 1-4, 109, 110; there have also been some

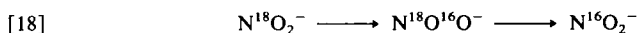
short reviews, including those oriented towards ^{15}N NMR of biomolecules.²²²⁻²²⁵ None of these covers any significant part of the data included in the present account of ^{15}N and ^{14}N NMR.

A. Isotope effects on nitrogen shielding

The *primary isotope effects* on nitrogen shieldings are those due to a change from ^{15}N to ^{14}N or vice versa. They are concerned directly with the important question of whether ^{14}N and ^{15}N shieldings can be used interchangeably, at least for most practical purposes. In principle, one can measure such effects by running the ^{14}N and ^{15}N NMR spectra of a given sample that gives rise to at least two nitrogen signals, under exactly the same experimental conditions; it is important that the signals should originate from the same sample, since the use of any external standard results in difficulties concerned with the necessity for the precise elimination of bulk-susceptibility effects. However, such measurements have not been carried out so far. One can estimate the order of magnitude of primary isotope effects on nitrogen shieldings indirectly, from *secondary isotope effects*; the latter are observed when an isotopic change occurs at atoms that are bound directly to the nitrogen atom involved. Since one may assume that the origin of isotope effects lies in changes of equilibrium bond distances, which in turn are affected by changes in the spacing of vibrational levels of anharmonic vibrations, it is reasonable to expect that primary and secondary isotope effects will be of the same order of magnitude. The secondary isotope effects on nitrogen shieldings are readily observed in the ^{15}N spectra of isotopomeric mixtures, because of the high resolution available, particularly at high magnetic fields; thus, such measurements rely on an internal calibration of the shieldings, and a precision of up to 0.001 ppm is possible. On the basis of secondary effects of about zero to 0.3 ppm observed in azo-type moieties, $-\text{}^{15}\text{N}=\text{}^{14}\text{N}-$ and $-\text{}^{15}\text{N}=\text{}^{15}\text{N}-$, one may expect that the primary effects are of a similar magnitude (ref. 1, p. 28, and references therein). Thus ^{15}N and ^{14}N shieldings should not differ by more than a few tenths of a ppm and are interchangeable for practical purposes. One should note, however, that the data quoted in ref. 1, p. 28, have been misread in ref. 110 (p. 76 therein), and this has led to the erroneous conclusion that the isotope effects may be in excess of 3 ppm.

Recently, secondary isotope effects of $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ on ^{15}N shieldings have been reported (Table 7, and references therein). They are of the order of 0.1 ppm per single ^{13}C or ^{18}O nucleus introduced, which is about the same as the $^{15}\text{N}/^{14}\text{N}$ secondary effects quoted above. The $^{18}\text{O}/^{16}\text{O}$ secondary effect on the ^{15}N shielding in the nitrite ion, NO_2^- , is large enough to produce well-resolved signals^{226,227} for the three isotopomers possible; the same is valid for the four isotopomers of the nitrate ion, NO_3^- .^{226,228} Thus ^{18}O can be employed as a tracer observed by ^{15}N NMR. Such studies

provide new ways of following the fate of oxygen in various reactions. The exchange of oxygen between H_2O and NO_2^- was observed by this method in the oxidation of ammonia to nitrite catalysed by the bacterium *Nitrosomopas*.²²⁶ Analogous investigations were carried out on the acid-catalysed exchange of oxygen between NO_2^- and H_2O ;²²⁷ the kinetics observed indicate that the exchange is sequential:



Still larger effects are found upon $^2\text{H}/^1\text{H}$ substitution in the NH_4^+ ion in 4 M ammonium nitrate/2 M HCl:²²⁹

Isotopomer	^{15}N shielding (in ppm) relative to NH_4^+
NH_4^+	0.000 (arbitrary)
NH_3D^+	+0.307
NH_2D_2^+	+0.605
NHD_3^+	+0.892
ND_4^+	+1.171

The effect is almost additive, about 0.03 ppm per D atom; a similar additivity is found in the secondary isotope effects presented in Table 7. The largest secondary effect is observed for the ^{15}N shielding in the case of a successive deuteration of ammonia, about +0.65 ppm per D atom introduced.³

The secondary isotope effects discussed above are obtained by internal calibration, that is from the ^{15}N spectra of isotopomeric mixtures. Caution is advisable, however, when one tries to assess such effects by the external calibration technique (Section III), because the errors involved can be of the same order as the isotope effects or larger. It is claimed¹²² that solvent-induced deuterium isotope effects on the ^{15}N shieldings of enamines can be measured upon changing from CF_3COOH to CF_3COOD as a solvent, using two independent samples, each referred externally to neat nitromethane; the reported values are of the order of 0.05 ppm, while the estimated, quite optimistic, accuracy of ± 0.03 ppm for a single measurement indicates clearly that the values obtained are within the experimental errors involved.

B. Absolute scale of nitrogen shielding

As far as the position of the absolute zero on the nitrogen shielding scale is concerned, one has to rely on theoretical calculations.^{1,56} However, one can include the corresponding spin-rotational coupling tensor into the calculation of the paramagnetic term in the shielding. So far, such calculations have yielded values that show significant deviations from the

experimentally observed relative shieldings of nitrogen nuclei in some simple molecules. Recently, the problem has been reconsidered⁵⁶ using the ^{15}N shieldings of some gaseous samples at 300 K, with an extrapolation to the zero-pressure limit; the compounds examined include N_2 , NNO , NH_3 and HCN . Since the most accurate value of the spin-rotation coupling available is that for NH_3 , the experimental shieldings quoted below are referred to the theoretical value of +264.54 ppm for NH_3 , while the errors quoted for the theoretical values reflect the reported errors in the spin rotation constants.⁵⁶

Molecule	Experimental shielding (ppm)	Absolute shielding calculated from spin rotation constants (ppm)
N_2	-61.6	-101 ± 20
NNO	+99.5	$+105 \pm 12$
NNO	+11.3	-44 ± 15
NH_3	(+264.5, assumed)	$+264.5 \pm 0.2$
HCN	-20.4	-31 ± 10

For a recalculation of the shieldings onto the neat nitromethane scale, the authors report a value of $+74.70 \pm 0.05$ for N_2 (gaseous, extrapolated to zero pressure) relative to neat MeNO_2 at 300 K; one can correct the latter for bulk-susceptibility effects, and obtain +73.9 ppm (Section III). Thus, with the assumption that the spin-rotation constant for NH_3 is correct, and that the theoretical calculations are valid, one obtains the absolute shielding of nitrogen nuclei in neat liquid MeNO_2 as -135 ppm; in other words, the absolute zero on the nitromethane scale of nitrogen shieldings should lie at +135 ppm. Nevertheless, there are severe discrepancies between the experimental and calculated values of absolute nitrogen shieldings quoted above, those for N_2 and for the central nitrogen atom in NNO . These are attributed to errors in the corresponding spin-rotation constants, in excess of those reported; however, unless more precise values of the latter constants are available, the question of the validity of the calculations seems to be still open, and the value of -135 ppm for the absolute nitrogen shielding in neat liquid nitromethane should be considered as a crude estimate.

C. Shift reagents in nitrogen NMR

Lanthanide chelates may be employed in order to induce shifts in nitrogen shieldings, which are often characteristic of various environments of the nitrogen atoms concerned (ref. 1, p. 29; ref. 4, p. 214 ref. 3, p. 254; and references therein). The shifts, which are mostly of contact origin, are largest if Dy chelates are used. Recently, some additional data have been

presented²³⁰ from ¹⁴N NMR studies:

Compound (2-3 M solution in CCl ₄)	¹⁴ N shielding induced by shift reagent specified (extrapolated to 1:1 reagent/substrate molar ratio)			
	Eu(fod) ₃	Ho(dpm) ₃	Pr(fod) ₃	Yb(fod) ₃
Pyrrolidine	+2190 ± 130	+1970 ± 150	—	—
Pr ⁿ NH ₂	+1850 ± 100	+2090 ± 150	—	—
Pyridine	+2280 ± 70	+2100 ± 80	-340 ± 20	-390 ± 50
<i>N</i> -Me-imidazole				
(N—Me)	+80 ± 30	0 ± 100	—	—
(—N=)	+2200 ± 50	+2080 ± 300	—	—
MeCN	+840 ± 10	+620 ± 170	—	-130 ± 30
Me ₂ NCHO	0 ± 30	0 ± 100	—	—
Me—N=N ⁺ =N ⁻				
(N—Me)	+720 ± 100	—	—	—
(=N ⁺ =)	0 ± 40	—	—	—
(=N ⁻)	0 ± 40	—	—	—

dpm = (Bu¹COCHCOBu¹)⁻, fod = (CF₃CF₂CF₂COCHCOBu¹)⁻

The magnitudes of the induced shifts can be explained in terms of the corresponding association constants, such as those reported for Eu chelates.²³¹

D. Nitrogen shielding assignments

Nitrogen shielding assignments may require non-trivial techniques or a combination of various methods in order to obtain unambiguous results. This happens because spin-spin couplings of nitrogen nuclei are often difficult to obtain or are not too informative, particularly in the case of long-range couplings of ¹⁵N in unsaturated or aromatic systems (ref. 1, p. 30; see also Tables 132-134 in the present account). One can consider the following general methods.

(i) *General correlations of nitrogen shieldings*, such as those inferred from Table 10: the large range of nitrogen shieldings for diamagnetic species, about 1000 ppm, frequently makes such assignments trivial.

(ii) *Selective ¹⁵N labelling*: this can be used not only for assignment purposes, provided that the label does really enter the site desired, but can also be employed in tracer studies, where the origin of the nitrogen atoms in reaction products can be followed by ¹⁵N labels.

(iii) *Spin-spin couplings* or, more generally, *spin connectivities*: modern polarization-transfer techniques (Section IV.A.C) relieve much of the problem of sensitivity in the case of coupled ¹⁵N spectra, and allow one to make use of multiplet patterns, couplings, and spin connectivities with ¹H spectra

in ^{15}N shielding assignments; such methods work best in cases of ^{15}N - ^1H couplings across one bond. Their magnitudes are much larger than those of long-range couplings, Table 130, and in some cases of two-bond couplings, $^2J(^{15}\text{N}-\text{H})$, where the latter attain magnitudes of about 10 Hz, Table 131.

(iv) *Changes in nitrogen shielding effected by lanthanide shift reagents* (Section V.C), *protonating media* (Section V.H), and *solvents* (Section V.J): these can be used mostly for the detection of basic, sterically non-hindered nitrogenous sites.

(v) *Relative widths of the ^{14}N resonance signals*: their use for nitrogen shielding assignments within a molecule that contains more than one nitrogen atom has already been considered in detail (ref. 1, p. 30 and Table 12 therein); in numerous cases, the electric field gradients and, consequently, the corresponding ^{14}N signal widths are small enough (nitro groups, various N -oxide moieties) in order to make a simple distinction, even if nitrogen shielding differences relative to other signals are small.

(vi) *Quantum-mechanical calculations*: even at the level of semi-empirical methods, such as INDO or CNDO, these can be employed in assignments of relative nitrogen shieldings within a given molecule²⁴⁻²⁶ (Section II).

(vii) *Empirical additivity of effects in nitrogen shieldings*: some effects on nitrogen shieldings are roughly additive, but their use for assignment purposes should be limited to cases where the effects are significantly larger than those due to molecular interactions (Section V.J): typical examples are the β -effects of alkyl substituents (Section V.F), and those due to nitrogen-nitrogen interactions in aromatic heterocycles (Section V.G).

An example of problems that can be encountered in nitrogen shielding assignments is provided by a study of azolopyridines,²⁴ where unambiguous results require the use of a combination of methods (iii), (v) and (vi).

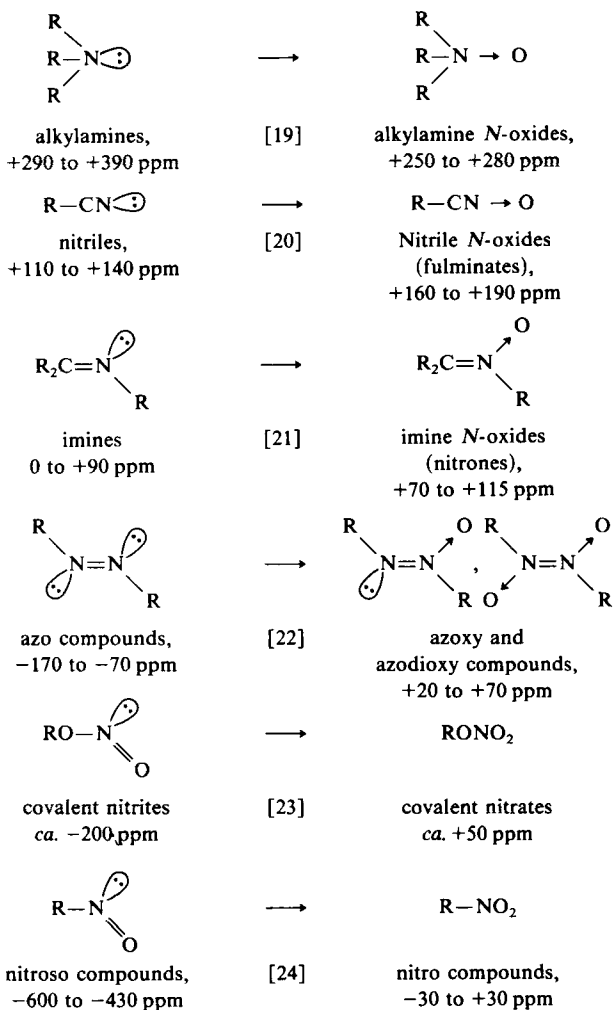
E. General characteristics of nitrogen shieldings in diamagnetic species

Nitrogen shieldings in diamagnetic molecules and ions span a range of slightly more than 1000 ppm, from +400 to about -600 ppm relative to neat nitromethane (Table 10). If one assumes that the absolute shielding in nitromethane is about -130 ppm (relative to a bare nitrogen nucleus, see Section V.B), this corresponds to absolute shieldings ranging from +270 to -750 ppm, and indicates clearly the role of the paramagnetic (deshielding) term in the overall nitrogen shielding (Section II.A).

It has already been noted (ref. 1, p. 30) that there is some parallelism between nitrogen and carbon shieldings; the most screened are the nitrogen nuclei in saturated moieties of the NR_3 (amino) and NR_4^+ (ammonium) types, the most deshielded are those in nitroso groups, $\text{R}-\text{N}=\text{O}$, and the nitrogen shieldings in doubly bonded moieties of the $-\text{N}=\text{CR}_2$ type are

found at intermediate positions. This resembles the deshielding sequence, CR_4 , $\text{R}_2\text{C}=\text{CR}_2$, $\text{R}-\text{C}=\text{O}$, observed in ^{13}C NMR.

If a nitrogen atom bears lone-pair electrons, characteristic changes in the nitrogen shielding take place upon involvement of the lone-pair in the formation of a covalent bond. The *N*-oxidation effects belong to this class, and they are observed when the nitrogen shielding in a given structure is compared with that of the corresponding *N*-oxide. A deshielding effect is characteristic of the *N*-oxidation of the saturated structures of alkylamines [19], (Tables 10, 11, 12, 33), but a significant shielding effect is observed when the nitrogen atom is a part of a multiply bonded or conjugated system and the lone-pair electrons can be thought of as a part of the σ -bond system concerned, [20]–[24]:

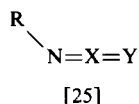


Analogous changes can be found upon the *N*-oxidation of pyridine-type nitrogen atoms in aromatic heterocycles.

Similar effects, and often more pronounced ones, can be found upon *N*-protonation or *N*-alkylation of nitrogenous structures which yield the corresponding cations (Section V.H).

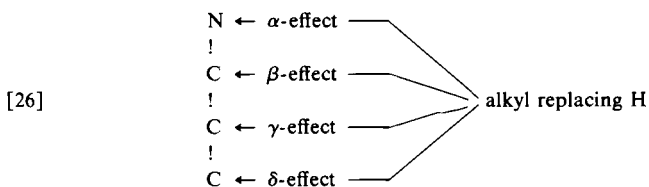
When the nitrogen atom in an —NR_2 group bears lone-pair electrons that can be involved in a delocalized π -electron system, the delocalization of the pair results in a deshielding effect on the nitrogen nucleus concerned. Thus arylamines, at least those that can assume nearly planar structures, show smaller shieldings of their nitrogen nuclei compared with alkylamines (Tables 12 and 34)); amide nitrogen atoms and, in turn, pyrrole-type nitrogen atoms show still smaller shieldings, in accord with the increasing delocalization of the lone-pair electrons (Table 10). In contrast, if there is any competition in the delocalization, such as that in ureas and carbamates, the deshielding effect is diminished; actually the nitrogen shieldings for the latter are found to be between those for amides and amines (Table 10). Thus the changes in nitrogen shieldings considered here can be termed as *lone-pair back-donation effects*.

One should notice that there is a clear distinction in the nitrogen shieldings of doubly bonded nitrogen atoms, such as those in the C=N and N=N type moieties. Structures of the type [25] where the N=X=Y moiety is linear (covalent azides, isocyanates, isothiocyanates, carbodiimides) are characterized by strong shieldings of their nitrogen nuclei, +270 to +390 ppm relative to nitromethane, while all other C=N and N=N moieties show nitrogen shieldings that are lower than +270 ppm (Table 10), including those for the bent structures of sulphodiimides, R—N=S=N—R .



F. Alkyl-group effects on nitrogen shielding

The most important and general effect of alkyl groups attached to a nitrogen atom on the shielding of the latter is the so-called β -effect (ref. 1, p. 31; ref. 4, p. 150). Let us recall the characteristics of α , β , γ and δ -effects on nitrogen shieldings of alkyl groups that replace hydrogen atoms at the relevant positions:



The α -effect is variable in both sign and magnitude, since it is concerned with changes in hydrogen bonding and the geometry of the bonds at the nitrogen atom concerned. The β -effect results generally in a significant deshielding, roughly -5 to -15 ppm per alkyl introduced. The γ -effect normally results in an increase in shielding, but its magnitude does not exceed about 1 ppm per alkyl group; the δ -effect can usually be neglected. All this applies to almost any type of nitrogen atom, and to saturated hydrocarbon chains attached to the nitrogen atom. The effects are roughly additive, provided that there is no significant steric hindrance: the latter tends to quench the β -effect (ref. 1, p. 32). One should remember, however, that the effects, with the exception of the β -effect, are usually smaller than those due to molecular interactions. Thus the latter and the β -effect are responsible for the range of nitrogen shieldings observed in *N*-alkyl derivatives of any given nitrogenous structure. Since the β -effect operates also for other nuclei, including ^{13}C , it constitutes a source of rather trivial correlations between nitrogen and carbon shieldings, if analogous alkyl substituents are considered (ref. 1, p. 32); the triviality stems from the fact that it is not necessary to compare "analogous" structures, say CH_3R and NH_3^+R for a variety of alkyl groups R. One can obtain linear correlations between nitrogen and carbon shieldings for quite different structures, for example NH_3^+R (nitrogen shieldings) and $\text{CH}_3\text{C}(=\text{O})\text{R}$ (carbonyl carbon shieldings), etc.

The considerations above refer to open-chain alkyl groups. In cases where the nitrogen atom is a part of a saturated ring system, complications arise owing to more precise geometrical relationships between various parts of the ring. Such effects on the nitrogen shieldings in decahydroquinoline derivatives are considered in terms of 14 parameters,²³² which comprise the effect of introducing methyl groups at various positions on the ring system concerned. One can have some doubt about the significance of such multi-parameter sets (ref. 1, p. 32), which, if the number of parameters is large, may constitute simply a restatement of the observed facts, under specific conditions (solvent, concentration); however, they can reveal some trends in nitrogen shielding changes upon molecular structure modification.

If one tries to assess the effects on nitrogen shielding of alkyl substituents in terms of parameters specific to individual alkyl groups, as was done for some amines and ammonium ions,²³³ one falls into the trap of numerous local correlations, for example, those for secondary amines, tertiary amines with three primary alkyls, and so on; such correlations usually reflect the approximate additivity of effects, mostly of the β -effect, under specific conditions, while the number of correlations is essentially governed by the variable α -effects and those due to steric hindrance.

In general, one should not ascribe too much significance to such correlations and regression analyses that try to rationalize nitrogen shieldings of *N*-alkyl derivatives in terms of alkyl structures alone.

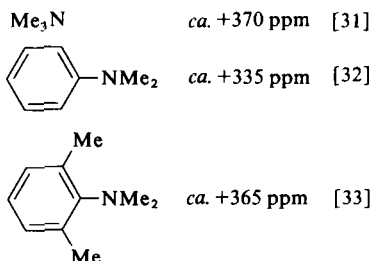
Nitrogen shieldings are so sensitive to molecular-interaction effects (Section V.J) that even consideration of a series of molecules in dilute solutions in the same solvent does not exclude contributions due to changes in the solvation shell that may be induced by changes in the alkyl groups bound to the nitrogen atom in question. Usually, only the β -effects are large enough to emerge clearly from those due to molecular interactions, and permit one to differentiate, from the point of view of nitrogen shielding between the structures $\text{N}-\text{CH}_3$, $\text{N}-\text{CH}_2\text{R}$, $\text{N}-\text{CHR}_2$, and $\text{N}-\text{CR}_3$, where R is an alkyl group. Examples can be found in numerous groups of compounds: alkylamines, and related structures, Tables 12, 14, 16, 25; enamines, Table 18; halogeno-amines, Table 27; alkylammonium ions, Table 30; hydroxyamines, Table 37; guanidinium ions, Table 41; ureas, Table 43; amides, Table 48; thioamides, Table 54; amino acids, peptides, and related structures, Tables 56, 60, 63, 64, 67, 73, 74; one should note here that the β -effect is responsible for the deshielding in amino-acid moieties of the type $-\text{NG}-\text{CR}(\text{R})-\text{CO}-$ relative to that for the glycine moiety, $-\text{NH}-\text{CH}_2-\text{CO}-$; alkyl azides, Table 77; alkyl isocyanides, Table 81; *N*-alkyl substituted sydnone structures, Table 92; immonium salts, Table 108; nitrones, Table 111; sulphinylamines, Table 112; nitramines, Table 113; nitroalkanes, Table 114; nitrosamines, Table 119. Additional examples can be found in older data.^{1,3,4,110}

G. Nitrogen shielding effects transmitted by conjugated ring systems

Effects of unsaturated, conjugated, hydrocarbon moieties on the shielding of nitrogen atoms attached to such moieties are complicated. If we replace an $\text{N}-\text{Me}$ moiety with an $\text{N}-\text{Ph}$ group, or any other conjugated system, considerable deshielding effects on the nitrogen nucleus are observed (relative to the $\text{N}-\text{Me}$ structure) if the lone-pair electrons at the nitrogen atom can be delocalized over the unsaturated system of π -electrons (the lone-pair back-donation effect, see Section V.E). If there is not such a lone-pair of electrons at the nitrogen atom or if the delocalization is obstructed by steric-hindrance effects, the deshielding is quenched, and even some shielding effects may be observed, as in the case of nitro compounds (Table 114) and nitroso compounds (Table 121):

MeNO_2	PhNO_2	
-2 to +7 ppm [27]	+10 to +12 ppm [28]	(no lone-pair electrons at N atom)
Bu^tNO	PhNO	
ca. -590 ppm [29]	ca. -530 ppm [30]	(lone-pair electrons at N atom are within the σ -bond systems)

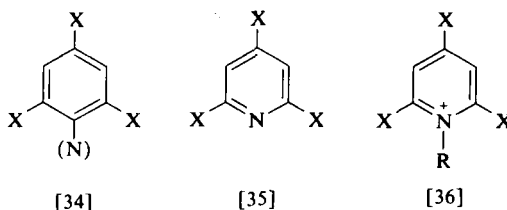
The back-donation, deshielding effect is clearly observed in simple amines (Tables 12 and 34):



The last value shows steric-hindrance effects which preclude the delocalization of the lone-pair electrons at the nitrogen atom concerned. Analogous deshielding effects have been found in a number of nitrogenous structures, upon replacing N—Me with N—Ph or other conjugated systems: hydrazines, Table 38; hydrazones, Table 39; guanidine structures, Table 41; ureas, Table 43; carbamates, Table 44; cyanamides, Table 46; isocyanides, Table 81; enaminones, Table 18.

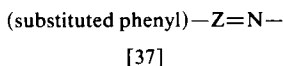
One should remember, however, that the deshielding effects are referred to replacement of an N—Me moiety with an N—Ph group; other alkyl groups can exert deshielding on the nitrogen nucleus (relative to that in the N—Me moiety) by the β -effect (Section V.F); thus the two effects are parallel, and it may be difficult to distinguish *N*-alkyl from *N*-phenyl groups on the basis of nitrogen shieldings if the alkyls are not methyl groups.

As far as the transmission of substituent effects on nitrogen shielding across a phenyl ring or an analogous system is concerned, the most pronounced effects are usually observed when substituents occupy any of the X-positions in the structures [34]–[36]:



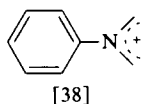
Usually, electron-releasing substituents X give rise to nitrogen shielding effects, while electron-attracting substituents X give deshielding effects, as is observed in aniline derivatives (Tables 34, 35), amides (ref. 1, Table 57 therein), pyridine derivatives (Table 95), pyridine *N*-oxide derivatives (Table 101), sulphonamides (ref. 1, Table 69 therein). Analogous effects are also transmitted in systems of the type [37] where Z = CH (imines, Table

108; hydrazones, ref. 1, Table 45 therein) or $Z = N$ (azo compounds, Table 117; triazines, Table 118).



However, the effects are reversed in some cases; that is, electron-attracting substituents give shielding effects, while electron-releasing groups result in deshielding effects (diazonium ions, Table 116; sulphinylamines, ref. 1, Table 131 therein; nitrogen atoms bound directly to the substituted phenyl in azo-type structures, Tables 117, 118).

Finally, there is a group of structures with *N*-phenyl groups where both electron-attracting and electron-donating substituents at the phenyl moiety seem to increase the shielding of the nitrogen atom. They include nitrobenzene derivatives (Table 114) and *N*-phenylpyridinium ions (Table 100), and their common feature is a formal positive charge at the nitrogen atom as in [38]

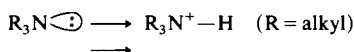


Thus there is no simple rule for predicting substituent effects on the nitrogen shielding in aromatic and conjugated systems, at least not within simple theories of electron charge distribution.

H. Protonation effects on nitrogen shielding

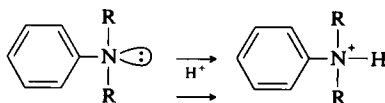
If a nitrogen atom undergoes protonation, the concomitant change in the nitrogen shielding is usually quite characteristic of the protonated structure involved, and can be used in studies on protonation sites and protonation equilibria. In numerous cases the protonation shifts in nitrogen shielding exceed 100 ppm, and cannot readily be confused with any other effect.

The protonation that takes place in a system of saturated bonds, like those in alkylamines, usually results in some deshielding of the nitrogen nuclei involved, and the quenching or reversing of the effect for sterically hindered nitrogen atoms can be attributed to significant changes in bond geometry that may result from the protonation. Examples can be found in Tables 11, 12 and 30 (see also ref. 1, pp. 33, 158, 212; and ref. 6). Such changes are large enough in most instances to provide a convenient method of detection of protonation processes, even in fairly complicated molecules, by means of nitrogen shielding titration curves (Tables 13, 28, 29, 32); the latter can yield information about individual pK_a values for various amino/ammonium protonation centres within a molecule.



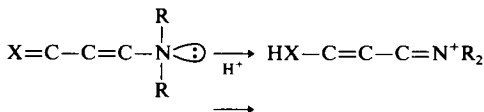
weak deshielding effect on nitrogen shielding,
typically about -10 ppm,
quenched or even reversed
if steric hindrance takes place
[39]

The situation becomes more complicated if an amino moiety, $-\text{NR}_2$, is attached to a conjugated system of double bonds or to an aromatic ring. If such an amino group is protonated, the effects on the nitrogen shieldings are variable, since the protonation engages the lone-pair electrons, and this results in a breakdown of the conjugation (if any) of the latter with the π -electron system of the unsaturated system. Examples can be found in Tables 34, 35, 36, and in ref. 1 (pp. 197, 212, 213, and references therein).



variable effect on nitrogen shielding,
typically -10 to $+10$ ppm
[40]

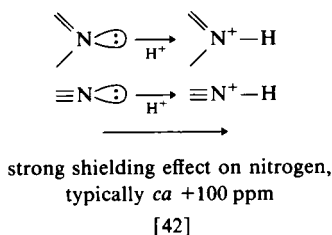
However, if such a conjugated system containing an amino moiety is protonated at some other site, this usually results in an increased delocalization of the lone-pair electrons of the amino moiety whose structure becomes close to that of an immonium ion, $=\text{N}^+\text{R}_2$; the increased delocalization yields a strong deshielding effect on the nitrogen nucleus (relative to that in the non-protonated species), which is illustrated in Table 18 for enaminone structures. This is simply another example of the lone-pair back-donation effect (Section V.E).



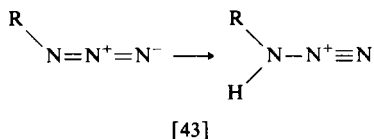
strong deshielding effect on nitrogen,
ca. -100 ppm
[41]

If protonation takes place at a nitrogen atom that is involved in a system of π -bonds and whose lone-pair electrons are not included in the π -bond system, there is invariably a strong shielding effect on the nitrogen nucleus, as indicated by the nitrogen shielding data for azine-type aromatic heterocycles (Tables 95-100), pyridine-type nitrogen atoms in azole ring systems (ref. 1, pp. 311-313), imines (Tables 108, 109), azo compounds

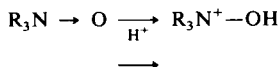
(Table 117, see also ref. 1, p. 390), nitriles (Table 81), the $=N-R$ moieties in guanidines (Table 41), nucleoside, nucleotide and related structures (Table 104) and oximes (Table 110).



One should note that the protonation of alkyl azides to yield the corresponding aminodiazonium ions (Table 77), [43], results in a deshielding of the nitrogen nucleus in the $R-N$ moiety, but in this case the lone-pair of electrons at the nitrogen atom concerned is formally retained in the protonated form.

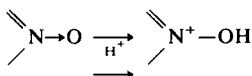


The directions of *N*-protonation effects on nitrogen shielding are parallel to those observed for analogous *N*-oxidation effects (Section V.E). The same directions are also found in the case of *O*-protonation of the corresponding *N*-oxide structures, but the magnitudes of the *O*-protonation effects on nitrogen shielding are usually much smaller than those due to *N*-protonation, and in the case of unsaturated structures it should be fairly simple to distinguish between *O*-protonation and *N*-protonation on the basis of the magnitudes of the shielding effects on the nitrogen nucleus. Thus, the large shielding effect (+200 ppm) observed upon the protonation of nitrous acid (Tables 121–123), HONO , seems to reveal *N*-protonation, while the rather weak (+15 ppm) effect upon the protonation of the hyponitrite ion, $\text{N}_2\text{O}_2^{2-}$, shows *O*-protonation (Table 123, see also ref. 234). However, on the basis of the shielding effect of about +24 ppm in the NO moiety of the trioxodinitrate ion, ONNO_2^{2-} when the latter undergoes monoprotection (Table 123),^{234,235} it is claimed that *N*-protonation takes place. This seems illusory, since the effect is well within the range of those due to *O*-protonation; additional arguments in favour of the *N*-protonation,²³⁵ which come from the observed $\text{NOEF} = -2.1$ in the NO moiety of the protonated species, are not convincing, since analogous NOEF values are observed in oxime moieties, $=N-OH$, for example those reported in ref. 110, p. 26, and references therein.



weak deshielding effect
on nitrogen, 0 to -10 ppm
(Tables 33, 37)

[44]



moderate shielding effect on nitrogen,
+10 to +50 ppm, ref. 1, Table 124 therein,
and references therein; see also Table 123

[45]

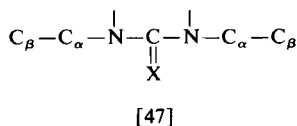
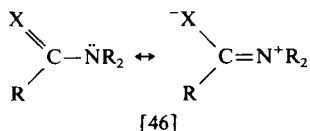
The deshielding effects on the nitrogen nuclei in amide-type structures that are observed in protonating media (Table 48) can be ascribed to *O*-protonation, which should augment the back-donation effect of the lone-pair electrons at the nitrogen atom (Section V.E); analogous, but stronger effects have already been considered in the present section for $\text{X}=\text{C}-\text{C}=\text{C}-\text{NR}_2$ structures.

It is clear from the considerations presented in this section that nitrogen shielding changes that occur on direct protonation of nitrogen atoms, and in some cases on protonation of other atoms, are usually so pronounced that it is fairly easy to follow such processes by means of nitrogen shielding titration curves. Even if we term some changes as weak, this is only on the relative scale of the huge shifts, in excess of 100 ppm, that are often observed. Such curves are employed in order to detect and characterize protonation sites in thermospermine and related polyamines, Table 13; in some polycyclic polyamines, Table 14, note (h), and Table 30, note (l); in neomycin-B and related aminoglycosides, Tables 28 and 29; in polyaminamide electrolytes, Table 32; in hydroxylamines, Table 37; in guanidino-moieties, Table 41, note (d); in sulphonamides, Table 55, note (f); in lysine, Table 57; in histidine, Table 59; in histidine residues of intact mycelia of *Neurospora crassa*,²³⁶ in angiotensin,²³⁷ Table 71; sydnone structures, Table 92; purine and adenine systems, Table 94, notes (e)–(g); nucleoside and nucleotide structures, Table 104, notes (b), (k), see also ref. 238; oximes, Table 110, notes (b), (c); and in nitrite ion and related species, Table 122; nitrogen shieldings are also employed in order to detect the protonation of imino-moieties in visual pigments (Table 109).

I. Correlations between barriers to internal rotation and nitrogen shielding

Since nitrogen shieldings are sensitive to the back-donation effects of lone-pair electrons at the nitrogen atoms concerned (Sections V.E, V.G,

and V.H), and since the delocalization of the pair increases the CN bond order, one may expect to observe some relationships between nitrogen shieldings and barriers to internal rotation in such systems as [46]. Some limited correlations of this kind have been reported (ref. 1, p. 34, and references therein), but their limitations are fairly obvious. First of all, alkyl groups R in the NR_2 moiety exert their own effects on the nitrogen shielding (Section V.F), which are not related in any simple way to the delocalization of the lone-pair electrons; thus the correlations must be limited to individual NR_2 moieties. Secondly, the nitrogen shielding cannot simply reflect any contributions to the height of the barrier that come from steric hindrance to the rotation. It is, therefore, not surprising that recent studies on ureas and thioureas,²³⁹ as well as those on aminophosphines, $\text{R}_2\text{N}-\text{PR}_2$,³⁶ failed to discover any useful correlations between nitrogen shieldings and rotational barriers if the two adverse effects are not accounted for. In the case of some ureas and thioureas²³⁹ [47], (Table 43, note (a)), reasonable correlations are obtained (recalculated here in order to conform to the nitromethane scale of nitrogen shieldings),



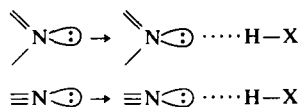
$$\begin{array}{ll} \text{ureas:} & \Delta G^\ddagger \text{ (kJ/mol)} = 333.0 - \sigma_{\text{N,corr.}} - 7.1 I_s (\pm 2.9) \\ \text{thioureas:} & \Delta G^\ddagger \text{ (kJ/mol)} = 568.3 - \sigma_{\text{N,corr.}} - 4.6 I_s (\pm 5.4) \end{array}$$

where $\sigma_{\text{N,corr.}}$ is the nitrogen shielding corrected for the effects of C_α (+4.9 ppm each), C_β (-14.3 ppm each) and for a thiourea structure (-30.6 ppm), if applicable; I_s is the total number of C_α s (on both nitrogen atoms) minus one, and is supposed to account for steric hindrance to the internal rotation: the α -, β - and thiourea structure effects on the shieldings are determined from an independent regression analysis, which also yields C_α and C_β effects on the shielding of the other nitrogen nucleus. Thus the regression analysis is actually performed for a linear function of as many as eight variables, as far as the barriers $\Delta G^\ddagger$ are concerned, and the numerical values obtained may be somewhat fortuitous; however, they seem to reflect a general trend of an increasing deshielding effect on the nitrogen nucleus with an increase in delocalization of the lone-pair electrons.

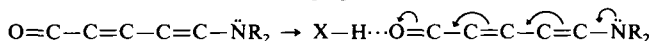
J. Solvent and temperature effects on nitrogen shielding

If we exclude protonation effects on nitrogen shielding (Section V.H), which can reach about 150 ppm, there is still a very significant contribution of solvent effects on nitrogen shielding variations, as can be seen from the data quoted in ref. 1, p. 35, and references therein, as well as in the present account in the following Tables: 6 (nitromethane); 16 (ammonia); 18 (enaminone structures); 20, 24 (silatrane structures and related compounds); 47 (amides); 51, 60, 63, 66, 69, 70, 76 (amino acids, peptides and related structures); 81 (nitriles); 85, 86, 87 (azole ring structures); 93, 94 (azoloazines); 95 (pyridine); 98, 100 (other azine systems); 101 (azine *N*-oxides); 106, 108 (imino-moieties); 110 (oximes); 120, 121 (nitroso moieties). The largest variations observed in nitrogen shieldings as a result of solvent effects reach about 45 ppm, as is found for $\text{Me}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{N}-\text{Bu}^n$, Table 108, note (a); the latter value is not exceptional, since pyridine (Table 95) shows a range of 33 ppm of solvent effects on its nitrogen shielding, and a similar variation is observed for $\text{O}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{NMe}_2$ (Table 18, note (a)).

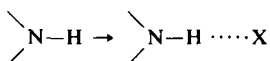
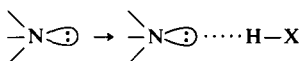
Such large effects can be attributed to hydrogen-bonding interactions, since they are observed when solutions in aprotic solvents are compared with those in strong hydrogen-bond donors. The nitrogen shielding data quoted above show that there is a simple analogy between hydrogen-bonding and protonation effects on nitrogen shielding (see Section V.H. for a comparison):



—————→
significant shielding effect on nitrogen
[48]

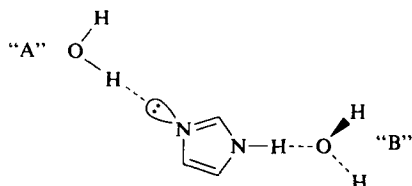


—————→
significant deshielding effect on nitrogen
[49]



—————→
weak or moderate deshielding of nitrogen
[50]

These empirical patterns have also been corroborated by *ab initio* MO calculations for isolated and hydrated molecules of imidazole¹⁸ [51] and formamide¹⁹ [52] (Section II.A).



[51]

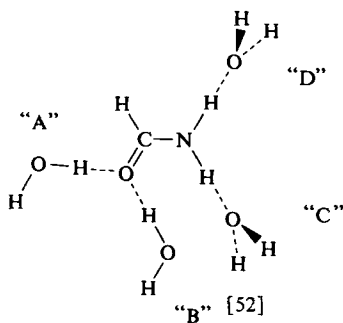
Number and position
of water molecules

Calculated solvation shift
of nitrogen shielding in ppm,
referred to isolated molecules

NH

=N—

none	0	0 (arbitrary)
1 (A)	-3.13	+17.58
1 (B)	-8.12	+1.67
2 (A + B)	-9.33	+18.60



[52]

Number and position
of water molecules

Calculated solvation shift
of nitrogen shielding in ppm,
referred to isolated molecule

none	0 (arbitrary)
1 (A)	-1.48
1 (B)	-3.54
1 (C)	-2.79
1 (D)	-0.75
2 (A + B)	-5.15
2 (C + D)	-3.56
4 (A + B + C + D)	-10.96

Such effects are actually employed in ^{15}N signal assignments and in the differentiation between solvent-exposed and solvent-shielded peptide groups in gramicidin $\text{S}^{240,241}$ (Table 70), and in actinomycin D^{242} (Table 51). A typical experiment involves nitrogen shielding measurements in a series of solutions, starting from hydrogen-bond acceptor solvents and ending up with a strong hydrogen-bond donor; this may mean a change from DMSO to MeOH, H_2O and, finally, $\text{CF}_3\text{CH}_2\text{OH}$. Deshielding effects on the nitrogen nuclei are observed in the case of solvent-exposed carbonyl groups of the peptide moieties concerned, and shielding effects in cases where the dominant role is played by the rupture of NH -DMSO hydrogen-bonding interactions. Significant shielding effects in the case of hydrogen-bonded pyridine-type nitrogen atoms can be employed for the detection of proton-acceptor sites in nucleoside base-pairing, for example, that of adenosine and uracil²⁴³ (Table 104, note (d)) as well as guanosine and cytidine¹⁴⁷ (Table 104, note (g)).

Even if one excludes hydrogen-bonding effects on nitrogen shieldings, there is still a considerable range of solvent effects on the latter. For example, nitromethane in aprotic solvents shows a nitrogen shielding range of about 9 ppm (Table 6), and for $\text{O}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{NMe}_2$ (Table 18, note (a)) the range is as large as 14 ppm. In the case of nitromethane as well as some other nitroalkanes, this range of nitrogen shieldings is reproduced by calculations within the INDO/S method combined with the solvation model of solute-solvent interactions.¹ The solvation model attempts to represent the oriented solvent distribution around the atoms of the solute in terms of induced charges within a medium characterized by a given dielectric constant. One can thus expect that nitrogen shielding variations, induced by changes in solvent polarity, can readily reach a range of about 10 ppm.

It has always been tempting to try to reproduce various solvent effects in terms of some simple parameters or combinations thereof. Recently, the system introduced by Taft and Kamlet has been employed for solvent effects on nitrogen shieldings (ref. 244, and references therein):

$$XYZ = XYZ_0 + s(\pi^* + d\delta) + a\alpha + b\beta \quad (19)$$

where XYZ is a given property (for example, the nitrogen shielding in a given molecule) of a solute in a solvent, XYZ_0 is the property in the reference state, a solution in cyclohexane; π^* is the polarity/polarizability of the solvent, α is its hydrogen-bond donor strength, β is its hydrogen-bond acceptor strength (these solvent parameters are expressed on three arbitrary scales, and for most solvents the parameters assume values between 0 and 1); δ is a correction for polychlorinated solvents ($\delta=0.5$) and aromatic solvents ($\delta=1.0$); the coefficients s , d , a and b represent the corresponding responses of the property (nitrogen shielding, in our case) of the solute to

the relevant solvent properties. One can argue about the merits and demerits of such simple models, and the corresponding values of solvent parameters (the latter usually undergo continuous modification with an increase in the body of experimental data available), but the system described may be useful in detecting certain trends and, what is even more important, exceptions from these.

The coefficients s , a and b (eventually d) are determined by the least-squares method, and they offer a simple estimate of polarity/polarizability and hydrogen-bonding effects that can be exerted by solvents on the nitrogen shielding in the solute. Since the solvent parameters vary within 0 to about 1 (in the case of the α parameter, the inclusion of $\text{CF}_3\text{CH}_2\text{OH}$ as a solvent extends the range to about 1.5), the range of solvent polarity/polarizability effects on nitrogen shielding is equal to s , that of solute-to-solvent hydrogen bonding is equal to b , and that of solvent-to-solute hydrogen bonding amounts to about $1.5a$. On the basis of the experimental nitrogen shieldings in pyridine (ref. 1, Table 120 therein, note (a)), and those in Si—Me silatrane (Table 20), the following values are calculated:²⁴⁴

	s	a	d
pyridine	+5.9 ppm	+19.5 ppm	—
Si—Me silatrane	-8.1	-2.9	-0.20

These can be compared with analogous values obtained for some amides²⁴⁵ (for experimental data, see ref. 1, Table 61 therein):

	s	a	d	b
HC(=O)NMe_2	-6.5 ppm	-7.2 ppm	—	—
MeC(=O)NMe_2	-6.3 ppm	-7.8 ppm	—	—
HC(=O)NH_2	-10.3 ppm	-4.5 ppm	—	-5.5 ppm

Similar calculations were performed for 1,3-dioxa-6-aza-2-silacyclo-octanes¹⁴⁰ (for experimental data see Table 24):

Substituents at Si and N	s	a	d	b
SiPh_2 , NH	-7.5 ppm	—	-0.16 ppm	-2.2 ppm
SiPh_2 , NMe	-3.1	—	-0.22	—
SiHPh, NMe	-8.8	—	-0.25	—

It is evident from the values quoted above that solvent polarity/polarizability has a significant effect on the nitrogen shieldings in solutes. The data also indicate the characteristic effects of hydrogen bonding, which were considered at the beginning of the present section.

While the Taft-Kamlet system presented above involves gross simplifications in the presentation of solvent effects on solutes, it is even more so in cases when single parameters are employed in order to explain solvent effects. A question arises as to why nitrogen shieldings seem to correlate in some cases with such single parameters as E_T , as is found for solutions of $\text{OC}=\text{CH}-\text{CH}=\text{CH}-\text{NMe}_2$,²⁴⁶ or some other parameters quoted in ref. 110, p. 73. The explanation is fairly simple, since such correlations can be observed only when the effects on nitrogen shieldings of both the increasing polarity and hydrogen bonding have the same sign; this happens frequently, as is shown by the s , a and b values obtained within the Taft-Kamlet scheme for some molecules.

Gas-to-liquid shifts of nitrogen shieldings in some simple molecules, like NH_3 (*ca.* -20 ppm),^{53,56} and HCN ^{54,56} (*ca.* +12 ppm) seem to reflect, at least qualitatively, the trends corresponding to hydrogen-bonding effects presented at the beginning of this section.

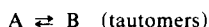
The temperature dependence of nitrogen shieldings (Table 9) can involve a variety of effects, including those due to changes in the population of rotation-vibrational levels, molecular interactions, association equilibria, etc., and some attempts have been made^{53,54} to rationalize the temperature dependence in terms of the latter, but this requires numerous assumptions to be made, particularly for the liquid state or solutions (Section II.A). Analogous interpretations of the temperature dependence of the nitrogen shieldings of amines, hydroxylamines and oximes²⁴⁷ (see Table 9, note (a)) in terms of hydrogen-bonding equilibria also involve oversimplifications, since the molecules concerned can act as hydrogen-bond donors and acceptors, and the respective effects on the nitrogen shieldings can differ in both sign and magnitude.

Attention is drawn to the high coefficients, *ca.* +0.07 ppm/deg, for the nitrogen shielding in liquid NH_3 (Table 9, note (b)), and for aqueous HNO_3 , *ca.* +0.04 ppm/deg (Table 9, note (a)); in the latter case the relationship is not linear. From this point of view, the two compounds are not suitable as references for nitrogen shielding scales (Section III).

K. Nitrogen shieldings in tautomeric systems

If we consider a tautomeric equilibrium [53] between nitrogenous compounds, and the corresponding model compounds where the tautomerism is prevented by, for example, replacing the mobile hydrogen atoms with

methyl groups:



[53]

A' (model compound for tautomer A)

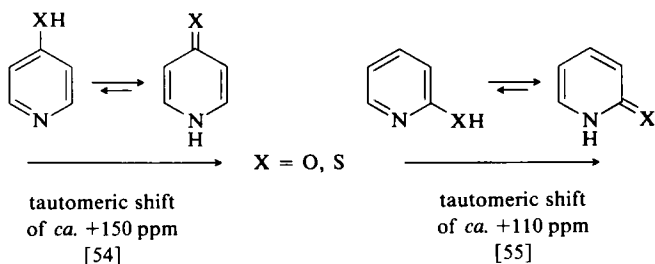
B' (model compound for tautomer B)

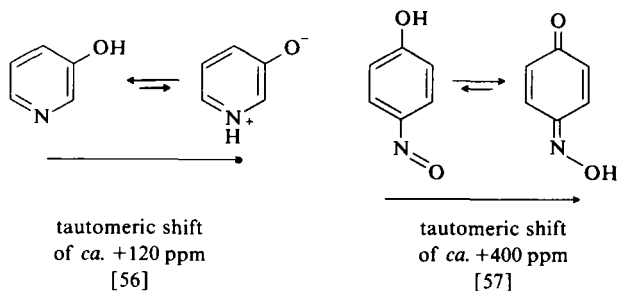
we often find that the relevant change ("tautomeric shift") in the nitrogen shielding, measured either directly as $\sigma_A - \sigma_B$ or indirectly as $\sigma_{A'} - \sigma_{B'}$, is quite large, and can exceed 100 ppm. Such large tautomeric shifts in nitrogen shieldings provide a sound basis for calculations of mole fractions of tautomers A and B under conditions where only a dynamically averaged value of the nitrogen shielding is observed:

$$x_A = \frac{\sigma_{(A \rightleftharpoons B)} - \sigma_B \text{ (or } \sigma_{B'})}{\sigma_A \text{ (or } \sigma_{A'}) - \sigma_B \text{ (or } \sigma_{B'})} \quad (20)$$

$$x_B = \frac{\sigma_{(A \rightleftharpoons B)} - \sigma_A \text{ (or } \sigma_{A'})}{\sigma_B \text{ (or } \sigma_{B'}) - \sigma_A \text{ (or } \sigma_{A'})} \quad (21)$$

Errors involved in such calculations result from replacing true values of σ_A and σ_B under the experimental conditions concerned with those found under some other conditions or those for A' and B', respectively. If the respective differences, $\Delta\sigma_A$ and $\Delta\sigma_B$, are small in comparison with the tautomeric shift that occurs in the denominators in equations (20) and (21), the errors in the mole fractions calculated, x_A and x_B , are equal to about $\Delta\sigma_B/(\text{tautomeric shift})$ and $\Delta\sigma_A/(\text{tautomeric shift})$ respectively. For example, if the uncertainty about the true values of σ_A and σ_B under given experimental conditions amounts to ± 5 ppm, and if the tautomeric shift concerned is about 150 ppm, the errors in the mole fractions should not exceed ± 0.03 . Such an approach is employed in the determination of the tautomeric equilibrium compositions in the systems [54]–[57] (ref. 4, pp. 194, 202; ref. 1, p. 88; and references therein): The tautomeric changes of nitrogen shielding in the case of 2- and 4-substituted pyridines are typical for analogous equilibria that may exist in more complicated heterocycles (Table 50), including those in nucleoside structures (Table 104). The large





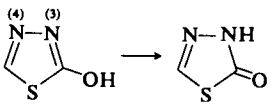
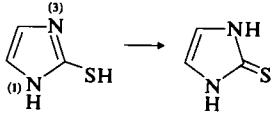
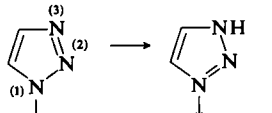
differences in nitrogen shielding between the tautomers allow one to detect the prevailing tautomers even if no effort is made towards an estimation of the equilibrium composition.

Substantial tautomeric changes of nitrogen shielding are observed in azole ring systems [58]–[62] (Table 87):

Type of rearrangement	Associated tautomeric shift of nitrogen shielding (from model compounds), in ppm			
	1-N	2-N	3-N	4-N
[58]	<i>ca.</i> -100	<i>ca.</i> +100	—	—
[59]	<i>ca.</i> -100	<i>ca.</i> +100	—	—
[60]	<i>ca.</i> -100	<i>ca.</i> +100	<i>ca.</i> +20	—
[61]	<i>ca.</i> -100	<i>ca.</i> -20	—	<i>ca.</i> +100
[62]	<i>ca.</i> -80	<i>ca.</i> +90	<i>ca.</i> +10	<i>ca.</i> 0

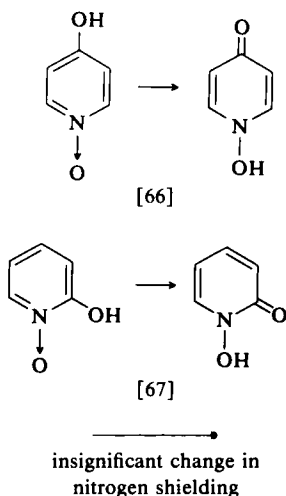
Such shifts, combined with differences in the nitrogen shieldings for individual atoms in azole ring systems are actually employed in calculations of the relevant equilibria, using either equation (20) or (21) as such²⁴⁸ or one of those with corrections for replacing NH with NMe and $-\text{NH}=\text{N}=\text{}$ with $-\text{NMe}-\text{N}=\text{}$ in the equations.²⁴⁹

Large tautomeric variations in nitrogen shielding are also involved when a hydrogen atom migrates between a nitrogen atom and an oxygen [65] (Table 87, notes (g, f)) or sulphur atom [63], [64] (Table 87, note (d)) within a substituted azole ring system:

Type of rearrangement	Associated tautomeric shift of nitrogen shielding, in ppm
 [63]	ca. +120 (3-N) ca. +40 (4-N)
 [64]	ca. 0 (1-N) ca. +100 (3-N)
 [65]	ca. -30 (1-N) ca. +30 (2-N) ca. +150 (3-N)

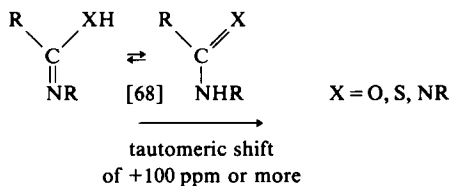
It is quite clear from the considerations above that large tautomeric changes in nitrogen shieldings are characteristic of protonation/deprotonation processes which directly involve nitrogen atoms. They are comparable to the protonation shifts in nitrogen shieldings, which were considered in Section V.H. They have been frequently employed in the field of nitrogen heterocycle chemistry in order to estimate either tautomeric equilibria or at least the preponderant tautomers in such systems.^{186,248-257}

Tautomeric variations in nitrogen shieldings are usually much smaller when the migration of a hydrogen atom does not include the nitrogen atom considered. This is illustrated by some of the data quoted above; an additional example is provided by substituted pyridine *N*-oxide structures²⁵⁸ [66], [67] (Table 101, note (b)), where the tautomeric shifts are negligible:



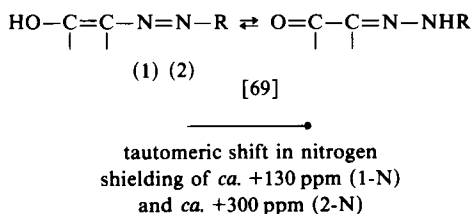
A notable exception to this rule, as far as conjugated or aromatic systems are concerned, is the huge tautomeric shift in nitrogen shielding in the case of oxime $\rightleftharpoons$ nitroso tautomerism, quoted at the beginning of this section; the latter case does not involve any direct protonation/deprotonation of the nitrogen atom concerned.

Thus large tautomeric shifts in nitrogen shieldings of unsaturated systems, with the exception quoted above, are typical of the rearrangement [68]



or that for any vinylogues of these structures. The structures are not limited to conjugated ring systems, but also include amide $\rightleftharpoons$ isoamide systems²⁵⁹ (Tables 47, 106), guanidines (Table 41) and isothiourea structures (Table 106).

Nitrogen shieldings can also be helpful in equilibrium estimates of azo-hydrazone tautomerism^{254,260} [69] (Tables 39, 117; ref. 1, p. 393):



and in the case of valence tautomerism between azido-substituted pyrimidine ring systems and the corresponding tetrazolopyrimidines, presented in Table 78.

VI. NITROGEN SHIELDING IN VARIOUS CLASSES OF MOLECULES AND IONS

A. Ammonia, alkylamines and alkylammonium ions

The nitrogen shielding in ammonia (Table 11) constitutes the high-shielding limit for nitrogen nuclei in diamagnetic molecules and ions (Table 10). It shows a gas-to-liquid shift of about -20 ppm. The gas-phase shielding changes linearly with pressure, -0.041 ± 0.002 ppm/amagat,⁵³ and the change significantly exceeds that expected from bulk-susceptibility effects upon changing the gas density. The temperature dependences of both gaseous and liquid NH_3 are given in Table 9. In the liquid, the relationship is not quite linear, and is actually described by the function $\sigma_T(\text{NH}_3) = \sigma_{300\text{K}}(\text{NH}_3) + 0.605(T - 300) + 0.111 \times 10^{-3}(T - 300)^2$, in ppm, within a range of 207–358 K.⁵³ The nitrogen shielding in NH_3 has so far constituted the only reasonable basis for attempts at setting up a scale of absolute values of nitrogen shielding constants (Section V.B).⁵⁶ Significant deshielding effects on the nitrogen nucleus in NH_3 have been found for NH_3 adsorbed in 88 HY-type zeolites (Table 11),^{261,262} these are attributed to the formation of ammonium ions due to interactions with the structural OH groups in the zeolites; however, the use of stabilized decationated zeolites results in deshielding effects up to -116 ppm relative to gaseous NH_3 which cannot be explained in terms of NH_4^+ ion formation.²⁶² Deshielding effects are also noted on the ^{14}N resonance of NH_3 solvent for Ti^+NO_3^- ion pairs²⁶³ (Table 11, note (g)). The solid-state ^{15}N spectra of complex solids that are obtained from the reaction of ammonia with HCN ¹⁸² show a variety of nitrogenous structures, including NH_4^+ , amino-type moieties, amide-type moieties, cyano groups and nitrogen-containing heterocycles.

The highest shieldings of nitrogen nuclei in NH_3 are found in amino complexes (Tables 127, 128). There are some characteristic patterns of the nitrogen shieldings of the amino-ligands (NH_3) for *cis*- and *trans*-relationships to other ligands in square-planar Pt complexes (Table 128); the largest effect is found for aquo-ligands (H_2O) which are in the *trans*-position relative to NH_3 .

The ammonium ion, NH_4^+ , shows a rather strong deshielding effect relative to NH_3 , about -20 to -60 ppm, depending on the presence of counterions (Tables 6, 30); this is the largest protonation shift of nitrogen shielding (Section V.H) as far as saturated structures, $\text{R}_3\text{N} \rightarrow \text{R}_3\text{NH}^+$, are concerned. The effect of counterions on the NH_4^+ shielding is quite remarkable, and this point is well illustrated by the solid-state data for ammonium

salts (Table 30, note (a)); the deshielding effects exerted by halide ions are particularly significant; they are also evident from the data on solutions (Table 6). Such changes in the nitrogen shielding are attributed to variations in the N-H bond lengths and geometry²⁶⁴ on the basis of some *ab initio* MO calculations; the latter suggests that if all four N-H bond lengths are changed, the response of the shielding is about 2.8 ppm per 0.01 Å.

The data for alkylamines and related structures (Tables 12-17) as well as those for alkylammonium ions (Table 30) provide examples of the effects of alkyl-group structure, protonation and molecular interactions in solutions that have been considered in Section V for saturated systems. Attention is drawn to the relatively strong shieldings observed in the case of the aziridine three-membered ring systems (Table 16).

The role of α -, β - and γ -effects exerted by alkyl groups (Section V.F) are well illustrated in the case of oligo- and polyethylene "imine" (actually, amino groups are involved) (Table 12, note (c)). The significance of spatial relationships between an amino substituent and methyl substituents on the nitrogen shielding is reported for 4-aminooxane and 4-aminothiane structures (Table 12, note (f)); there are clear differences between the shieldings for axial and equatorial amino groups as well as significant shielding effects (*ca.* +10 ppm) exerted by alkyl substituents in position 3 on the axial amino group, NH₂, while in the case of the NMe₂ group, the effect is observed for the equatorial position of the latter. Attempts are made²⁶⁵ to explain this in terms of conformations and internal rotations of the amino moieties, but one should be cautious in drawing conclusions based on geometrical considerations alone, since the replacement of NH₂ with NMe₂ can bring substantial changes to the solvation sphere. As far as axial-equatorial equilibria are concerned, ¹⁵N NMR turns out to be the only means of direct detection of the axial conformer of aminocyclohexane (Table 12, note (m)), and a value of 1.4 kcal/mol is found for the conformational free energy, $-\Delta G^0(\text{NH}_2)$, on the basis of the integral intensities of the corresponding ¹⁵N resonances.²⁶⁶

If an amino moiety constitutes a part of an alicyclic system, there are remarkable conformational effects on the nitrogen shielding involved. These are shown in Table 14, note (j), and Table 15. In the case of *trans*-decahydroquinoline derivatives (ref. 128, Table 15), the effects on the nitrogen shielding of introducing methyl groups in various positions are presented, using a linear regression analysis, in terms of as many as 14 parameters. This comes close to a restatement of the facts observed for quite concentrated solutions in benzene. Some trends, however, are noteworthy, since they show that the β -effect (Section V.F) invariably leads to deshielding, which is more pronounced in the case of an equatorial Me group; they also show that there is a significant (shielding) γ -effect of an axial Me group, but practically none in the case of an equatorial Me group.

The nitrogen shieldings for 2-substituted aziridines (Table 16, note (a)) are claimed to correlate linearly with the Taft inductive constants of the substituents involved and the steric constants E_s , but this seems to be a misunderstanding, since the major part of the changes in the shielding comes from the β -effect of alkyl substituents in position 2. The same origin is involved in the observed correlation between the nitrogen shieldings and three ^{13}C shieldings.

There are some clear differences in the nitrogen shieldings for geometrical isomers of substituted azetidine and oxaziridine ring systems (Table 16). One should note that the shieldings for oxaziridine systems are close to those observed for hydroxylamines (Table 37), but are remarkably different from those for their isomers, nitrones (Table 111).

The amino moieties in nitrogen-containing crown ethers and cryptands (Table 17) show some characteristic shifts in their nitrogen shieldings on complexation with ions. Deshielding effects are found with an increase in the charge of the ion, while shielding effects are typical of the increasing polarizability of the complexed ion.²⁶⁷

Protonation of amino moieties in alkylamines, which yields the corresponding ammonium ions, usually leads to some decrease in the nitrogen shielding involved (as shown in Tables 13, 29, 30, 32). Some exceptions to this rule are found for sterically hindered systems or those where adamantane-type structures are involved (ref. 1, p. 192). This is the case for hexamethylenetetramine (urotropine), where a protonation shift of about +4 ppm in its nitrogen shielding is reported.⁴⁵ The protonation shifts (Section V.H) can be employed for recording ^{15}N NMR titration curves (Tables 13, 29), which provide detailed information about protonation processes. Analogous titrations were carried out for polyelectrolytes based on polyaminamides (Table 32). In the latter case, nitrogen shieldings are also helpful in tracing the processes of *N*-alkylation of the polyelectrolytes by various alkylating agents. Two stages of protonation are detected by means of ^{15}N NMR titration curves of diazabicyclo[2.2.2]octane (DABCO, See Table 30, note (1)) while only monoprotection is found in hexamethylenetetramine.⁴⁵

A considerable amount of data has been reported on silatrane structures and analogues thereof (Tables 20–24). They contain transannular dative bonds, $\text{N} \rightarrow \text{Si}$ (or analogous bonds with other heteroatoms), and there seems to be an increasing deshielding effect on the nitrogen nuclei with an increase in the strength of the trans-annular bonds.^{137,268,269} The nitrogen shieldings can be correlated linearly with the Taft inductive constants σ^* of substituents at the silicon atom of 1,3-dioxa-6-aza-2-silacyclooctane structures²⁶⁹ (Table 24), and of those at the germanium atom in the geratrane structure¹³⁸ (Table 21). The correlations, together with those reported earlier for silatrane structures (ref. 1, p. 40, and references therein) are clearly

indicative of the presence of the transannular bonds. There is also a linear relationship between solvent-induced shifts of the nitrogen shieldings in silatranes and those for the corresponding ^{29}Si nuclei.¹³⁷ The solvent effects on the nitrogen shieldings can be reproduced in terms of a linear combination of parameters that characterize solvent polarity and hydrogen-bond donor strength. The latter presentation has been recently recalculated in terms of the Taft-Kamlet system of solvent parameters²⁴⁴ (Section V.J) for methylsilatrane. The same approach is employed for the solvent-induced effects on the nitrogen shieldings in Table 24 (Section V.J).¹⁴⁰ The compounds concerned can exist in various conformational equilibria (Table 24), one of which has a transannular bond between N and Si. The equilibrium constants are available from the proton spectra; they are used in the calculation of the nitrogen shielding changes that take place upon the formation of the transannular bond [70]:²⁶⁹

$\text{Ph}_2\text{Si}(\text{OCH}_2\text{CH}_2)_2\text{NR} \rightarrow \text{Ph}_2\text{Si}(\text{OCH}_2\text{CH}_2)_2\text{NR}$ [70]	
R	Nitrogen shielding change (ppm)
H	-11.7
Me	-18.4
Et	-17.9
Pr ⁿ	-10.1
Bu ^t	-6.0

The calculations are based on the assumption that the nitrogen shieldings in the crown conformation (that without the transannular bond) are equal to the experimentally observed shieldings of some related $\text{RN}(\text{CH}_2\text{CH}_2\text{OH})_2$ compounds (Table 12, note (e)).

The deshielding effects on the nitrogen nuclei in silatranes, observed upon passing from the gas phase to solutions and then to the solid phase (Table 20, note (b)) are attributed to the concurrent decrease in the transannular N $\rightarrow$ Si bond length.²⁷⁰ The same explanation is invoked for the deshielding observed in the silatrane analogues in Table 23, as compared with the corresponding silatranes.²⁶⁸

The involvement of the lone-pair electrons of the nitrogen atom in an alkylamine in the formation of a covalent bond results in a significant deshielding effect on the nitrogen nucleus, as is shown for some trimethylamine adducts of mixed trihalides of boron (Table 31); however, there is no simple correlation of the nitrogen shieldings with the B-N bond strength,¹²⁴ since fluorine seems to exert some specific effect on the shielding. The data in Table 31 can be fitted into a simple additivity scheme¹²⁴ of the following contributions of substituent pairs at the boron atom:

Pair of substituents R in $\text{Me}_3\text{N} \rightarrow \text{BR}_3$	Contribution of each pair to nitrogen shielding (ppm) referred to neat nitromethane
F, F	+114.0
Cl, Cl	+111.4
Br, Br	+112.4
I, I	+116.0
I, Br	+113.6
I, Cl	+112.3
I, F	+115.3
Br, Cl	+111.5
Br, F	+113.3
Cl, F	+112.1

Thus, for example, the shielding of N in $\text{Me}_3\text{N}-\text{BFCl}_2$ can be reproduced as the sum of three contributions, $(\text{Cl}, \text{Cl}) + (\text{Cl}, \text{F}) + (\text{Cl}, \text{F})$.

The quadrupolar relaxation of ^{14}N in alkylammonium ions is frequently slow enough that the corresponding ^{14}N signals are detectable, owing to their relatively small widths, even in large molecules or biological samples with millimolar concentrations of the ions per litre; trimethylammonium moieties of choline and derivatives thereof can be distinguished in ^{14}N spectra from NH_4^+ , urea derivatives, amino acids in mammalian tissues *in vivo* and *in vitro*²⁷¹ rat and rabbit kidneys, rat liver, brain and legs. The nitrogen shieldings in choline-type groups are presented in Table 30, notes (m) and (n).

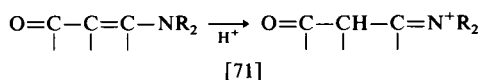
It is not possible to detect the ^{15}N signal of NH_4^+ in the reduction process of N_2 by nitrogenase from *Klebsiella pneumoniae*.²⁷² This is ascribed to signal nulling by the unfavourable NOE (Section IV.A), since the NH_4^+ signal could be observed after enzyme separation.

Ethylenediamine ligands in complexes with Co(III) reveal rather strong shieldings of their nitrogen nuclei (Table 65, note (b)), comparable to those observed in ammino-type complexes (NH_3 ligands, Tables 127, 128); the shieldings are sensitive to *cis* and *trans* relationships with respect to other ligands. However, complexes of 1,4,8,11-tetra-azacyclotetradecane (Table 129, notes (a, d)) show small deshielding effects on their nitrogen nuclei as compared with the parent compound (Table 14, note (f)); in the case of the Pb complex, axial and equatorial NH ligands are clearly distinguished in the ^{15}N spectrum (Table 129, note (a)), while for the Cd complex, an equilibrium between two structures is observed²⁷³ Table 129, note (d)). The coordination shifts in nitrogen shielding of complexes of 1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetate ion (Table 129, note (d)) are also in the deshielding direction as compared with the parent ion.

B. Enamines and enaminones

The nitrogen shieldings in amino moieties which are attached to an unsaturated system of carbon-carbon bonds are generally smaller than those for alkylamines (Tables 18, 19, as compared with Table 12). The shieldings in enamines are comparable to those in arylamines (Tables 34, 35). If an enamino-type moiety, $-\text{CR}=\text{CR}-\text{NR}_2$, is conjugated with a carbonyl group, there is a further decrease in the nitrogen shielding, which attains values comparable to those for amides (Table 47). All this is a typical example of the lone-pair back-donation effect considered in Section V.E. The effect is augmented by hydrogen bonding of the carbonyl moiety of a conjugated enaminone, and even more so in the case of the *O*-protonation at the carbonyl group, and this is reflected by considerable deshielding effects on the nitrogen nucleus involved (Tables 18, 19; see also Sections V.H, V.J). In contrast, if the conjugation is weakened by a non-planar conformation (Table 18, structure "C", *trans-s-skew*), the shielding increases owing to a reduction of the back-donation effect, as indicated by the data in Table 18, note (b). The ^{15}N spectra of enaminones, taken at low temperatures, reveal separate signals for individual conformers (Table 18, note (b); Table 19).

The largest deshielding effects on the nitrogen nuclei in enaminones are found when *C*-protonation takes place (Table 18, note (d)), since the protonated species has essentially the structure of an immonium ion [71] (Table 108):



and a nitrogen shielding that corresponds exactly to that of immonium ions.

It has been reported that solvent-induced deuterium isotope effects can be observed in the nitrogen shieldings of enaminones if CF_3COOH as a solvent is replaced with CF_3COOD .¹²² The values obtained, of the order of 0.05 ppm, are actually within the experimental errors quoted in ref. 122, and can hardly be considered as significant (see also the comments in Section V.A).

C. Amino groups bound to elements other than carbon

The situation where an amino-type moiety is bound intramolecularly to a silicon atom by a dative $\text{N} \rightarrow \text{Si}$ bond has already been considered in Section VI.A (silatrane structures and their analogues).

The amino groups in amino-phosphine structures (Table 25, notes (a, b)) are characterized by nitrogen shieldings that do not differ appreciably from

those for alkylamines, at least when the phosphine moiety does not bear any halogen atoms. The shieldings display typical alkyl-group effects, considered in Section V.F. There are local linear correlations (limited to a given type of the NR_2 moiety in $\text{R}_2\text{P}-\text{NR}_2$) between the nitrogen shieldings and those for ^{31}P , and also between the nitrogen shieldings and the corresponding $^1\text{J}(^{31}\text{P}-^{15}\text{N})$ couplings.³⁶

The phosphoramidate structures, $\text{R}_2\text{N}-\text{P}(=\text{O})(\text{OR})_2$, are also characterized by nitrogen shieldings (Table 25, notes (d, e); Table 26) that come close to those for the corresponding amines (Table 34); the shieldings for the former are slightly smaller than in the corresponding amines, but the effect is far weaker than in the amide structures, $\text{R}_2\text{N}-\text{C}(=\text{O})\text{R}$ (Tables 43, 47). The same holds true for some cyclic analogues of phosphoramidates, shown in Table 25, notes (f, g).

The most striking difference between nitrogen shieldings for phosphorus-nitrogen and for carbon-nitrogen moieties is observed in the case of $\text{P}=\text{N}$ and $\text{C}=\text{N}$ double bonds. The $\text{P}=\text{N}$ moieties are characterized by nitrogen shieldings that are practically within the range characteristic of amino groups (Table 25, notes (d, h-j)), while the $\text{C}=\text{N}$ moieties of imines show deshielding effects of about -200 ppm relative to amines (Tables 10, 108).

There is little effect due to Sn, Pb and Si bound to an amino group on the nitrogen shielding of the latter, as compared with the corresponding amines (Table 27, notes (a, d)), but deshielding effects are observed in the case of aminoboranes and related structures (Table 27, notes (f-i)); the latter effects can be simply ascribed to the back-donation of the lone-pair electrons from the nitrogen atom to boron (Section V.E).

Halogen atoms in halogeno-amines, $\text{R}_2\text{N}-\text{X}$, where $\text{X} = \text{Cl}, \text{Br}$, exert quite significant deshielding effects on the nitrogen nuclei relative to those in amines (Table 27, note (a)); the data also show typical effects of the alkyl groups R in $\text{R}_2\text{N}-\text{X}$ structures (Section V.F).

D. Aminosugars and related structures

The potential use of nitrogen NMR in structural investigations of complicated amino derivatives is well illustrated by the ^{15}N spectra of neomycin B and related aminoglycosides (Table 28).²⁷⁴ First, it is quite simple to distinguish, on the basis of nitrogen shieldings, the $-\text{CH}_2\text{NH}_2$ moieties from the amino groups that are bound directly to the carbohydrate ring systems; the former are more shielded. This is a simple manifestation of the β -effect (Section V.F). Secondly, it is possible to resolve the ^{15}N signals of all inequivalent NH_2 groups owing to conformational and other effects. Then, having the means of observation of all individual amino moieties, one can make use of the protonation shifts of nitrogen shieldings in amino moieties (usually about -10 ppm) and follow the protonation processes by

^{15}N NMR titration curves; the latter yield the corresponding $\text{p}K_a$ values for the individual ammonium moieties concerned (Table 29).

It is also fairly simple to trace *N*-acetylation processes of amino derivatives of carbohydrates, since there is a considerable difference in the nitrogen shieldings of amine/ammonium moieties and amide-type structures (Table 28).

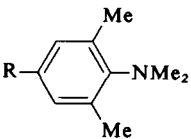
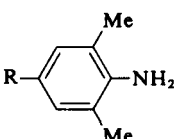
E. Arylamines, arylammonium ions and related structures

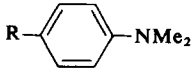
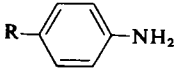
The nitrogen nuclei in arylamines are generally less shielded than those in alkylamines (Tables 34, 35). This may be ascribed to the lone-pair back-donation effect in the former (Section V.E). If an arylamine cannot assume a coplanar conformation of its NR_2 moiety and the phenyl ring, as in the case of *N,N*,2,6-tetramethylaniline (Table 34, notes (a, c)), the effect vanishes and the nitrogen shielding increases significantly, approaching that of the corresponding alkylamine (Section V.G). For 2,4,6-tri-Bu^t-*N,N*-dimethylaniline (Table 34, note (a)), the shielding is even stronger than in most alkylamines.

Substituents in the *para*-position exert shielding effects if they are electron donors, and deshielding effects if they are electron acceptors. The effects can be explained in terms of Taft's constants, σ_I (inductive) and σ_R (resonance), using equation (22),

$$\sigma(\text{aniline}) - \sigma(\textit{para}\text{-substituted aniline}) = \rho_I \sigma_I + \rho_R \sigma_R \quad (22)$$

where the σ s are the corresponding nitrogen shieldings, and the ρ s are the shielding responses to the substituent parameters σ_I and σ_R respectively; the following values are obtained for the data presented in Table 34, note (a):²⁷⁵

	ρ_I	ρ_R	rms error (ppm)
 [72]	4.18	10.44	2.3
 [73]	17.29	25.03	1.3

	ρ_I	ρ_R	rms error (ppm)
 [74]	18.05	20.19	1.9
 [75]	12.95	21.79	0.8

It is evident that steric effects that decrease the delocalization of the lone-pair electrons of the NR_2 moiety, also quench *para*-substituent effects on the nitrogen shielding. The shielding effect of fluorine substituents is also seen from the data on polyfluorinated arylamines (Table 35, note (c)).

Rather high shieldings, *ca.* +385 ppm from nitromethane, are observed for aniline ligands in ammino-type complexes of Pt(II) ,²⁷⁶ the shielding effect is analogous to those for the NH_3 ligands relative to free NH_3 (Table 127).

The presence of a ^{15}N signal at about +325 ppm (from nitromethane) in the spectrum of a *p*-benzoquinone polymer, obtained by air oxidation of *p*-benzoquinone in the presence of $^{15}\text{NH}_4\text{Cl}$ and some amino acids, is considered as an indication of the formation of arylamine moieties.²⁷⁷

The nitrogen shieldings in arylammonium ions (Table 36) indicate that the protonation effects on the shieldings of arylamines reflect, at least partly, the cancellation of the lone-pair back-donation effect, since increased shieldings are usually observed in the corresponding ions. The increase in nitrogen shielding is especially pronounced if electron-attracting *para*-substituents are present. However, complications can arise because of possible changes in bond geometry at the nitrogen atoms involved, and sometimes the protonation leads to negligible shielding or even deshielding effects.

F. Amine *N*-oxides

The *N*-oxidation of an amine leads to a substantial decrease in its nitrogen shielding, by about -100 ppm (Table 33). This is just opposite to *N*-oxidation effects in cases where the nitrogen atom is part of an unsaturated system and the lone-pair electrons are not involved in the delocalized π -electron system (Section V.E). The protonation of an amine *N*-oxide to yield the corresponding hydroxylammonium ion (Table 37) does not seem to significantly change the nitrogen shielding. However, the shieldings in amine *N*-oxides are significantly greater than those in the corresponding isomeric structures of hydroxylamines (Tables 33, 37). Attention is drawn

to the estimated value of nitrogen shielding in ammonia *N*-oxide (Table 37, note (a)).

G. Hydroxylamines, hydrazines, hydrazides and related structures

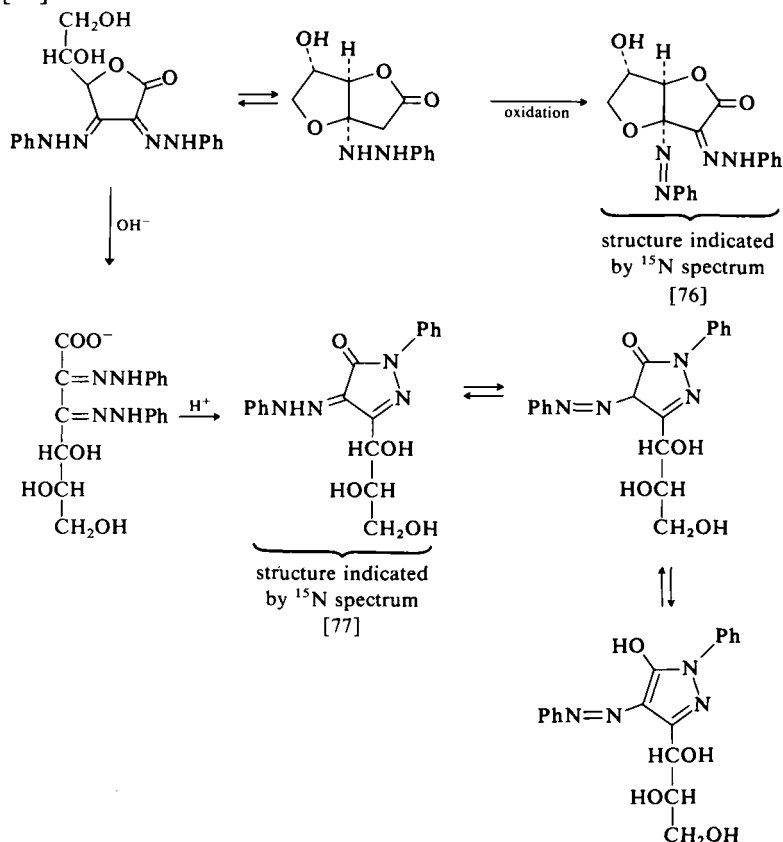
The nitrogen shieldings in hydroxylamines (Table 37) are significantly smaller than those in amines, and the difference amounts, on the average, to about 100 ppm. The protonation of a hydroxylamine, which yields the corresponding hydroxylammonium ion, invariably results in a shielding effect observed on protonation of alkylamines and ammonia (Section VI.A), effect of about +30 to +50 ppm. This is opposite to the usual deshielding. In contrast, the deprotonation of hydroxylamine (Table 37, note (a)), which gives the NH_2O^- ion, results in a shielding increase of the nitrogen nucleus; it is possible to estimate the nitrogen shielding in the anion from the data presented in Table 37.²⁷⁸ The temperature dependence of the nitrogen shielding of hydroxylamine is tentatively ascribed to a tautomeric equilibrium with the ammonia *N*-oxide form (Table 37).²⁷⁸ *N*-alkyl derivatives of hydroxylamine and the hydroxylammonium ion show the typical effects of alkyl groups on the nitrogen shieldings.

In hydrazines, the nitrogen shieldings do not differ appreciably from those in amines, as indicated by the data in Table 38 (ref. 1, pp. 46–48). There seems to be some deshielding effect relative to amines, but there is a significant overlap between the nitrogen shielding ranges for hydrazines and amines. As far as hydrazides are concerned (Table 38, notes (c–e)), there is a simple distinction, on the basis of the nitrogen shieldings, between the amide-type moiety and the amino-type moiety. The difference is similar to that observed between amides (Table 47) and amines (Table 12), but the shieldings in hydrazides are slightly smaller than those in amides and amines.

H. Hydrazones

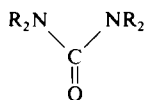
Hydrazones (Table 39) contain imino- and enamino-type moieties, $\text{R}_2\text{C}=\text{N}-$ and $-\text{NR}_2$ respectively, and the nitrogen shieldings concerned are quite analogous to those found in imines (Table 108) and amino groups bound to unsaturated systems (Table 35), but are smaller relative to the latter, especially in the case of the amino-type moieties. The latter effect can be ascribed to delocalization of the lone-pair electrons of the $-\text{NR}_2$ moiety, particularly when the hydrazone structure is conjugated with an unsaturated system of bonds (Table 39, notes (b, c)). There is a considerable difference between the *Z* and *E* isomers of the $\text{R}_2\text{C}=\text{N}-\text{NHR}$ structure as far as nitrogen shieldings are concerned (Table 39, note (c)). Nitrogen shieldings are quite useful in studies on azo-hydrazone tautomerism (Section V.K), since there are large tautomeric shifts of the shieldings involved. It is shown, on the basis of nitrogen shieldings, that the product of a mild

oxidation of dehydro-L-ascorbic acid bis(phenylhydrazone) has a bicyclic structure with an azo-moiety [76] (Table 39, note (b)), whereas, the cyclization product of the bis(phenylhydrazone) (Table 39, note (b)) is shown to contain only hydrazone-like moieties rather than an azo-type moiety [77]:²⁷⁹

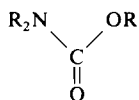


I. Ureas, guanidines, amidines and related structures

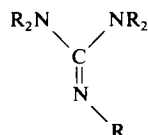
In structures [78]–[80], one can think of a competition between the delocalization of the lone-pair electrons from the two NR₂ moieties or the NR₂ and OR moieties; therefore the lone-pair back-donation effect (Section V.E) is weaker than in amides, and the nitrogen shieldings in ureas, and in the NR₂ moieties of guanidines, are smaller than those in amines, but are larger than those in amides (Table 43, ureas; Table 41, guanidines). Carbamates (Table 44) show nitrogen shieldings comparable to those found in



(ureas)
[78]

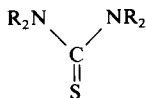


(carbamates,
urethanes)
[79]



(guanidines)
[80]

ureas, but the NR_2 moieties in guanidines reveal slightly higher shieldings. In thioureas [81] (Table 54), the nitrogen nuclei are less shielded, by about 30 ppm on the average, as compared with the corresponding ureas. Correlations can be found between the shieldings in ureas and thioureas, and the barriers to internal rotation of their NR_2 moieties, provided that alkyl group effects on the shieldings are accounted for²³⁹ (Section V.I) as well as some steric effects. The protonation of ureas and the formation of adducts of Lewis acids with ureas and thioureas leads to deshielding effects on the nitrogen nuclei (Table 43, note (a); Table 54, note (c)).



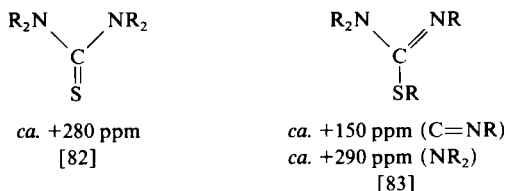
[81]

The data in Tables 43 and 44 seem to indicate that there are only small solvent effects on the nitrogen shieldings in ureas and carbamates, but the measurements are limited largely to polar, hydrogen bonding media, and hydrogen-bond acceptors. One should note that tetramethylurea (Table 43, notes (a, g)) shows an appreciable difference in nitrogen shielding between neat liquid and CH_2Cl_2 solution.

It has been demonstrated that nitrogen shieldings observed in polyurethanes (Table 45) show differences that are large enough to resolve signals representing various carbamate and urea-type moieties in such polymers; the resolution is superior to that in ^{13}C spectra.²⁸⁰ The nitrogen shieldings in biotin (Table 43, note (f)) allow one to observe individually the two NH moieties of the urea system there; since biotin is an essential cofactor for enzymes involving carboxylation and carbonyl exchange, the ^{15}N spectra can provide a convenient means of following interactions between biotin and protein systems.²⁸¹ Dynamic ^{15}N NMR spectra (proton-coupled) are employed in order to estimate the rates of proton exchange in urea and thiourea (Section IV.I).²¹⁵

The *N*-nitrosation of ureas and thioureas (Table 120) only affects appreciably the nitrogen shieldings of the nitrosated moieties; the other NR_2 type moieties show little change in their nitrogen shieldings.

There is a vast difference in the nitrogen shielding between thiourea [82] and isothiurea structures [83] (Tables 54 and 106):



which is concerned with the presence of an imino-type moiety in the latter.

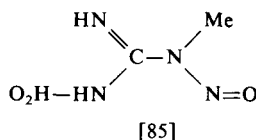
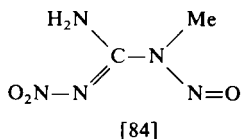
Guanidines contain both enamino-type moieties, NR₂, and imino-type moieties, C=N—R (Table 41). The nitrogen shieldings of the former do not depart appreciably from those for conjugated amines, but the latter are the highest among various imino-moieties, such as those found in isoamide structures (Table 106), and even more so as compared with simple imines (Table 108). In fact, they come close to the shieldings observed in immonium ions which are higher by more than 100 ppm than those for imines (Table 108).

If a guanidinium ion, (R₂N)₃C⁺, is formed from a guanidine structure, (R₂N)₂C=NR, the nitrogen shielding of the former is slightly below those for the NR₂ moieties in the guanidine, but it is much higher than that for the C=NR moiety in the guanidine. The latter shielding effect is typical for the structures concerned (Section V.H), and is also found for other imino-type moieties (Tables 106, 108) on the formation of the corresponding immonium-type ions. The same effect is observed in amidines and amidinium ions (Table 40).

No useful correlation is found between the nitrogen shieldings in guanidinium salts (Table 41, note (c)) and the barriers to internal rotation of their NR₂ moieties, even if attempts are made to account for alkyl-group effects on the shieldings.²⁸² This is attributed to steric effects, which affect the transition state for the rotation. Dynamic ¹⁵N spectra yield the barriers to isomerization about guanidinium and guanidino carbon-nitrogen bonds in L-arginine²¹⁶ (Table 41, note (d), and the discussion in Section IV.I).

The proton-coupled spectra of *N*-hydroxy-*N'*-aminoguanidine and derivatives thereof (Table 41, note (e)) suggest the assignments of the nitrogen shieldings as indicated in the Table. The ¹⁵N titration curves for the compounds²⁸³ show that they are weaker bases than guanidines, and the spectra of the cations suggest the presence of NHOH moieties, and exclude that of —NH₃⁺ moieties.

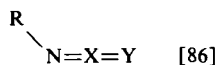
The nitrogen shieldings for *N*-methyl-*N*-nitroso-*N'*-nitroguanidine (Table 120, note (i)) clearly indicate the presence of an enamino-type NH₂ moiety and show the structure [84] to be correct rather than [85]. Analogous structures have already been shown for nitroarginine derivatives (ref. 1, Table 74 therein, and references therein).²⁸⁴



The structures of some neurotoxins that contain guanidinium moieties (Table 42) have been amply corroborated by means of the ^{15}N spectra of ^{15}N labelled substances.²⁸⁵

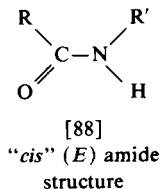
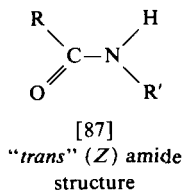
J. Cyanamides and carbodiimides

Essentially no new data on these structures have been reported recently (Table 46). We only recall that in cyanamides, $\text{R}_2\text{N}-\text{CN}$, the NR_2 moiety is characterized by a rather high shielding of nitrogen, comparable to that in alkylamines; the cyano group there also exhibits the strongest shielding among $-\text{C}\equiv\text{N}$ moieties, comparable to that found in covalent cyanates, $\text{R}-\text{O}-\text{CN}$ (Table 79). Carbodiimides, $\text{R}-\text{N}=\text{C}=\text{N}-\text{R}$, are structural isomers of cyanamides, and are clearly differentiated from the latter by the nitrogen shieldings (Table 46). As far as $\text{R}-\text{N}=\text{C}$ moieties are concerned, carbodiimides are characterized by rather high shieldings of their nitrogen nuclei, but this is a characteristic of structure [86] with a linear $\text{N}=\text{X}=\text{Y}$ moiety (Section V.E).



K. Amides, thioamides, sulphonamides and related structures

The deshielding effect of the delocalization of the lone-pair electrons from an NR_2 type moiety (Section V.E) is clearly demonstrated by the nitrogen nuclei in amide-type structures (Table 47) and their vinylogues (Tables 18, 19). The amide structures show more deshielding of their nitrogen nuclei, relative to those in alkylamines, than do ureas (and related structures), enamines and arylamines. Thus it is fairly easy to distinguish amide and amino moieties on the basis of nitrogen shieldings, since the difference amounts to about 100 ppm (Table 32). It is also possible, in numerous cases, to observe separate nitrogen resonances for the *Z* and *E* isomers of amides [87] and [88] (Table 47, note (b); see also ref. 1, Table 60 therein):

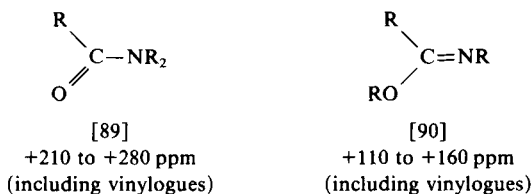


but the difference in the nitrogen shielding between *Z* and *E* structures does not exceed 4 ppm.

Thioamide structures show a deshielding effect relative to amides (Table 54), by about 50 ppm, which is analogous to that observed for thioureas relative to ureas (Section VI.I).

The nitrogen shieldings in amides are quite susceptible to solvent effects (Table 47), and the detailed consideration in Section V.J indicates that the increasing polarity of the medium, hydrogen bonding from solvent to the carbonyl group as well as hydrogen bonding from NH amide moieties to solvent result in deshielding effects on the nitrogen nuclei in amides.

Amide structures [89] are isomeric, or potentially tautomeric, to isoamide structures [90] (Table 47, notes (i, h); Table 106), and nitrogen shieldings provide a simple means of distinction between the two isomeric or tautomeric structures (Table 50):



Deshielding effects on the nitrogen nuclei in amides and polyamides are observed in protonating media (Tables 48, 52), they can be explained as those due to the increasing delocalization of the lone-pair electrons from the nitrogen atom when the oxygen atom is protonated (Section V.H).

Dynamic ^{15}N spectra provide a convenient means for study of proton exchange rates at amide moieties, as shown for acetamide and thioacetamide (Section IV.I).²¹⁵

Saturated lactams (Table 49) show nitrogen shieldings that are essentially the same as those for non-cyclic amides. In contrast, the nitrogen shieldings in conjugated lactams are especially interesting (Table 50), since such lactams are often involved in tautomeric equilibria with the corresponding OH-substituted azole and azine ring systems. The same applies to conjugated thiolactams and conjugated cyclic amidines (Table 50), which may be in tautomeric equilibria with SH- and NH_2 -substituted, respectively, azoles and azines. Tautomeric shifts of nitrogen shieldings in such equilibria are large, often in excess of 100 ppm, and afford a simple tool for estimating either the equilibrium constants involved or at least the detection of preponderant tautomers (Section V.K).

Potentially tautomeric pyrimidone derivatives, which are shown in Table 50, notes (o), (p), (q), have structures (those reported in the Table) indicated unambiguously by the nitrogen shieldings, on the basis of the large differences between the amido and imino moieties which can be directly involved

in the tautomerism. The nitrogen shielding assignments for tetrahydrofolic acid and its derivative containing a methylene bridge (Table 50, note (r)), together with experimental data on ^{13}C - ^{15}N couplings²⁸⁶ provide proof of the location of the bridge between 5-N and 10-N.

The structures of flavins contain pyrimidodione moieties (Table 50A). The nitrogen shieldings of flavins, including riboflavin, show quite large changes upon the oxidation or reduction of the corresponding reduced and oxidized forms, respectively. For 5-N the change amounts to about 300 ppm (Table 50 A); these are concerned with the conversion of NH (amido- or enamino-type) moieties to imino-type moieties, or vice versa. A comparison of the 1-N and 5-N shieldings between flavin solutions in CHCl_3 and H_2O reveals a typical shielding effect on hydrogen bonding in the case of the oxidized forms (Section V.J). The ^{15}N shielding titration curve for 7-methyl-10-ribityl-isoalloxazine-5'-phosphate in its reduced form shows that protonation occurs at 1-N, and that the $\text{p}K_a = 6.8$.²⁸⁷

The ^{15}N CP-MASS spectra of solid samples of ^{15}N -labelled melanoidins (dark brown nitrogenous polymers obtained from xylose or glucose, by reaction with ^{15}N -labelled glycine or ammonium sulphate) and ^{15}N -labelled humic acids reveal the presence of secondary amide groups (*ca.* +260 ppm from neat nitromethane) and of pyrrole-type nitrogens (*ca.* +205 and +230 ppm from neat nitromethane); in the melanoidin obtained from xylose and ammonium sulphate, a minor peak is observed at *ca.* +50 ppm from nitromethane. This is assigned to pyridine-type nitrogen atoms.²⁸⁸ The formation of amides is also indicated by the ^{15}N spectrum of a synthetic humic acid,²⁷⁷ obtained by air oxidation of *p*-benzoquinone with the addition of $^{15}\text{NH}_4\text{Cl}$.

N-hydroxy derivatives of amides, $\text{R}-\text{CO}-\text{N}(\text{OH})\text{R}$ (Table 53), show nitrogen shieldings which are smaller than those in amides. There is also some differentiation of the shieldings between the *cis* and *trans* amide structures (Table 53, note (a)).

Sulphonamide structures, $\text{R}_2\text{N}-\text{SO}_2\text{R}'$ (Tables 55, 55 A), reveal slightly higher shieldings of their nitrogen nuclei as compared with amides. There are typical effects of alkyl groups (such as those considered in Section V.F) on the nitrogen shieldings in *N*-alkyl sulphonamides (Table 55 A).

The shieldings in sulphenamide structures, $\text{R}_2\text{N}-\text{SR}'$ (Table 55 A) are still higher, and come close to those observed in conjugated amino groups. In contrast, the shieldings in sulphinamides, $\text{R}_2\text{N}-\text{SO}-\text{R}'$ (Table 55 A), are smaller than those in the corresponding sulphonamides.

Various products that are obtained in the reaction of SO_3 with NH_3 (Table 55, note (a)) can be readily identified by means of nitrogen shieldings. A study of the binding of benzenesulphonamide inhibitor to the active-site zinc of human carbonic anhydrase B (Table 55, note (f))²⁸⁹ indicates that the inhibitor is bound as PhSO_2NH^- , since the ^{15}N signal is a doublet in

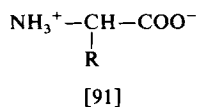
the proton-coupled spectrum; the signal reveals a shielding increase of about 18 ppm relative to that in the free anion. On the basis of the shieldings of model compounds, 2-aminobenzenesulphonamide and *N*-(2-aminophenyl)benzenesulphonamide, which are known to coordinate to Zn *via* N and O atoms respectively, the shielding effect in the PhSO_2NH^- anion bound to the enzyme, relative to that in the free anion, is indicative of binding through the nitrogen atom of the sulphonamide.

Oxidation of $(\text{R}_2\text{SO}_2)_3\text{N}$ to $(\text{R}_2\text{SO}_2)_3\text{N} \rightarrow \text{O}$ (Table 55, note (e); Table 33, note (c)) leads to a decreased shielding of the nitrogen nucleus. The effect is much smaller than for *N*-oxidation of amines, and this can be explained as a result of cancelling the delocalization of the lone-pair electrons from the nitrogen atom, because of their involvement in the formation of the $\text{N} \rightarrow \text{O}$ bond.

It is interesting to note that there is only a small difference in the nitrogen shieldings between $\text{HN}(\text{SO}_2\text{F})_2$ and $\text{FXeN}(\text{SO}_2\text{F})_2$; the latter compound contains a direct Xe-N bond, as indicated by the observation of ^{129}Xe - ^{15}N coupling (Table 55, notes (b-d)).²⁹⁰⁻²⁹²

L. Amino acids, peptides, polypeptides and related structures

Amino acids are usually involved in protonation-deprotonation equilibria, and thus their nitrogen shieldings fall into the range characteristic of amino and ammonium moieties (Table 56); there can be some additional resonances which come from side-chain moieties, such as imidazole rings, guanidino groups or amido groups. In most of the α -amino acids, under conditions where the α -amino groups are protonated to form the corresponding ammonium moieties (amino-acid cations and amphions or "zwitterions"), the nitrogen shieldings fall close to a value of +340 ppm from neat nitromethane. This is the case for a general structure [91] where R is an alkyl group, which exerts a typical β -effect (Section V.F) on the nitrogen shielding of the NH_3^+ moiety. If $\text{R} = \text{H}$, as in the case of glycine, the effect vanishes, and the shielding increases to about +350 ppm; analogous shieldings are observed for side-chain $\text{NH}_3^+ - \text{CH}_2 -$ groups (lysine, hydroxylysine, ornithine, Table 56), and for such groups in β -, γ -, δ - and ϵ -amino acids (Table 56). The secondary ammonium group of proline exhibits a characteristic shielding of about +325 ppm.



Much more information can be drawn from ^{15}N titration curves of amino acids, where the nitrogen shieldings are plotted against pH. Such experiments yield individual shieldings for the species involved and also the

corresponding pK_a values for individual ammonium moieties, as indicated by recent studies on lysine-type structures (Table 57) and on histidine-type moieties (Table 59). The latter case includes also the detection of tautomeric forms of histidine, in aqueous solutions as well as in the solid state (Table 59). Solid-state studies (Table 59)¹⁹¹ show that the nitrogen shielding tensors are quite different for the two tautomeric forms of the imidazole moiety of histidine hydrochloride monohydrate. While the observation of various species of histidine by means of ^{15}N NMR studies of solutions is complicated by the dynamic effects of proton exchange, the solid-state spectra of lyophilized powders prepared from solutions of histidine in H_2O with pH varying from 2 to 12.5¹⁸⁶ show clearly the individual species involved (Table 59), owing to the negligible rate of proton exchange in the solid state. The latter spectra indicate that the τ -NH tautomeric forms (structures "B" and "D" in Table 59) are the only ones that can be observed as far as histidine amphions and anions in the solid state are concerned.

The ^{15}N spectra of lysine hydrochloride and an amorphous polymer of lysine-formaldehyde-urea²⁹³ (Table 58) seem to indicate that the binding of lysine in the polymer occurs via the ϵ -N atom. The polymer was synthesized as an additive to ruminant diet in order to provide the infusion of essential amino acids to a ruminant's abomasum (true stomach) and to provide protection against the deamination of the amino acids by rumen microorganisms on the way to the abomasum.

^{15}N NMR was employed in order to follow the production of amino acids, and derivatives thereof, by microorganisms (Table 72). Such measurements can be carried out *in vivo*, particularly if ^{15}N labels are used. In the case of the fermentative production of glutamic acid by *Brevibacterium lactofermentum*²⁰⁷ (Table 72), it was possible to monitor free amino acids within the bacterial cells as well as those excreted into the medium. It was shown that under conditions of high oxygen supply and normal biotin concentration, the glutamic acid produced is first accumulated within the cells, together with some other amino acids, and after the preliminary stage, the excretion of the glutamic acid takes place; low oxygen supply changes the latter stage into the excretion of alanine and only small amounts of the glutamic acid accumulated. High biotin concentrations in the growth medium result in a significant decrease in the accumulation and excretion of glutamic acids by the cells. Amino acids that are metabolites of NH_4^+ assimilation by the intact mycelia of *Neurospora crassa* were also observed by means of ^{15}N NMR spectra²⁹⁴ (Table 72); similar studies²⁹⁵ reveal that the rates of biosynthesis of glutamine and alanine by the mycelia depend significantly on the nitrogen sources employed. As far as the synthesis of glutamine is concerned, the fastest rate is observed when the culture is grown on glutamic acid or on ammonium nitrate followed by 3 h of nitrogen starvation; the rate slows down when ammonium nitrate is employed, and

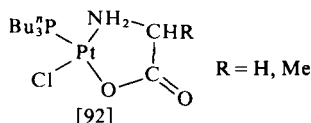
even more so if a combination of ammonium nitrate with glutamic acid and glutamine is used. The reverse trend is found for the rates of biosynthesis of alanine. All such studies rely, to varying degrees, on the relation between the concentrations of nitrogen nuclei and the intensities of the corresponding ^{15}N resonance signals. One should be cautious with stretching too far any conclusions that may result from ^{15}N signal intensities, because of the role of relaxation and nuclear Overhauser effects (Section IV.E). However, provided that such effects are either accounted for or non-significant (as in the case of the growth or decay of any single resonance peak under given experimental conditions), ^{15}N NMR can be very useful in tracing down various biosynthetic pathways, including those concerned with amino acids and their derivatives. The uptake of $^{15}\text{NO}_3^-$ ions by *Neurospora crassa*, and the resulting distribution of the ^{15}N label between the protein components and amino acid metabolites is shown clearly by the ^{15}N CP-MASS spectra of lyophilized mycelia of the microorganisms¹⁷⁷ measured as such and after an extraction of soluble components with ethanol; the study also indicates that there must be an induction period of contact with NO_3^- ions, in order to produce significant amounts of nitrate reductase in the microorganisms, before the utilization of the nitrate by the latter. Since the nitrogen shieldings of the imidazole moiety of histidine are quite sensitive to pH (Table 59), they can be employed in intracellular pH measurements. This technique coupled with that based on proton-exchange effects observed for ^{15}N resonances of some other amino acids (arginine, alanine, proline) was employed for intact mycelia of *Neurospora crassa* (in aqueous suspensions) to yield a value of $\text{pH} = 6.1 \pm 0.4$ for vacuoles, and 7.15 ± 0.10 for cytoplasm.²³⁶

The nitrogen shieldings of the ammonium moieties in amino acids can be studied, from the point of view of substituent effects, using amino-acid ester hydrochlorides (Table 60); this relieves one from complications that result from protonation/deprotonation equilibria between amino and COOH moieties. The effects, relative to the shieldings in the corresponding glycine derivatives, are shown in Table 64; they reveal a significant contribution of solvent effects and, therefore, they can be used for assignment purposes only if differences in excess of 3 ppm are observed,²⁹⁶ contrary to earlier expectations, which were based on studies of rather concentrated solutions.

The *N*-hydroxymethylation of amino acids by aqueous formaldehyde induces characteristic deshielding effects (by -22 to -26 ppm) on the resonances of the amino groups (Table 61). Thus it is fairly easy to observe such processes by means of nitrogen NMR.

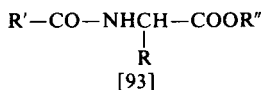
Appreciable shielding effects on the nitrogen nuclei are observed in the case of Co(III) complexes with amino acids (Table 65), as compared with the shieldings of the free ligands. The coordination shifts of the nitrogen shieldings depend significantly on the geometry of the complexes. In general,

the shielding effect is much larger when the amino group of an amino acid is in the *trans* position relative to an oxygen atom than in arrangements where the amino group is *trans* relative to a nitrogen atom. Rather high shieldings are also observed in Pt(II) complexes of some amino acids [92]



in whose spectra the ^{15}N resonances lie at about +403 ppm ($\text{R} = \text{H}$) and +388 ppm ($\text{R} = \text{Me}$) from neat nitromethane.²⁹⁷ The ^{15}N shielding titration curves of cysteine and its 2:1 complex with Zn(II) indicate that the pK_a value of NH_3^+ changes from 10.8 for the free ligand to 9.5 for the complex;²⁹⁸ however, in this case the nitrogen shieldings are not very informative about the existence or non-existence of Zn-N bonds in the complex. A method was proposed to detect such bonds in complexes by labelling the latter with ^{67}Zn (spin $\frac{5}{2}$) and the eventual observation of ^{15}N signal broadening;²⁹⁸ in the case of the cysteine- Zn complex, this gave a small broadening of about 2 Hz, which was used as an argument in favour of the NH_2 coordination to zinc at high pH values. However, the broadening seems to be too small for a serious evidence of the coordination.

In peptide systems the nitrogen atoms of amino-acid residues are involved in amide-type bonds, apart from terminal $\text{NH}_2/\text{NH}_3^+$ moieties and side-chain moieties. Since the nitrogen shieldings in amides (Section VI.K) are appreciably smaller than those in amino and ammonium moieties (Section VI.A, see also Table 10), it is fairly easy, on the basis of nitrogen shieldings, to distinguish peptide bridges from other nitrogenous moieties in peptides. An examination of *N*-acetyl amino acids (amide-type moieties) and *N*-carbobenzyloxy amino acids (urethane or carbamate-type moieties) [93] indicates that effects of substituents R relative to $\text{R} = \text{H}$ (glycine moieties) are quite analogous to those observed for ammonium moieties in amino-acid ester hydrochlorides (Tables 62, 64), as far as changes in the nitrogen shieldings are concerned. The origin of the effects presented in Table 64 is, in most of the cases, the β -effect of alkyl group R (Section V.F). Thus glycine moieties in peptides are characterized by relatively high nitrogen shieldings. One should note, however, that the substituent effects are sensitive to solvent influences. Attention is drawn also to the fact that the nitrogen shieldings in amino acids, whose amino moieties are protected by the formation of carbamate-type structures, are 20–30 ppm higher than those in amide-type peptide bridges (Table 62).



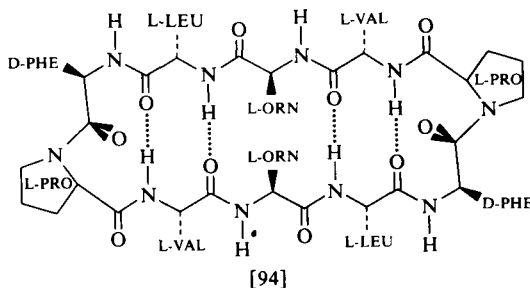
In general, one can expect significant solvent and concentration effects on the nitrogen shieldings of peptides and their analogues, on the basis of such effects observed for amides (Section VI.K; see also Section V.J). The effects are shown clearly in recent studies on peptides (Tables 48, 63, 66).^{296,299}

A large body of nitrogen shielding data on oligopeptides (Table 66) was employed in an attempt²⁹⁶ to construct a system of neighbouring residue effects, that is, differences in nitrogen shieldings of amino-acid residues Y between structures X—Y and Y—Y, where X and Y represent different amino-acid residues. Such effects can theoretically be helpful in nitrogen shielding assignments and sequence analyses of copolypeptides (Table 74). However, it was found that there is a rather poor correspondence between the effects in model oligopeptides and copolypeptides.²⁹⁶ As far as the neighbouring residue effects (NREs) in oligopeptides are concerned, they are susceptible to solvent effects, steric crowding of residues, etc. As a general rule, the NRE that X exerts on Y always has the opposite sign to the NRE which Y exerts on X;²⁹⁶ there are also other, more limited, rules, such as the shielding direction of NREs when X = Gly, and the deshielding direction when Y = Gly and X = any other residue.

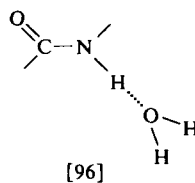
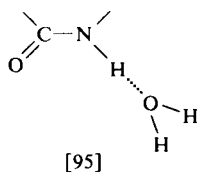
The *cis*-amide and *trans*-amide isomers in peptides can be observed in ¹⁵N spectra if proline moieties are present, as shown in Table 67, and Table 66, note (f).

The similarity of the nitrogen shieldings in oxytocin and 8-arginine vasopressin (Table 68) suggest that the two peptide hormones have similar conformations.³⁰⁰ A study of the nitrogen shieldings of enkephalin derivatives (Table 69) suggests that the molecules of the cationic and anionic forms have unfolded, flexible conformations, with all of the amide groups exposed to interactions with solvents; the amphion should have a cyclic structure,³⁰¹ owing to a hydrogen bond between the NH of Phe⁴ and the CO of Tyr¹. Such conclusions are usually based on solvent-induced shifts in the nitrogen shieldings of peptide bridges. As indicated in Section V.J, one can expect deshielding effects on amide nitrogen nuclei upon hydrogen bond donation by the amide NH moiety as well as upon the acceptance of a hydrogen bond by the corresponding carbonyl moiety. There can be a competition of the latter effects induced by intra- and inter-molecular hydrogen bonds. Thus if one changes solvents from hydrogen-bond donors to hydrogen-bond acceptors, the resulting shifts in the nitrogen shieldings of individual amino-acid residues in a peptide can represent a complicated combination of hydrogen-bonding effects, which act in the deshielding direction. One should then be rather cautious in inferring any positive conclusions about the structure of the peptide, since it is often difficult to distinguish convincing proofs from mere speculations. A good deal of discussion of this kind has taken place as far as the nitrogen

shieldings of gramicidin-S are concerned (Table 70, and references therein). The data in Table 70 indicate clearly that there is a significant deshielding of the amide-type moieties of L-Val, L-Leu, and L-Pro residues upon changing solvents in the sequence: DMSO, MeOH, H₂O and CF₃CH₂OH. This is in a perfect agreement with the postulated structure of gramicidin-S [94],



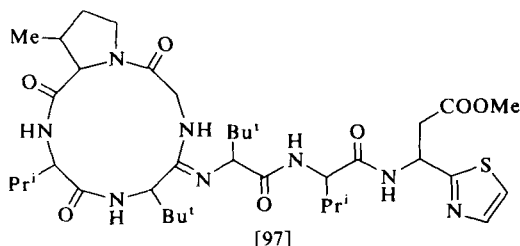
since the hydrogen-bonding donation from solvent molecules to the carbonyl groups of L-Pro, L-Orn and D-Phe should result in significant deshielding effects on the nitrogen nuclei in the adjacent nitrogen atoms, according to the considerations of amide groups in Section V.J. However, the nitrogen shieldings of the amide moieties in L-Orn and D-Phe do not show any substantial variations upon changing solvents in the sequence mentioned, while in theory there should be shielding effects upon passing from DMSO to CF₃CH₂OH as a solvent, since the hydrogen-bond donation by the peptide NH moieties should be impaired by the decreasing hydrogen-bond accepting properties of the solvent employed. In order to explain this, some authors³⁰² resort to invoking a chain of perturbations generated by the hydrogen bonding to the CO groups across the internal hydrogen bonds as a compensating effect. We think we can offer a much simpler rationalization of the lack of sensitivity of the shieldings of the solvent-exposed NH moieties in gramicidin-S to changes in the hydrogen-bond acceptor strength of the solvent. Theoretical calculations suggest¹⁹ (Section V.J) that there is a significant deshielding effect on the nitrogen nucleus on the hydrogen-bond donation in [95], while the effect should be negligible in [96]. Since the



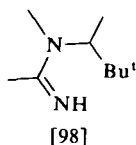
latter occurs in the case of the NH moieties considered, the explanation of the lack of response of the nitrogen shieldings to solvent changes becomes rather trivial. There seems to be a still unsolved problem of the significant

deshielding of the nitrogen nuclei in L-Pro and L-Leu in gramicidin-S relative to model peptides;²⁹⁶ the effect does not change its sign on changing the solvent from DMSO to formic acid, and it is ascribed tentatively to steric hindrance of the bulky side-chains in the neighbourhood of the moieties considered.²⁹⁶

The structure of the antibiotic, bottromycin A2 [97] has been revised on the basis of ¹H-coupled ¹⁵N spectra.³⁰³



The presence of five doublets at about +298, +270, +267, +260, and +256, a split signal at +245 ppm, and two singlets at about +150 and +67 ppm indicate clearly the arrangement of the amidine moiety to be as shown above rather than as in [98], which was postulated in earlier studies.



The nitrogen shieldings in angiotensin amide (Table 71) were examined from the point of view of their pH dependence.²³⁷ The shieldings of the Arg² moiety are practically constant throughout a broad range of pH values (2–10), thus indicating that this group does not interact with other charged groups; only a small effect is observed for Tyr⁴. There is some increase in the shieldings of Val³ and Val⁵ at high pH, probably because of interactions with the ring moieties of Tyr⁴ and His⁶.

The incorporation of ¹⁵N-labelled glycine into peptide bonds of reduced glutathione of intact human erythrocytes was followed by means of ¹⁵N spectra (Table 72).³⁰⁴ Various amino-acid residues are observed in the CP-MASS ¹⁵N spectra of solid pellets of bacteriophage fd virus (Table 72).¹⁷⁸ The signals of the coat protein of the virus can be clearly distinguished from those due to DNA, since there is a large difference in the nitrogen shieldings involved. While the ¹⁵N spectrum of the protein part is dominated by a strong signal at about +270 ppm (Gly and side-chain Gly), the single proline moiety Pro⁶ (+241 ppm) and terminal Ala¹ (+346 ppm) can also be observed. If the coat protein is labelled with ¹⁵N at the tryptophan

moiety, Trp²⁶, a single signal is observed in the CP-MASS spectrum of ¹⁵N;¹⁷⁹ this means that in all 2700 coat protein subunits the environment around Trp²⁶ is the same. The two-dimensional ¹⁵N spectra (nitrogen shieldings versus dipolar splitting) of magnetic-field-oriented solutions of viruses fd and Pf1 indicate³⁰⁵ that the N-H bonds of the amide groups in virus fd are almost parallel to the filament axis of the virus, and to the α -helix axis; for virus Pf1, the ¹⁵N data show two distinct sections of the α -helix of the coat protein, and this contradicts earlier conclusions based on X-ray diffraction data.

The ¹⁵N powder spectra of the coat protein of virus fd show that the nitrogen shielding anisotropy is about the same as in crystalline amino acids and peptides, and this excludes any large-amplitude motions of the peptide backbone at frequencies larger than 10⁴ Hz, while ¹⁵N relaxation and NOE measurements suggest motions at a rate of about 10⁹ Hz;¹⁹⁸ this apparent discrepancy is explained in terms of rapid, but small-amplitude, motions of the polypeptide backbone.

Peptide bridges and various amino-acid moieties have been observed by means of CP-MASS spectra of ¹⁵N in soybeans (Table 72, references in footnote (e)). Quantitative measurements of the utilization of glycine in the presence of glutamine for the synthesis of storage protein in soybean cotyledons,¹⁷⁶ using ¹⁵N CP-MASS spectra, indicate that the presence of glycine (¹⁵N-labelled) in the culture medium impairs the utilization of glutamine; the incorporation of the ¹⁵N labels of the glycine substrate into the protein includes not only glycine residues, but also other residues. Since the incorporation of ¹³C labels of glycine is much smaller than that of ¹⁵N, the glycine substrate must be involved in transamination processes in the plant tissue. Analogous studies¹⁷⁵ were carried out for asparagine and glutamine utilization in the synthesis of the protein. The ¹⁵N-labelled amino and amide nitrogen atoms of glutamine are incorporated almost equally into the protein, but in the case of asparagine the use of the amide nitrogen atoms is reduced; the latter observation suggests that asparagine is involved in transamination processes. CP-MASS spectra of ¹⁵N with double cross-polarization (Section IV.G) were employed in order to follow the incorporation and turnover of ¹³C-¹⁵N double labels in the protein of soybean leaves;¹⁸⁴ the plants are uniformly labelled with ¹⁵N, and exposed to a ¹³CO₂ atmosphere. The results show that the proteins of mature, fully expanded leaves of soybean has a lifetime of about 30 days.

Studies on nitrogen shieldings of some imidazole derivatives²⁵¹ (Table 88) provide support for the explanation of the preponderance of the π -NH tautomer (Table 59) in the histidine residues of the catalytic triad Ser-His-Asp in α -lytic protease as a result of hydrogen bonding within the triad.

Two ¹⁵N resonances are observed in the spectra of wheat proteins in solution, one at about +311 ppm from neat nitromethane (NH₂ moieties)

and another at *ca.* +299 ppm (NH moieties), and irreversible changes in their intensities are found after a heating and cooling cycle.³⁰⁶

Solvent effects on the nitrogen shieldings of actinomycin-D (Table 51) show that when one replaces DMSO with H₂O as a solvent, the shieldings decrease significantly for the L-(NMe)Val, Sar and L-Pro moieties while those for the other amino acid residues are hardly affected. This seems to indicate that the carbonyl groups of Sar, L-Pro, and D-Val are solvent-exposed,²⁴² with an alternative explanation of these effects in terms of hydrogen bond formation within a dimer which may exist in aqueous solutions. In some instances, separate ¹⁵N signals are observed for the two non-equivalent peptide moieties of actinomycin-D (Table 51). Some minor changes in the nitrogen shieldings of actinomycin-D in an aqueous buffer are found upon an addition of the dinucleotide d(pGpC) or calf thymus DNA³⁰⁷ (Table 51), and attempts were made to present these as an example of the potential of ¹⁵N NMR for providing a great deal of information on the structure of actinomycin-nucleic acid complexes, but one should be rather cautious with conclusions based on nitrogen shielding changes of about 1 ppm, which, at best, can provide some weak support to data from other sources.

The CP-MASS spectrum of ¹⁵N-labelled protein of carrot cell¹⁸² reveals, in addition to a dominant peak at about +260 ppm from neat nitromethane (peptide bridges), signals of side-chain His, Arg and Lys moieties.

It is claimed that ¹⁵N spectra,³⁰⁸ in addition to other techniques, confirm unambiguously the structure of ¹⁵N-labelled methyl α -(isocyano)propionate, prepared from ¹⁵N-alanine, but the nitrogen shielding reported, *ca.* +339 ppm from neat nitromethane (after recalculation from the original NO₃⁻ reference) is simply that of alanine (see Table 56), while the isocyano group is characterized by a nitrogen shielding of about +200 ppm (Table 81).

The CP-MASS ¹⁵N spectra of solid polypeptides (Table 73) reveal differences of about 10 ppm in the nitrogen shieldings of β -sheet and α -helix secondary structures. In some cases, it is possible to estimate contributions of the two secondary structures, as in the case of (L-Leu)_n, where about 10% β -sheet and 90% α -helix is found.¹⁸⁰ Usually, the shieldings of the β -sheet structures are smaller than those of the corresponding α -helices, with an exception for (Gly)_n (Table 73). Interesting results were obtained for host-guest copolypeptides (Table 73). Polyvaline forms β -sheets (*ca.* +251 ppm), but when L-valine is incorporated into the α -helix structures of (L-Ala)_n or (L-Leu)_n, the nitrogen shielding of Val residues, *ca.* +260 ppm, indicates that, in the copolymers, valine also assumes the helical structure. The situation is more complicated if glycine is introduced as the guest into a polypeptide; when Gly is incorporated into an α -helical structure the nitrogen shielding of Gly becomes *ca.* +270 ppm, which corresponds apparently to the shielding of β -sheet (Gly)_n; however, if Gly is incorporated

into a β -sheet polymer the Gly shielding becomes *ca.* +264 ppm, and this indicates that the nitrogen shielding in the guest Gly is simply influenced by the neighbouring amino-acid residues, and that Gly units are actually built in between the blocks of the host polymer.¹⁸⁰

While the nitrogen shieldings in solid peptide polymers are influenced significantly by secondary structures of the solid, the shieldings in solutions of such polymers reveal effects of neighbouring amino-acid residues (Tables 74, 75). On the basis of a large amount of data, it is possible to present a set of nitrogen shieldings characteristic of individual peptide linkages in peptide polymers, dissolved in CF_3COOH (Table 75); attention is drawn to bulk-susceptibility effects on the values of the shieldings obtained by the external reference technique (see the specifications in Table 75). For any pair X—Y of amino-acid residues, the nitrogen shielding in Table 75 is that of Y, influenced by X. Thus only the direct neighbouring residue effects are considered here, and this is the favourable case (α -amino-acid polymers) when the effects of more remote residues are small. This is important from the point of view of sequence analysis of copolypeptides, since ^{15}N resonance signals of individual peptide bonds can be observed with good resolution,³⁰⁹ as indicated by the data in Table 74, note (e). Thus, for a binary copolypeptide (that made of two kinds of amino-acid residues, X and Y), one should observe four signals corresponding to X—X, Y—Y, X—Y and Y—X peptide linkages, and the average lengths of homogeneous blocks (e.g., —X—X—X...) can be calculated from the corresponding signal intensities I according to^{309,310}

$$L_X = \frac{I_{X-X}}{I_{Y-X}} + 1 \quad (23)$$

provided that the inverse-gated decoupling technique is used in order to quench nuclear Overhauser effects (Section IV). Proton resonance intensities can then be employed as a check of the L_X/L_Y ratio obtained from ^{15}N NMR. In the case of a ternary copolypeptide (that made of three kinds of residues, X, Y and Z), nine ^{15}N signals should be found,^{309,310} and the equations for the average length of homogenous blocks assume the form

$$L_X = \frac{I_{X-X}}{I_{Y-X} + I_{Z-X}} + 1 \quad (24)$$

Actually, it is sufficient if three signals are resolved for a binary copolypeptide, and seven signals for a ternary copolypeptide. From the point of view of sequence analysis of polypeptides and polyamides, not only are differences in nuclear shieldings important, but also the corresponding signal widths, which affect the spectral resolution available. Long-range effects (those other than the direct neighbouring-residue effects) can result in minor non-equivalences of nitrogen shieldings, and consequently in increasing the

widths of the nitrogen signals concerned, thus deteriorating the spectral resolution. The following comparison shows the merits and demerits of ^{15}N and ^{13}C spectra in such analyses:³⁰⁹

Type of amino-acid residues in copolymer	Neighbouring residue effects (NREs) on shielding and consequences thereof	
	^{15}N NMR	^{13}C NMR
α - and ω -amino-acid residues, varying side chains:		
direct NREs	large	small
long-range NREs	small	large
resolution	good	poor
ω -amino-acid residues, varying number of bonds intervening between the amide and carbonyl moieties:		
direct NREs	large	large
long-range NREs	large	small
resolution	poor	good

Thus, ^{13}C spectra are superior, in sequence analyses, to ^{15}N NMR when the sequences include ω -amino acids with different chain lengths, while ^{15}N spectra provide a better means of analysis in cases when monomeric units differ only in side chains, and this includes obviously α -amino-acid polymers.^{130,309,310} The spectral resolution is usually better in natural polypeptides, as far as ^{15}N spectra are concerned, and it turns out that it may be easier to observe 20 individual peptide bonds in bovine insulin-A chain³¹¹ (Table 76) than 9 peptide groups in a ternary copolypeptide,^{296,310} (Table 74, note (e)).

It seems also that ^{15}N NMR is superior to ^{13}C NMR in the investigation of the tacticity of polymers of D,L-amino acids (Table 74, note (d)),^{309,312,313} provided that appropriate solvents are employed in order to resolve individual ^{15}N resonance signals representing various combinations of syndiotactic (s) and isotactic (i) sequences:

diads:	$\text{L}_\text{N}\text{L}$	(i)	$\text{L}_\text{N}\text{D}$	(s)
triads:	$\text{L}_\text{N}\text{LL}$	(ii)	$\text{L}_\text{N}\text{DL}$	(ss)
	$\text{L}_\text{N}\text{LD}$	(is)	$\text{L}_\text{N}\text{DD}$	(si)
tetrads:	$\text{LL}_\text{N}\text{LL}$	(iii)	$\text{LL}_\text{N}\text{DL}$	(iss)
	$\text{DL}_\text{N}\text{LL}$	(sii)	$\text{DL}_\text{N}\text{DL}$	(sss)
	$\text{LL}_\text{N}\text{LD}$	(iis)	$\text{LL}_\text{N}\text{DD}$	(isi)
	$\text{DL}_\text{N}\text{LD}$	(sis)	$\text{DL}_\text{N}\text{DD}$	(ssi)

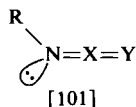
where N represents the nitrogen atom in a given peptide bridge, while D and L represent the configurations of the amino acid residues involved (the corresponding enantiomers, like $D_N D$, etc., are not listed here). It is found that, as a rule, the nitrogen shieldings of isotactic sequences are smaller than those for the corresponding syndiotactic sequences.^{309,312}

M. Azides and their protonated forms

The nitrogen shieldings of the terminal nitrogen atoms of the azide ion [99] are appreciably higher than that of the central atom (Table 77). In covalent azides [100], the most shielded nitrogen nuclei are those in the

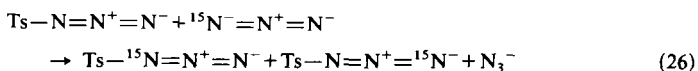
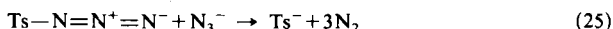


$R-N=$ moieties (Table 77, see also ref. 1, p. 70); the latter shieldings are comparable to those observed in carbodiimides and covalent isocyanates and covalent isothiocyanates (Table 10). Such high shieldings are typical of the singly bent structures [101], as indicated in Section V.E. The least-shielded nitrogen nucleus in a covalent azide is usually that in the central atom $=N^+=$ (ref. 1, Table 103 therein), but if group R is a strong electron acceptor, the least shielded becomes $=N^-$ (Table 77).

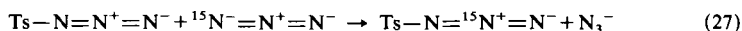


The nitrogen shieldings of the azido moiety are quite characteristic and allow one to distinguish the moiety from any other structures. It is therefore straightforward to observe valence tautomerism that involves an azido group, such as that presented in Table 78, using nitrogen NMR.³¹⁴

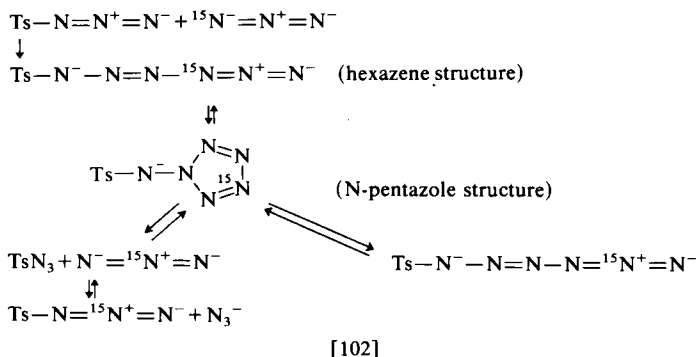
Tracer studies that employ ^{15}N labels and ^{15}N NMR spectra can be used in the investigations of reaction mechanisms of *p*-toluenesulphonyl azide with nucleophiles, including the azide ion (see ref. 1, p. 71, and references therein). It is shown that in DMSO solution the following reactions take place (Ts = *p*-toluenesulphonyl group):



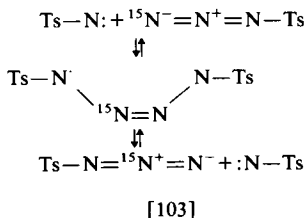
but more recent studies³¹⁵ show that in CH_2Cl_2 (using potassium azide solubilized with a crown ether) only reaction (26) takes place and, in addition, there is a slow reaction



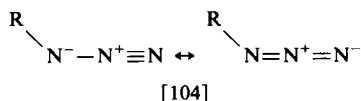
The relevant nitrogen shieldings are given in Table 77, note (c). In order to explain reaction (27), a scheme [102] is postulated³¹⁵ that involves the formation of hexazene and N-pentazole structures:



Alternatively, either the hexazene or N-pentazole structures can generate *p*-toluenesulphonyl nitrene, $\text{Ts}-\text{N}:$, which is likely to react in the following way:³¹⁵

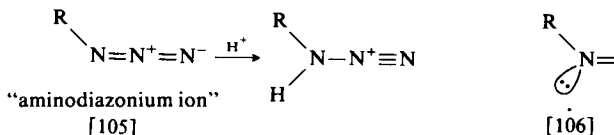


The nitrogen shieldings of the central $=\text{N}^+=$ atoms in azido groups seem to be the least affected by the nature of the group R in $\text{R}-\text{N}_3$. The shieldings of the two other nitrogen atoms reveal much more variation, and attempts have been made³¹⁶ to explain this in terms of electron orbital energies, UV transitions, and contributions of the resonance structures [104], to the actual structure for a given group R.



However, one should be cautious with such explanations, which do not involve really any calculation of the shieldings concerned. For example, alkyl azides (Table 77) reveal a typical β -effect (see Section V.F), about -15 ppm for $\text{R}-\text{N}=\text{N}$ upon replacing $\text{R}=\text{Me}$ with $\text{R}=\text{Et}$, and this effect cannot be explained in terms of any simple theories or correlations with simple physico-chemical properties.

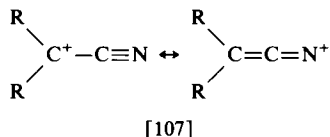
The protonation of a covalent azide [105], which leads to a structure that may be termed an aminodiazonium ion, results in some deshielding of the nitrogen nucleus in the R—N moiety, but induces a strong deshielding effect on the terminal nitrogen atom (Table 77).³¹⁷ As far as protonation effects on nitrogen shieldings are concerned in the case of [106],



this is an exception from the general rules (see the discussion in Section V.H).

N. Cyanocarbenium ions

The structure of cyanocarbenium ions [107] bears a formal resemblance to that of the protonated forms of covalent azides (Section VI.M), and actually their nitrogen shieldings (Table 80) are very close to those of the



latter (terminal nitrogen atoms, Table 77, note (f)). On the other hand, the shieldings in the ions do not depart significantly from those in nitriles (Table 81). The scarce data available (Table 80) seem to indicate that there is a significant effect on the nitrogen shielding exerted by the *para* substituents in *para*-substituted phenyl groups R,³¹⁸ and that the nitrogen shieldings correlate with the corresponding ¹³C shieldings of the carbon atom R₂C. The increased nitrogen shielding in the case of the *p*-methoxyphenyl derivative (Table 80) was taken as evidence of the reduced contribution of the "nitrenium ion" resonance structure, R₂C=C=N⁺, in the actual structure of the ion.

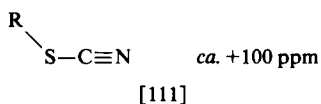
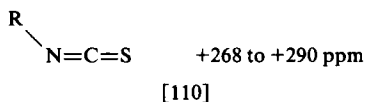
O. Cyanates, isocyanates, thiocyanates and isothiocyanates

The ambidentate (iso)cyanate ion, NCO⁻, is characterized by a nitrogen shielding of about +303 ppm (from neat nitromethane), but the formation of covalent bonds to yield covalent isocyanates, R—N=C=O, and covalent cyanates, R—O—CN, gives significant shielding [108] and deshielding [109] effects on the nitrogen nucleus, respectively (Table 79):



Thus the mode of binding of the (iso)cyanate ion is clearly indicated by nitrogen shielding, and the values of about +338 ppm observed for NCO^- bound to human carbonic anhydrase B,²⁸⁹ shown in Table 79, note (b), can be interpreted as due to the binding through the nitrogen atom to the zinc atom in the metalloenzyme. The insensitivity of the nitrogen shielding of the bound cyanate to changes in pH seems to indicate that the cyanate ion replaces the H_2O molecule at the fourth ligand site of Zn.²⁸⁹

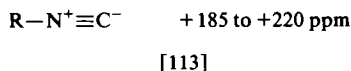
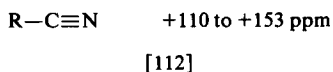
The free (iso)thiocyanate ion, NCS^- , is characterized by a nitrogen shielding of about +172 ppm (Table 79), but the latter value is more susceptible to molecular interaction effects in solutions than that of the cyanate ion. The formation of covalent bonds yields analogous effects on the nitrogen shieldings which clearly differentiate isothiocyanates, [110] from thiocyanates [111],



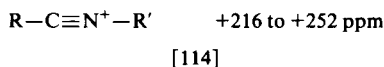
Thus the mode of binding of NCS^- in complexes can be predicted for the *N*-binding (a shielding effect) and the *S*-binding (a deshielding effect). In a solution of the thiocyanate-Pd complex shown in Table 79 (note (d)), the ^{15}N signal of non-complexed NCS^- is found at +223 ppm, and therefore the two other signals at +302 and +197 ppm should be assigned to the *N*-bound and *S*-bound thiocyanate ion, respectively, contrary to the given³¹⁹ reverse assignment.

P. Cyanides, isocyanides, related ions and *N*-oxides (fulminates)

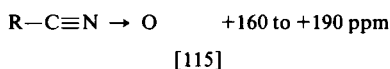
The nitrogen shielding in the cyanide ion, CN^- (ca. +104 ppm, Tables 81) appears at the low-shielding limit of various cyano moieties. Covalent cyanides or nitriles, $\text{R}-\text{CN}$, where R contains a carbon atom bound directly to the CN moiety, are characterized by higher shieldings of the nitrogen nuclei, as compared with that of the CN^- ion, but in isocyanides, $\text{R}-\text{NC}$, the shieldings are still higher, and provide an easy distinction between cyanides [112] and isocyanides [113] (Tables 81 and 10):



The protonation or *N*-alkylation of a covalent cyanide (nitrile), which yields the corresponding nitrilium ion [114] (Table 81), results in a considerable shielding effect (by about 100 ppm):



which is typical from the point of view of the considerations presented in Section V.H. The *N*-oxidation of a nitrile, which gives the corresponding nitrile *N*-oxide (fulminate) [115], also results in a significant increase in the nitrogen shielding,



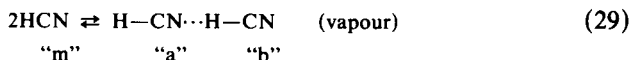
according to the data presented in Table 82, and this shift is also typical from the point of view of the *N*-oxide effect considered in Section V.E.

It is evident from the above data that nitrogen shieldings afford a simple means of differentiation among all of the species considered, since there is little or no overlap of their spectral ranges. One should note, however, that nitrogen shieldings of about +200 ppm (from neat nitromethane) are also typical of the cyano moieties in cyanamides, $\text{R}_2\text{N}-\text{CN}$ (Table 46), and covalent cyanates, $\text{R}-\text{O}-\text{CN}$ (Table 79).

The gas-to-liquid shift of the nitrogen shielding in HCN at 346 K is found to be +10.4 ppm,⁵⁴ which is comparable to that in acetonitrile and pyridine, but opposite in sign compared with ammonia and trimethylamine. The temperature dependence of the nitrogen shielding in liquid HCN obeys the equation⁵⁴

$$\sigma_{\text{N}}(\text{liq. HCN}, T) - \sigma_{\text{N}}(\text{liq. HCN}, 300 \text{ K}) \\ = -2.1775 \times 10^{-2}(T - 300) - 5.508 \times 10^{-5}(T - 300)^2 \quad (28)$$

within the limits 265–340 K, while the shielding of the vapour in equilibrium with the liquid shows a linear dependence, $+2.8097 \times 10^{-2}$ ppm/deg (within the range 340–376 K). An analysis of these data yielded the association shift of the nitrogen shielding in HCN vapour, on the assumption of the simple equilibrium⁵⁴



$$\frac{1}{2}[\sigma_{\text{N}}(\text{a}) + \sigma_{\text{N}}(\text{b})] - \sigma_{\text{N}}(\text{m}) = +14.08 \text{ ppm} \quad (\text{average})$$

The sign of this hydrogen-bonding effect is consistent with that of *N*-protonation of cyano groups (Table 81) and the general considerations of hydrogen-bonding effects on nitrogen shielding (Section V.J). Analogous observations were made for solutions of benzonitrile, PhCN, in a variety

of solvents (Table 81, note (d));³²⁰ the increasing acidity of the solvent results in an increased shielding of the nitrogen nucleus in PhCN.

If the lone electron pair at the nitrogen atom in acetonitrile, MeCN, is involved in interactions with cationic centres, one again observes significant increases in the nitrogen shielding, as was shown (Table 84) for acetonitrile adsorbed in various cation-exchanged zeolites; the magnitude of the increase correlates linearly with the electrostatic potential e/r , where e is the elementary charge and r is the radius of the cation concerned.³²¹ Thus nitrogen shieldings can be used conveniently for tracing down interactions of cyano groups with their environment. In contrast, the nitrogen shieldings in the $-\text{CMe}_2\text{CN}$ end groups in polystyrene and polymethylmethacrylate whose polymerization is initiated with aza-isobutyronitrile³²² (Table 81, note (h)) do not show any detailed information about the structure of the polymers in the vicinity of the cyano groups.

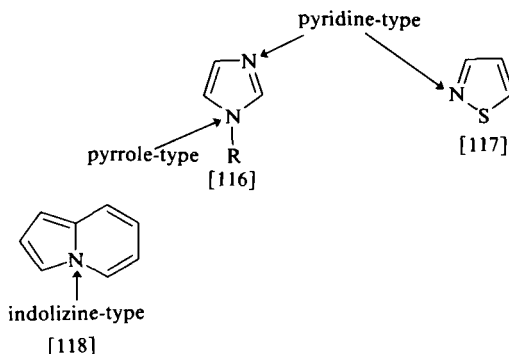
The nitrogen shieldings of the cyano group afford a simple means of observation of rearrangements of sydnone-imine structures into the isomeric *N*-alkyl-*N*-cyanomethylnitrosamines (Table 92, note (d)).

The nitrogen shieldings in the cyanide ligands in complexes with various metal ions (Table 83) are within ± 15 ppm of the shielding for the free CN^- ion (Table 81), but some general trends can be observed:³²³ for isoelectronic complexes the deshielding direction corresponds to increasing oxidation number of the metal; within periodic families the shielding of nitrogen increases upon going down the periodic table, except for the Zn family.

Secondary isotope effects ($^{13}\text{C}/^{12}\text{C}$) on the ^{15}N shieldings of the cyanide ligand in some complexes are shown in Table 7 (note (a)).

Q. Azole ring systems, azolium ions and azolo-azines

One can distinguish three essential types of nitrogen atoms in azole ring systems, those of five-membered rings of a significant aromatic character, which include at least one nitrogen atom, and eventually additional nitrogen atoms or heteroatoms like O or S:



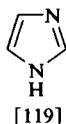
From the point of view of simple electron-distribution theories, pyrrole-type and indolizine type nitrogen atoms supply two electrons to the delocalized π -electron system of an azole, while pyridine-type nitrogen atoms contribute only one electron to the π -system; in the latter type the lone-pair electrons can be considered as a part of the σ -bond system involved.

Generally, the nitrogen shielding decreases in the order:

pyrrole-type nitrogen atoms	+273 to +101 ppm;
indolizine type nitrogen atoms	+190 to +100 ppm;
pyridine-type nitrogen atoms	+140 to -75 ppm;

according to the data in Table 85-87 and 93. There is some overlap between their spectral ranges, but for any given molecule that contains two or more nitrogen atoms, this order of nitrogen shielding is usually maintained.

There have been a number of successful explanations of the nitrogen shieldings in azoles in terms of various molecular-orbital theories. Non-empirical methods¹⁸ show clearly the much higher shielding of the nitrogen nucleus in the pyrrole-type nitrogen atom of imidazole [119] compared with that in the pyridine-type nitrogen atom:



Absolute shielding (in ppm) calculated by *ab initio* self-consistent perturbation method with Gaussian basis functions¹⁸

Nitrogen nucleus	Absolute shielding (in ppm) calculated by <i>ab initio</i> self-consistent perturbation method with Gaussian basis functions ¹⁸	
	Minimal basis set	Split valence shell basis
NH	+181.12	+139.65
-N=	-5.66	-19.04

Semi-empirical methods, such as INDO/S, explain quite well the sequence of nitrogen shieldings in any given azole system that contains more than one nitrogen atom (Table 85, note (a));²⁶ the same holds for azolo-azine ring systems (Table 93, note (b); Table 94, note (c)).^{24,324} Additional correlations of this kind were found for some azole derivatives (Table 86, note (f); Table 87, note (d))²⁴⁸ as well as for *N*-hydroxybenzotriazole and their isomeric forms (Table 85, note (i); Table 86, note (m); Table 87, note (f)).²⁵³ Calculations of this kind that employ the INDO/S method combined with the sum-over-states (SOS) approach in the evaluation of the shielding seem

to provide a simple means of nitrogen shielding assignments within a given azole system with two or more nitrogen atoms; the origin of the success lies probably in the fact that the method of calculation of the shieldings operates on a fixed set of energy levels (obtained by the INDO/S method) for the molecule involved. Results are not so good when one tries to compare different molecules, since then the energy level sets are also different; however, in some cases the method works even when different molecules are examined. For example, *N*-vinylpyrroles substituted at position 2 (Table 86, note (a)) show an increase in the nitrogen shielding relative to that in the parent *N*-vinylpyrrole. In the former, steric interactions can force the vinyl group out of the plane of the ring system, at least in one of the conformers, and the calculations³⁷ show that such effects should actually result in an increased shielding of the nitrogen nuclei.

Apart from theoretical explanations of the nitrogen shieldings in azoles, some rough but simple empirical additivity rules were found, particularly for pyrrole-type nitrogen atoms; the rules present the effects of pyridine-type nitrogen atoms, in various positions in the ring system of an azole or indolizine, on the nitrogen shielding of the pyrrole- or indolizine type nitrogen atom respectively. For a detailed consideration see ref. 1, p. 77. It has already been shown (see ref. 4, p. 187, reference 63 therein) that the nitrogen shieldings of the indolizine-type nitrogen atoms in aza-indolizines that contain pyridine-type nitrogen atoms within the five-membered ring moiety correlate linearly with the shieldings in the pyrrole-type nitrogen atoms in the corresponding aza-pyrroles. Recently, an analogous correlation has been found between the nitrogen shieldings of the indolizine-type nitrogen atoms in aza-indolizines that contain pyridine-type nitrogen atoms within the six-membered ring, and the corresponding shieldings in analogous azines (six-membered aza-aromatic heterocycles), as indicated,³²⁵ but some exceptions have also been noticed.

Nitrogen shieldings differentiate clearly between various isomeric structures of azoles, oxazoles, and thiazoles (Table 85). This is important from the point of view of spectral identification of such structures (see also ref. 1, p. 78) as well as of investigations of tautomeric equilibria in azoles (Table 87).

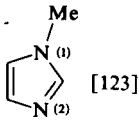
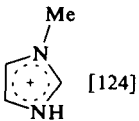
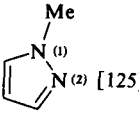
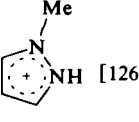
While the nitrogen shieldings of the pyrrole-type nitrogen atoms in azoles are fairly insensitive to molecular interactions, such effects are quite pronounced for pyridine-type nitrogen atoms; the latter have their lone-pair electrons exposed to interactions with the environment (Tables 85, 86). The formation of hydrogen bonds from solvent molecules to pyridine-type nitrogen atoms in azoles results in a considerable increase in the nitrogen shielding, and this has been explained in terms of *ab initio* molecular-orbital calculations of the shieldings in hydrated imidazole molecules (Section V.J and scheme therein).¹⁸ Similar results are obtained for a larger number of

azole structures, using the SOS method for calculations of the shieldings, combined with the semi-empirical INDO/S method and the supermolecule approach;²⁹ examples are shown below.

Molecule	Nitrogen atom	INDO/S-SOS calculated solvation shift of nitrogen shielding (in ppm) referred to isolated molecule	Experimental difference in nitrogen shieldings on hydrogen bonding
 [120]	1-N	-1.9	-4.6
	2-N	+10.7	+9.2
 [121]	1-N	+2.7	+1.4
	2-N	+10.5	+17.9
 [122]	1-N	+2.9	+6.6
	2-N	+22.1	+25.7

The protonation (or *N*-alkylation) of a pyridine-type nitrogen atom in an azole yields the corresponding azolium ion, and there is a remarkable increase in the nitrogen shielding in the atom concerned while the nitrogen shielding of the pyrrole-type nitrogen atom is usually somewhat decreased (see ref. 1, p. 79, and references therein). This is typical from the point of view of the considerations in Section V.H. In azole systems where rapid tautomerization takes place, and only dynamically averaged shieldings are observed (Table 88), the net result of the protonation is still a significant increase in the averaged shieldings of the nitrogen nuclei. Thus nitrogen NMR provides a sensitive tool for investigations of protonation processes in azole systems. Recently, the protonation effects on the nitrogen shieldings in azoles have been explained in terms of INDO/S calculations combined

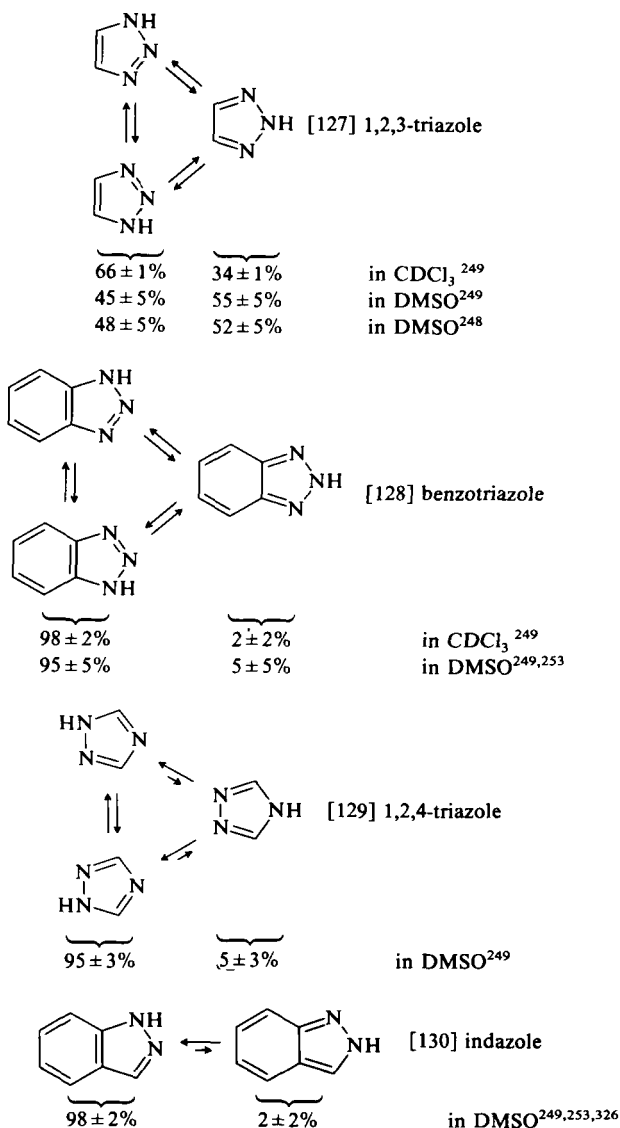
with the sum-over-states method of evaluation of the shieldings:²⁹

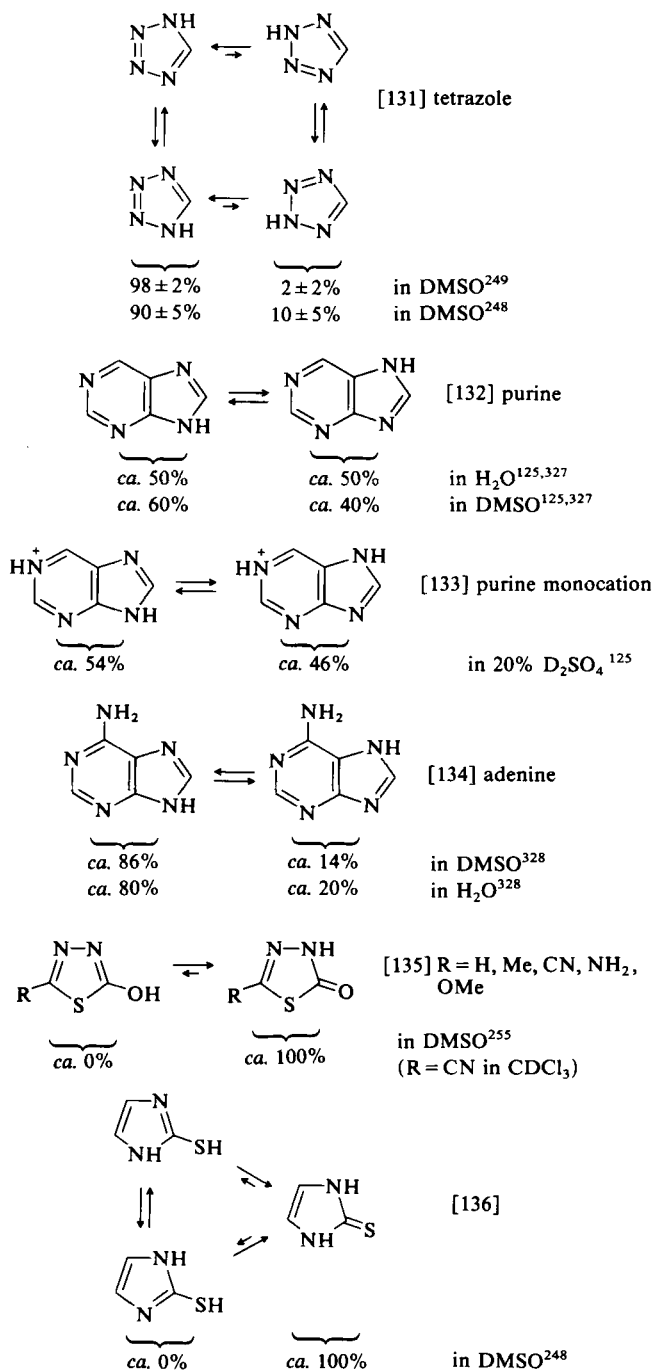
Azolium ion	Nitrogen atom	Effect of protonation upon nitrogen shielding (in ppm) referred to parent azole in protic solvent	
		Calculated by INDO/S-SOS	Experimental
 [123]			
	1-N	-2.2	-1
	2-N	+38.0	+62
 [124]			
 [125]			
	1-N	+8.9	+1
	2-N	+44.3	+52
 [126]			

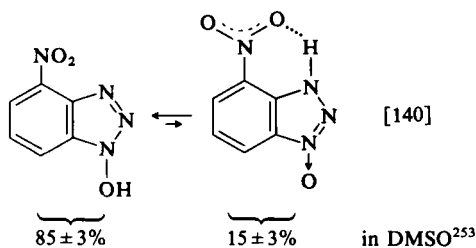
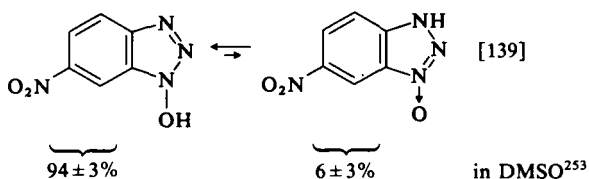
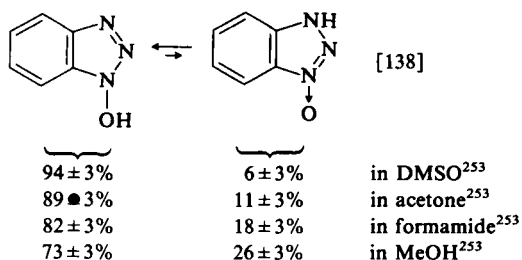
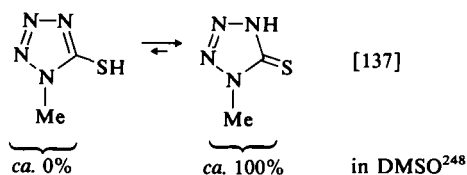
Thus the protonation effects on the nitrogen shieldings are much stronger than those due to hydrogen bonding, but both follow the same pattern, which is typical for the involvement of the lone-pair electrons at a pyridine-type nitrogen atom in some kind of bonding. The same effect is observed (Table 90) on the formation of nitrogen-boron dative bonds in azole derivatives, and the formation of complexes of azoles with Zn(II) and Cd(II) (Table 89).

In view of the large protonation shifts in the nitrogen shieldings in azoles, as well as the large difference in the nitrogen shieldings of pyrrole-type and pyridine-type nitrogen atoms, it is not surprising that in tautomeric azole systems (those containing NH, OH or SH moieties and at least one pyridine-type nitrogen atom) changes in the nitrogen shieldings associated with proton migrations are usually large, and can be used for estimations of tautomeric equilibria. This point is considered in detail in Section V.K, and

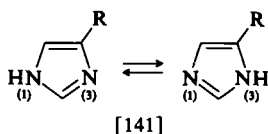
the relevant data are presented in Table 87; for azolo-azine systems, the data are shown in Table 94. On the basis of nitrogen shieldings in tautomeric systems compared with those for model compounds (for example, *N*-methyl derivatives or OMe and SMe derivatives) with or without attempts to account for shielding changes that may result from replacing NH and NMe moieties, etc., the following estimates of tautomeric equilibria in azole systems are reported:







The nitrogen shieldings in substituted imidazoles [141] where R contains a carbonyl or amino group which can be hydrogen-bonded by 3-NH (see Table 88) show that the 3-NH tautomer is more stable than the 1-NH



tautomer;²⁵¹ this is in accord with the preponderance of the former in the histidine residues of the catalytic triad (Ser-His-Asp) of α -lytic protease; the ¹⁵N shielding titration curves of the imidazole derivatives considered

yield the following values of pK_a for the NH moieties in protonated imidazole rings:²⁵¹

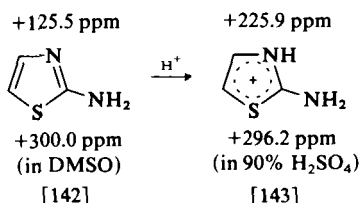
R	pK_a values		3-NH/1-NH tautomer ratio in neutral
	NH in cation	NH in anion	
—CH ₂ CH ₂ NH ₂	6.3 (dication)		0.26 (cation, NH ₃ ⁺)
	10.6 (monocation)		0.60 (neutral molecule)
—CH ₂ CH ₂ COOH	not measured	7.7	0.61 (anion)
—CH ₂ COOH	2.9	7.5	0.53 (anion)
— <i>cis</i> -CH=CHCOOH	3.3	7.0	5.2 (anion)
— <i>trans</i> -CH=CHCOOH	4.0	6.1	0.37 (anion)
— <i>endo-cis</i> -C ₇ H ₈ COOH (see Table 88)	not measured	8.2	1.5 (anion)

The use of nitrogen shielding differences between azole systems and azido groups in the detection of azoloazine–azidoazine valence tautomerism is clearly demonstrated in Table 78. Nitrogen shieldings were also employed in the determination of the actual structure of the pyrazole moiety in the cyclic derivative (Table 39, note (b)) of dehydro-L-ascorbic acid bis(phenylhydrazine), as discussed in Section VI.H.

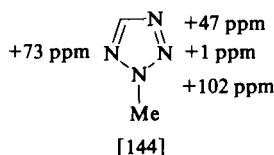
A rather high shielding of the nitrogen nuclei in a 1:1 complex of imidazole with trimethylphosphate (Table 86, note (e)) is assumed as an indication of strong hydrogen bonding between the NH moiety of imidazole and the O=P moiety of the phosphate, but the shielding reported, *ca.* +214 ppm from neat nitromethane, suggests that the imidazolium ion (protonated imidazole) is actually observed (see the data in Table 88 for comparison), possibly owing to the presence of (MeO)₂PO₂H, since the complex contained some residual water.³²⁹

The structure of the bipyrazole shown in Table 86, note (d), is proved largely from the corresponding nitrogen shieldings obtained for the ¹⁵N-labelled compound.³³⁰ A similar technique, using proton-coupled ¹⁵N spectra of ¹⁵N-labelled compounds, was employed in order to establish the structures of thiadiazole derivatives presented in Table 86, note (k).³³¹

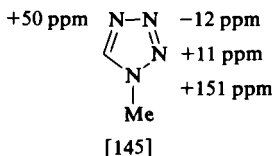
The nitrogen shieldings in 2-amino-1,3-thiadiazole [142] suggest that in acidic solvents, the protonation takes place at the nitrogen atom in the ring system,³³² on the basis of the typical, large, increase in the shielding in the latter atom, but one cannot exclude the formation of the corresponding dication, with an NH₃⁺ moiety; nevertheless, the protonation of the ring system leaves no doubt.



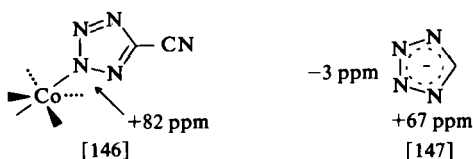
The site of coordination of the cyanotetrazole anion in 5-cyanotetrazolato-pentaamminecobalt(III) bromide was established on the basis of the nitrogen shieldings in the tetrazole ligand (Table 86, note (h)). The identification of the ^{15}N resonance signal corresponding to the tetrazole nitrogen that is bound directly to Co(III) is quite straightforward, owing the signal broadening by the quadrupole relaxation of Co, and the pattern of the nitrogen shieldings in the tetrazole ligand follows that observed in the corresponding *N*-methyltetrazole [144] according to the data in Table 85, notes (a, c); this



assignment of the nitrogen shieldings in the Co complex (Table 86, note (h)) yields a regular deshielding effect on the nitrogen nuclei in the complex relative to those in the *N*-methyltetrazole shown above, and this is in accord with analogous ^{13}C deshielding effects for similar complexes relative to the corresponding *N*-methylazole systems.³³³ One cannot attain such an agreement when the other isomeric *N*-methyltetrazole [145] is taken as the basis

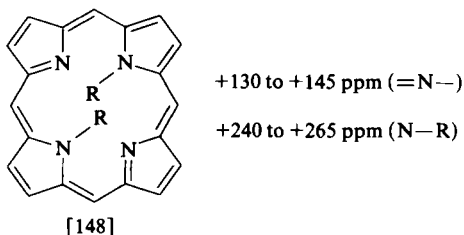


of nitrogen shielding assignments in the Co complex considered. Thus, if one compares the nitrogen shieldings in the Co complex [146] (Table 86, note (h)) and the tetrazole anion [147] (Table 87, note (d)), one finds a substantial shielding effect on the nitrogen nucleus bound to Co as a result



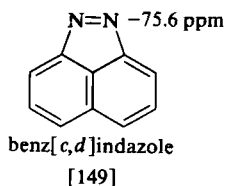
of the involvement of the lone-pair electrons in the formation of the Co-N bond.

Porphyrin ring systems [148] contain usually both pyrrole-type and pyridine-type nitrogen atoms within their five-membered ring moieties which



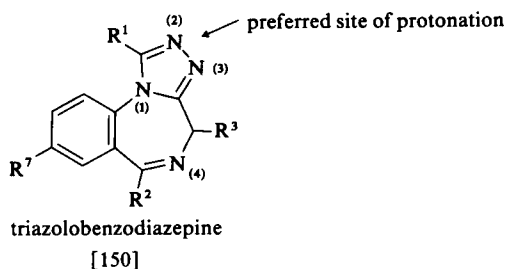
are clearly distinguished by their nitrogen shieldings (ref. 1, p. 80, and Table 116 therein); it is also fairly easy to detect protonation processes, hydrogen bonding, proton exchange and coordination with metals from modifications of the shieldings quoted above. Some additional data are presented in Table 91 on uroporphyrinogen systems (those containing only pyrrole-type moieties) and a pyridine adduct of cadmium *meso*-tetraphenylporphyrin. Attempts have been made to correlate the nitrogen shieldings in porphyrin systems with calculated π -electron densities and ring currents,¹⁰⁷ but such procedures are generally unsound since nitrogen shieldings depend heavily on the total distribution of electron charge in a molecule, and the corresponding pattern of energy levels (see Section I). More promising may be a search for correlations of nitrogen shieldings in paramagnetic metalloporphyrins with the unpaired spin density distributions.³³⁴

The structure of benz[*c,d*]indazole [149] (Table 85, note (h)) obtained by the low-temperature photolysis of 1,8-diazidonaphthalene is proved by, in addition to other spectral data, the single ^{15}N signal at -75.6 ppm (from neat nitromethane). This is an interesting example of an azole structure with only pyridine-type nitrogen atoms and no other heteroatoms.



Some nitrogen shielding data have been reported for azole ring systems fused with the benzodiazepine structure (Table 102). Large increase in the nitrogen shieldings of the pyridine-type nitrogen atoms in these structures was observed upon the addition of CF_3COOH or the lanthanide shift reagent $\text{Yb}(\text{dpm})_3$.³³⁵ The data suggest that the preferred site of protonation in these

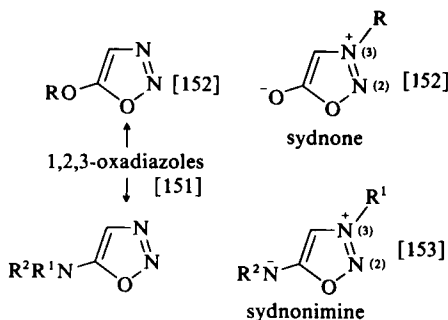
structures [150] is the 2-N atom:



The CP-MASS ^{15}N spectra of complex solids that are formed in the reaction of HCN with ammonia show, among others, a resonance signal at about +230 ppm (from neat nitromethane) which is assigned tentatively to pyrrole-type nitrogen atoms.¹⁸² Analogous signals are observed in the CP-MASS ^{15}N spectra of *p*-benzoquinone polymers with nitrogen incorporated by the addition of NH_4Cl or amino acids ("synthetic humic acids").^{277,288}

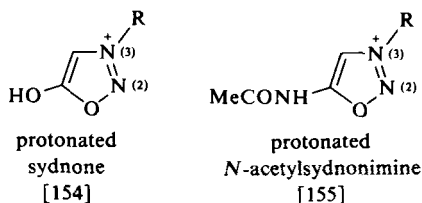
The nitrogen shielding tensors for the two possible tautomers of the imidazole moiety in solid histidine hydrochloride monohydrate are given in Table 59. The isotropic shieldings in the tautomers of histidine are also available from the CP-MASS ^{15}N spectra of lyophilized powders prepared from aqueous solutions of histidine, within a pH range 2–12.5 (Table 59, note (b)).

Sydnone [152] and sydnonimines [153] can be considered as betaine-type isomers (internal salts) of the corresponding 5-substituted 1,2,3-oxadiazoles [151].

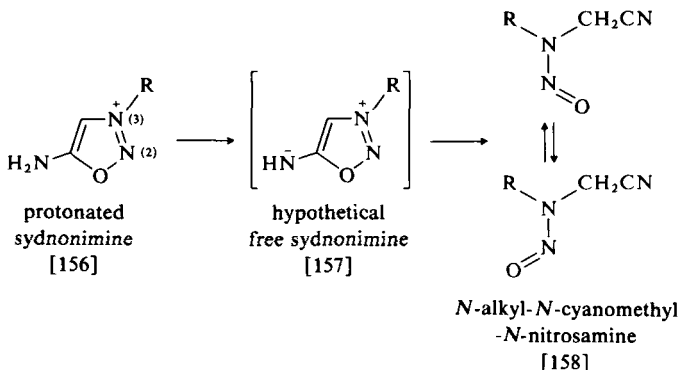


There have already been data galore on the ^{14}N and ^{15}N NMR of such structures (ref. 1, p. 83, and Table 119 therein), and additional results are presented in Table 92. The nitrogen shieldings differentiate clearly the two types of nitrogen atoms within the sydnone ring as well as the exocyclic nitrogen atom in sydnonimine structures. They also show that sydnones and *N*-acetylsydnonimines ($\text{R}^2 = \text{MeCO}-$) exist as such in solutions, and

that they are protonated in acidic solvents at the exocyclic O and N atoms, [154], [155] respectively,



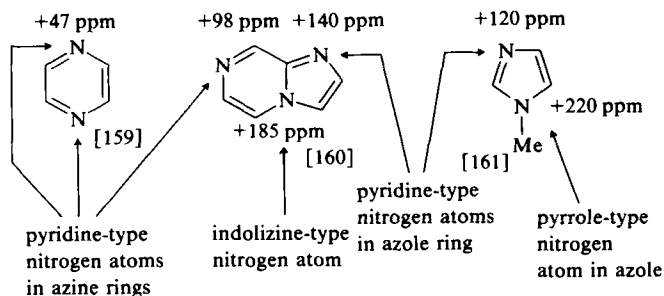
The nitrogen shieldings (Table 92) exclude the possibility of protonation at 2-N, which should result in a remarkable increase of the nitrogen shielding concerned. In the case of *N*-acetylsydnonimines, the protonation at the exocyclic N atom is shown independently by the *ca.* 55 ppm increase in the nitrogen shielding of this atom. All this is corroborated further by a combination of ^{15}N , ^{14}N , ^{17}O , and ^{13}C data for sydnone-type structures.³³⁶ In contrast, the nitrogen spectra show that free sydnonimines ($\text{R}^1 = \text{R}^2 = \text{H}$) are unstable and rearrange into the corresponding open-chain structures of *N*-cyanomethyl-*N*-nitrosamines [158], while protonated sydnonimines [156] exist as such, and contain an exocyclic NH_2 moiety:



The existence of the exocyclic NH_2 moiety in the protonated sydnimine structure is shown by the nitrogen shielding of about +310 ppm, characteristic of arylamino structures, as well as by observable spin-spin coupling patterns (see ref. 1, p. 83, and references therein). It has not been possible to date to observe any nitrogen spectrum of the free sydnimine structure (Table 92, note (d)),³³⁷ but using ^{15}N singly labelled sydnimine hydrochlorides, it is shown unequivocally that 2-N goes into the $\text{N}=\text{O}$ moiety of the nitrosamine, 3-N becomes the amino nitrogen in the latter, and the exocyclic nitrogen atom appears in the cyano group, and there is no scrambling of the labels among the three sites. The data in Table 92, notes (a-c), show that there is a clear β -effect (Section V.F) on the 3-N shielding of the alkyl groups attached to the nitrogen atom involved in sydnones.

R. Azine ring systems, related ions and *N*-oxides

Azine structures involve six-membered heteroaromatic ring systems with at least one pyridine-type (Section VI.Q) nitrogen atom within the ring structure. The nitrogen shieldings of the pyridine-type nitrogen atoms in azines do not depart appreciably (see Tables 10, 94–99) from those for imines (Table 108) and the pyridine-type nitrogen atoms in azole ring systems (Tables 85–87), but they are generally much smaller than the nitrogen shieldings of the pyrrole-type nitrogen atoms in azole rings. There is, however, an important exception to the rule. The nitrogen atoms located at the ring junctions in azolo-azines of the indolizine type (Table 93) formally constitute a part of both the azole and the azine moiety, and they are characterized by much higher shieldings of their nuclei relative to pyridine-type nitrogen atoms. This is not surprising, since such indolizine-type nitrogen atoms are bound directly to three neighbouring atoms and formally supply two electrons to the delocalized π -electron system of the aromatic structure involved. From this point of view they resemble the pyrrole-type nitrogen atoms in azoles and their nitrogen shieldings come close to those in the latter atoms (Section VI.Q), for example,

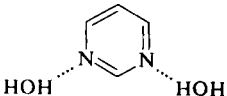


The nitrogen shielding ranges for the three types of nitrogen atoms in aromatic heterocycles (Section VI.Q and Table 10) show some overlap, but in a given molecule, the shielding usually increases in the sequence: pyridine-type (both in azine and azole moieties), indolizine-type and pyrrole-type nitrogen atoms. As far as azine ring systems are concerned, there are some rough, but simple, additivity rules in the nitrogen shieldings which are based on relative positions of nitrogen atoms within an azine ring (ref. 1, p. 84):

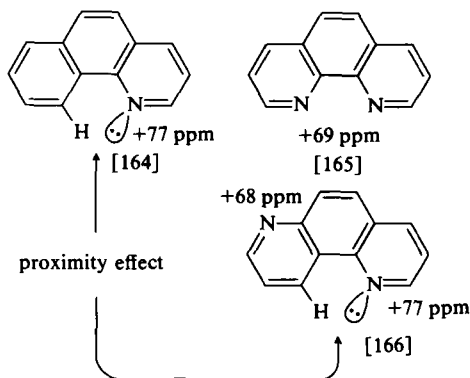
Relative position of a pair of N atoms in azine ring	Nitrogen shielding increment (in ppm) relative pyridine shielding, concerned with nitrogen atom arrangement specified
1,2	ca. -90
1,3	ca. +30
1,4	ca. -12

Such empirical rules are helpful in nitrogen shielding assignments for heteroaromatic structures that contain more than one nitrogen atom. Recently it has been shown that theoretical calculations of nitrogen shieldings using the SOS method combined with INDO/S calculations of molecular orbitals give also a sound basis for nitrogen shielding assignments within a given molecule containing azine rings (Tables 93-95, 98, 99).^{23-25,324}

General considerations of nitrogen shieldings (Section V) indicate that the nitrogen shieldings of pyridine-type nitrogen atoms in azine ring systems should be quite sensitive to any sort of involvement of the lone-pair electrons in molecular interactions or to the formation of covalent bonds by these electrons (*N*-oxidation, *N*-alkylation or *N*-protonation). A good example of this sensitivity is provided by the nitrogen shieldings in pyridine (Table 95), which span a range of about 40 ppm if gaseous pyridine is included, and about 30 ppm when only liquid pyridine and its solutions are considered. This range of solvent effects on the shielding in pyridine has been rationalized in terms of the Kamlet-Taft²⁴⁴ system of empirical parameters (Section V.J), and it has been shown that solvent polarity/polarizability effects (relative to those in hydrocarbon solvents) can exert a shielding influence on the nitrogen nucleus in pyridine, up to about +6 ppm, while hydrogen-bonding effects can reach +30 ppm. The latter shielding effect is quite remarkable and can be employed as a means of the detection of hydrogen bonding of solvent molecules to azine nitrogen atoms. It is also typical for the structure of the nitrogen bonding system concerned, according to the considerations in Section V.J. Theoretical calculations based on the supermolecule approach, with use of the SOS method and INDO/S scheme, also indicate clearly that the nitrogen shielding in azines should be augmented upon the formation of hydrogen bonds with H₂O molecules:²⁹

	INDO/S-SOS calculated absolute nitrogen shieldings (in ppm)	Experimental shieldings (in ppm) referred to MeNO ₂
 [162]	+117.2	+84.8 (in DMSO)
 [163]	+127.0	+92.0 (in H ₂ O)

It is also interesting to note that an increased shielding in azine nitrogen atoms is observed when one of the hydrogen atoms that are bound to the aromatic ring of an azine comes close to the lone-pair electrons of the nitrogen atoms; this may be called "the proximity effect" (Table 98, note (a)).²⁵

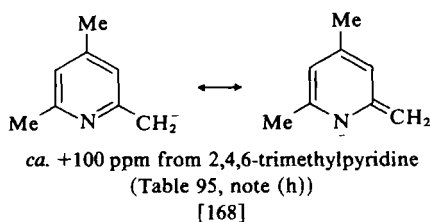
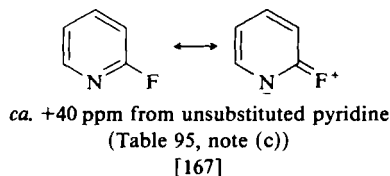


The proximity effect may have its origin in weak interactions of the hydrogen-bonding type.²⁹

It has already been shown (see ref. 1, p. 85, and references therein) that the effects of substituents that are bound to an azine ring of the nitrogen shieldings of azine nitrogen atoms reveal certain trends, but cannot be fitted into any simple and general pattern. Numerous examples are also shown in Tables 95 and 99. Electron-attracting substituents in the 4-position relative to the nitrogen atom tend to exert deshielding effects, while electron donors at the same position give rise to shielding effects, relative to the nitrogen shielding in the parent azine. This is also observed to some extent for substituents in position 2, but the general picture is less clear here. Substituents at position 3 relative to the azine nitrogen atom concerned seem to exert only little influence on the nitrogen shielding. One should also note, however, that effects on the shielding of substituents that are not very strong electron donors are fairly small compared with effects of molecular interactions. For example, the large body of nitrogen shielding data on substituted pyrazines³³⁸ (Table 99, note (e))³³⁸ shows that only substituents like NR_2 , OR and F exert shielding effects that are clearly out of the range of solvent effects on nitrogen shieldings in azines. Smaller changes, those up to about 10 ppm, observed on introducing some substituents into an azine ring, even if the relevant data refer to solutions in the same solvent, can include a considerable share of effects that originate from modifications of the solvation sphere that are induced by the presence of the substituents.

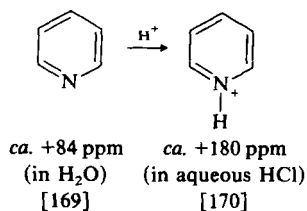
Especially large increases in the azine nitrogen shieldings, relative to parent azines, are found on the aggregation of amino, hydroxy (or alkoxy)

and fluorine substituents at positions 2, 4, and 6 (see Table 95). Fluorine substituents seem to exert the largest effects when they occupy positions 2 and/or 6, and the effect is smaller for 4-F substituents. The latter effects on nitrogen shieldings are likely to originate from the back-donation effect of the lone-pair electrons at the fluorine atoms, for example,



Anions of the type shown (Table 95, note (h))¹⁴² reveal a huge increase in the nitrogen shielding relative to the parent azine, and the effect is certainly due to the back-donation of the lone-pair electrons from CH_2^- to the ring system; however, they cannot be explained simply in terms of an increased electron density at the nitrogen atoms concerned, as done elsewhere,¹⁴² in view of the fact that the *N*-protonation of azines, which yields the corresponding azinium cations, also gives rise to a similar enhancement of the nitrogen shielding.

The high shieldings of the nitrogen nuclei in azinium ions, referred to those in the parent azines (Tables 95, 98, 100) are analogous to those observed in pyridine-type nitrogen atoms in azole rings (Section VI.Q) on protonation of the latter, and those in *N*-protonated imines (Table 108). They are in accord with the predictions from quantum-mechanical calculations for protonated azoles (Section VI.Q),²⁹ and the general empirical rules presented in Section V.H. Needless to say, all this is valid also for the corresponding *N*-alkyl or *N*-aryl azinium ions (Table 100). Such large shifts in the nitrogen shieldings, involving changes that amount to about 100 ppm,



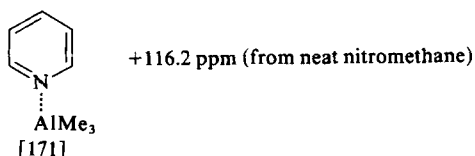
make nitrogen NMR a sensitive tool for the detection and localization of protonation-deprotonation processes in heteroaromatic ring systems. This applies also to investigations of interactions with acid sites on solid surfaces (Table 96). Thus separate ^{15}N signals are observed in the ^{15}N CP-MASS spectra of pyridine sorbed on γ -alumina and acid-leached calcined mor-denite (Table 96, note (a)) for various pyridine/pyridinium moieties bound to different sites on the surfaces of the solids.¹⁸¹ The nitrogen shieldings in pyridine molecules adsorbed on a partially dehydroxylated silica gel (Table 96, note (b))³³⁹ indicate that strong hydrogen bonds are formed between the pyridine nitrogen atoms and the OH groups of the gel, since the nitrogen shielding increases significantly with the decreasing coverage of the gel (in terms of statistical monolayers), up to about 0.5 monolayer; the latter fact allows one to calculate the number of active sites—about 1 per nm^2 .³³⁹ In samples of the gel that are also treated with PCl_3 , the nitrogen shieldings of the adsorbed pyridine indicate that formation of the pyridinium ions takes place, and the number of the latter can be estimated as about 0.05 per nm^2 . Analogous studies were performed for pyridine adsorbed on NaY and 88 HY-type zeolites.²⁶² In the case of NaY zeolites (Table 96, note (c)) the nitrogen shielding of the adsorbed pyridine does not depend significantly on the pore-filling factor, and can be used as a reference for estimations of the number of pyridinium ions formed in 88 HY zeolites, since in NaY only non-protonated pyridine molecules occur. The shieldings observed in the case of pyridine adsorbed on 88 HY zeolites²⁶² allow one to calculate the percentage of protonated pyridine molecules (pyridinium ions), if one takes +90 ppm for adsorbed pyridine shielding and +180 ppm for that in the pyridinium ion:

Number of pyridine molecules per large cavity of 88 HY zeolite	Nitrogen shielding (in ppm) (referred to MeNO_2)	Calculated percentage of protonation of pyridine molecules
2.1	+171.2	91.2
3.0	+165.4	84.7
4.6	+147.9	65.0

All these studies indicate the advantage of using nitrogen shieldings, as compared with ^{13}C shieldings, since the protonation effects on the former are much larger than those for the latter.

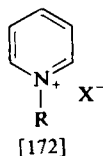
Similar results are obtained from the ^{15}N CP-MASS spectra of pyridine adsorbed on silica-alumina (Table 96, notes (d, e)).^{340,341} The nitrogen shieldings show that hydrogen-bonding-type interactions dominate the adsorption at high surface coverages, 0.5–1 monolayer.³⁴⁰ In the case of HCl-pretreated silica-alumina, two distinct ^{15}N resonance signals were

observed, a major peak at +115.2 ppm (Table 96, note (d)), and a minor signal at +182.2 ppm (from neat nitromethane). The former is just halfway between those for pyridine and the pyridinium ion, and must represent pyridine/pyridinium-exchanging species, while the other corresponds to that of the pyridinium ion, and should represent a non-exchanging Brønsted surface complex.³⁴⁰ The success in the observation of discrete species at the surface must also be assigned to the large difference in the nitrogen shieldings between pyridine and the pyridinium ion. At low coverages, about 0.08 monolayer, only the nitrogen resonance of the Brønsted surface complex is observed (+182 ppm, Table 96, note (e)), and this signal vanishes upon the addition of *n*-butylamine,³⁴¹ while that characteristic of hydrogen-bonded pyridine appears at +77 to +91 ppm (Table 96). When the ratio of $\text{Bu}^n\text{NH}_2/\text{pyridine}$ is less than 1, there is also an additional broad signal at about +115 ppm, which may be ascribed to pyridine coordinated to Lewis-acid sites, as indicated by the nitrogen shielding in the complex of pyridine with AlMe_3 [171]:³⁴⁰



The complexation of alkali-metal cations with cryptand structures which contain azine rings also results in an increase in the nitrogen shielding in the latter (Table 97).²⁶⁷

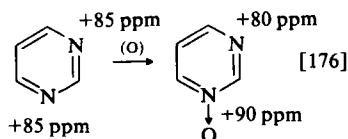
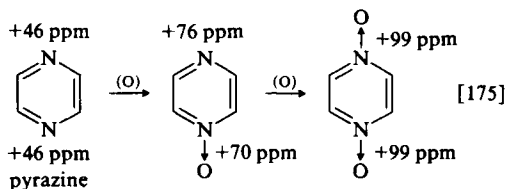
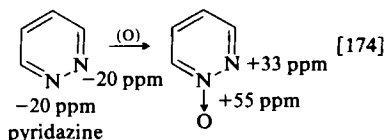
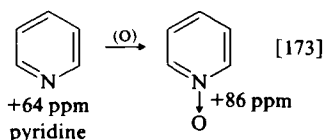
Alkylpyridinium ions [172] reveal a clear β -effect of the alkyl groups on the nitrogen shielding (Section V.F), and a recent example can be found elsewhere³⁴² (experimental details are given in Table 100, note (b)):



R	X	Solvent	Nitrogen shielding (in ppm) referred to neat nitromethane
H	CF_3COO^-	D_2O	+178.6
Me	I	D_2O	+178.2
Me	I	MeOH-d_3	+178.0
Et	I	D_2O	+164.0
Et	I	MeOH-d_3	+163.5

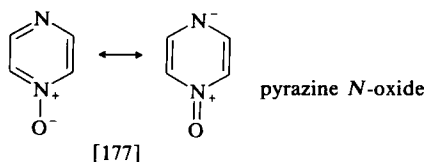
N-phenylpyridinium salts substituted at the phenyl ring (Table 100, note (b)) do not show any correlation of their nitrogen shieldings with the σ^0 constants of the substituents.³⁴²

The oxidation of nitrogen atoms in azines, which yields the corresponding azine *N*-oxides (Table 101), gives rise to an increase in the nitrogen shielding in the oxidized atom, and this is in accord with the general rules (Sections V.E, V.H, V.J) concerning the involvement of the lone-pair electrons at the nitrogen atoms in such structures in the formation of any kind of bonds. However, the magnitude of this *N*-oxidation effect is quite variable, and moreover the shieldings of any other nitrogen atoms that may be present in the azine ring concerned can experience also significant changes; the latter are sometimes larger than those in the nitrogen atom that undergoes the oxidation; typical examples of such effects are shown below (data from Tables 98 and 101 for solutions in DMSO) [173]–[176]:



The complications arise probably from the electron distribution in azine *N*-oxides, which can be influenced by the back-donation effect of the lone-pair electrons from the oxygen atom to the ring structure, especially when there are additional nitrogen atoms in positions 2 or 4 relative to the

NO moiety, for example,

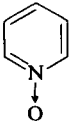
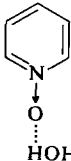
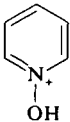


Such effects are in accord with the recent calculations of electron charge density distribution (*ab initio* method, STO-3G minimal basis set),³⁴³ which show clearly a significant increase of the electron charge at the non-oxidized nitrogen atoms in the *N*-oxides of 1,2-diazine (pyridazine) and 1,4-diazine (pyrazine), compared with those in the parent azines, while a reverse effect is predicted for pyrimidine (1,3-diazine) *N*-oxide. All this is reflected in the relevant nitrogen shieldings quoted above. The back-donation effects should also affect the nitrogen shieldings in the N-O moieties of azine *N*-oxides, and they should act in the direction of deshielding, as can be estimated from the reported correlation between the N-O stretching frequencies and the N-O nitrogen shieldings for a number of azine *N*-oxides;³⁴⁴ the former are shown to increase linearly with the decreasing shielding. Thus the nitrogen shieldings in the N-O moieties of azine *N*-oxides are affected by various factors, some of which can act in opposite directions, and thus it is not surprising that the numerical values of the nitrogen shielding increase which occurs upon the *N*-oxidation of an azine covers a range of 5–80 ppm. In some cases, even a small relative deshielding can take place, as was found for N-3 in the 3-*N*-oxides of 2,4-diaminopyrimidine derivatives (Table 101, note (g); Table 99, note (d)).³⁴⁵

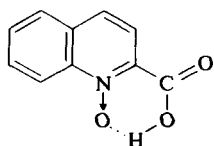
In view of this, nitrogen shielding changes that occur on the *N*-oxidation of azine rings cannot be used simply for the identification of the *N*-oxidation site, and there can be serious difficulties in the assignments of the shieldings if they are based on ¹⁵N spectra. However, ¹⁴N NMR is quite helpful from this point of view, since the ¹⁴N resonance signals of the N-O moieties in azine *N*-oxides are generally much sharper (that is, the corresponding quadrupolar relaxation times are much longer) than those representing other moieties (see also ref. 1, p. 90, and references therein),³⁴⁶ this experimental finding is in a good agreement with theoretical estimates of relative gradients of the electric field at the nitrogen nuclei concerned. Thus it is fairly easy to localize the ¹⁴N resonance signals of the N-O moieties in azine *N*-oxides, and the relevant nitrogen shieldings as such, rather than the corresponding shielding changes referred to parent azines, can be employed in the detection of *N*-oxidation sites (ref. 1, p. 91).

The formation of hydrogen bonds from solvent to the O-atom of the N—O moiety (Table 101) leads to a significant increase in the nitrogen

shielding, for example [178]–[180]:

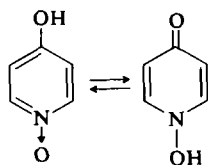
		
+86 ppm (in DMSO, Table 101, note (a))	+99 ppm (in H ₂ O, Table 101, note (a))	+136 ppm (ref. 1, Table 124, note (d))
[178]	[179]	[180]

and the *O*-protonation causes a still larger effect in this direction. This is in accord with the considerations above, since the hydrogen bonding or the protonation should hamper the back-donation of the lone-pair electrons from the oxygen atom to the ring system. Calculations have even been attempted of the contributions of the back-donation to the overall electronic structure of individual azine *N*-oxides and derivatives thereof, on the basis of nitrogen shielding differences between the *N*-oxides and their conjugate acids (*N*-hydroxy-azinium ions),³⁴⁴ but one should be rather cautious in assigning too much significance to the results, since the relevant shieldings and their differences can be governed by other factors. The rather high shielding of the nitrogen nucleus in [181], compared with those for other derivatives of quinoline *N*-oxide, indicates the formation of a strong internal hydrogen bond.³⁴⁷



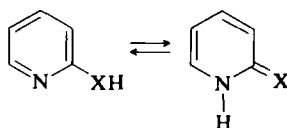
ca. +125 ppm
(Table 101, note (c))
[181]

Effects of substituents on the nitrogen shieldings in azine *N*-oxides (Table 101) are similar to those observed in parent azines.³⁴⁷ They are within the range of solvent effects on the shieldings, and caution should be exercised in any rationalizations thereof, but some simple trends can be observed; for example, the shieldings in substituted pyridine *N*-oxides correlate linearly with those for analogous quinoline *N*-oxides.³⁴⁷ Azine *N*-oxides that bear substituents like OH and NH₂ are potentially tautomeric, for example [182], but the relevant changes in the nitrogen shieldings between such tautomers are rather small, as estimated from a study of the corresponding model compounds containing OMe and *N*–OMe moieties, respectively (Table 101, note (b)).²⁵⁸



[182]

Azine ring systems that bear substituents like OH, SH or NHR are also capable of tautomerism, which may be depicted by [183]–[185] using pyridine derivatives as examples:



[183]

X = O

ca. +110 ppm

ca. +215 ppm

X = S

ca. +80 ppm

ca. +190 ppm

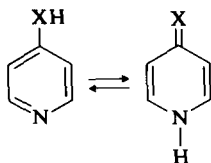
X = NH

ca. +115 ppm

ca. +240 ppm

ca. +310 ppm (NH₂)

ca. +195 ppm (=NH)



[184]

X = O

ca. +90 ppm

ca. +245 ppm

X = S

ca. +70 ppm

ca. +225 ppm

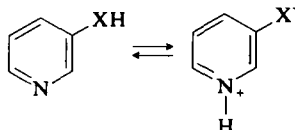
X = NH

ca. +105 ppm

ca. +260 ppm

ca. +320 ppm (NH₂)

ca. +170 ppm (=NH)



[185]

X = O

ca. +65 ppm

ca. +180 ppm

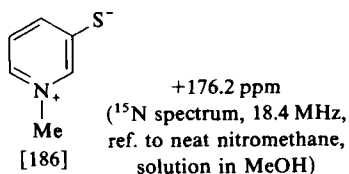
X = S

ca. +65 ppm

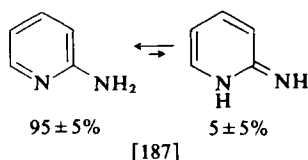
ca. +175 ppm

The estimates of the nitrogen shieldings for the tautomers involved are based on studies of the corresponding N—Me and X—Me derivatives (Table 95, 50, and references therein; see also ref. 1, p. 88, and Tables 64,

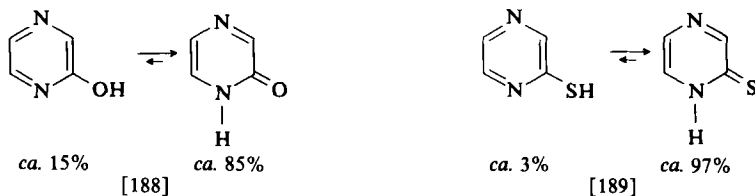
120 therein). The last of the estimates comes from our unpublished data:



The changes in nitrogen shieldings that occur upon the tautomeric shifts of protons in such substituted azines are large, often in excess of 100 ppm, and thus they can be employed in estimating the equilibria concerned. It has already been shown (ref. 1, pp. 88, 89), on the basis of dynamically averaged nitrogen shieldings, that 2-OH, 4-OH, 2-SH and 4-SH substituted pyridines exist in solutions essentially as the corresponding pyridone (lactam) tautomers, while analogous 3-substituted derivatives exist largely as such rather than the corresponding "betaine-type" tautomers; however, the nitrogen shieldings in 4-OH-pyridines fully substituted with fluorine, chlorine and methoxy substituents (see Table 95, note (e); also ref. 1, Table 120 therein) suggest a clear preponderance of the hydroxypyridine tautomers at the equilibria. In the case of amino derivatives of pyridine, the estimates can be made independently for the two tautomeric pairs of nitrogen atoms involved, exocyclic and endocyclic respectively, and they indicate that aminopyridines in solutions exist mainly ($95 \pm 5\%$) as such [187] (Table 95, note (e); and references therein; see also ref. 1, p. 88).³⁴⁸



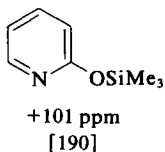
Analogous results are obtained from the nitrogen shieldings for pyrazine derivatives [188], [189] (Table 99, note (f)) in DMSO.²⁵⁶



A large amount of nitrogen shielding data for lactam-type tautomers of azine ring systems are presented in Table 50 (Section VI.K). The nitrogen shieldings in pyridine-type nitrogen atoms which may occur in such systems can be used conveniently for the localization of protonation sites. Thus it

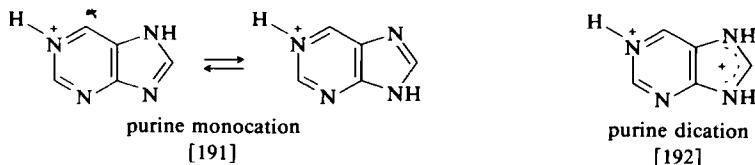
was shown (Table 50, notes (r, s)) that tetrahydrofolic acid undergoes protonation essentially at 1-N, and that 5-azacytidine (Table 104, note (k)) is protonated mainly at 3-N.³⁴⁹ Numerous examples from the field of nucleoside structures (Table 104) will be considered in Section VI.S. The structure of riboflavin (Table 50 A) in its reduced form includes a pyrimidodione moiety, and the nitrogen shieldings of the reduced and oxidized forms of riboflavin derivatives show evidently that, on oxidation, two pyridine-type nitrogen atoms are formed at positions 1-N and 5-N (Table 50 A).²⁸⁷

The nitrogen shielding in the trimethylsilyl derivative of 2-hydroxypyridine, which in solution exists essentially as the corresponding pyridone tautomer, proves that the derivative has the structure of 2-trimethylsilyloxy-pyridine [190] rather than that of *N*-methyl-2-pyridone (Table 95, note (d)).³⁵⁰



The valence tautomerism between azido-azine and azolo-azine structures, presented in Table 78, is also reflected clearly in the nitrogen shielding changes concerned; from the point of view of the azine nitrogen atoms in the 2-azido-pyrimidine derivative studied (Table 78),³¹⁴ one of them is converted to the indolizine-type nitrogen atom in the tautomeric azolo-pyrimidine, and this change is associated with a remarkable increase in the nitrogen shielding.

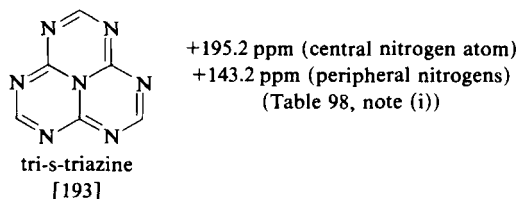
The changes observed in the nitrogen shieldings of purine and some derivatives thereof that occur upon the addition of acids (Table 94, notes (e, f))^{125,327} show that the first stage of protonation, leading to a monocation, takes place at the azine moiety, at the 1-N position [191], but the second stage involves protonation of the azole ring [192], (Table 94, note (f), data for solutions in 90% D₂SO₄ and in HSO₃F):¹²⁵



There is an appreciable increase in the nitrogen shielding of pyridine when the latter is complexed with Pt(II), as shown for *cis*-[Pt(NH₃)₃(pyridine)₂]²⁺ (Table 127, note (a)). In the latter complex, the pyridine nitrogen shielding becomes +180.8 ppm (from neat nitromethane),

while for aqueous pyridine the shielding is about +83 ppm (Table 95). This shielding enhancement is also typical of any kind of involvement of the lone-pair electrons of the pyridine-type nitrogen atoms in the formation of dative bonds, as has already been considered in the present section.

The interesting structure of tri-s-triazine [193] reveals two values of the nitrogen shieldings:³⁵¹



One should note that the rather high shieldings observed can be explained simply in terms of the general considerations of azine nitrogen shieldings. As far as the peripheral nitrogen atoms are concerned, there are three 1,3-nitrogen-nitrogen interactions for each of them, and thus the shieldings should be larger than those in s-triazine, where only two such interactions occur. The central atom cannot be considered as a pyridine-type nitrogen atom, since it is bound directly to three carbon atoms, and supplies two electrons to the delocalized π -electron system of the molecule; from this point of view, it can be assigned to the indolizine type, which is characterized by appreciably higher shieldings, as compared with the pyridine-type nitrogen atoms (in this case, the peripheral nitrogens). Actually, the value of +195.2 ppm for the central nitrogen is very close to those for indolizine-type nitrogen atoms (Table 93).

S. Nucleosides, nucleotides and related structures

These highly specialized structures include azolo-azine and azine rings or lactam-type tautomers thereof, but they are considered separately owing to their significance in biochemistry and molecular biology. The relevant data on their nitrogen shieldings are presented in Table 104.

There is a clear distinction between the individual types of nitrogenous moieties in such systems as far as the nitrogen shieldings are concerned:

pyridine-type nitrogen atoms	+130 to +190 ppm
pyrrole- and lactam-type nitrogen atoms	+200 to +260 ppm
amino/ammonium substituents	+280 to +310 ppm

Also, the identification of individual nucleosides or nucleoside moieties by means of nitrogen shieldings is fairly simple, since the latter form characteristic sets (Table 104). The protonation of pyridine-type nitrogen atoms

leads to large increases in the relevant nitrogen shieldings (Section VI.R), and therefore nitrogen NMR can be considered as a standard method of localization of protonation also for nucleoside structures and derivatives thereof.

The assignments of the nitrogen shieldings in individual nucleoside structures, based on ^{15}N -H couplings, protonation shifts, NOE and structural analogies (see ref. 1, p. 93), leave little doubt; and some uncertainty about the 1-N and 3-N assignments in the case of adenine derivatives has been cleared recently (Table 104, note (b)) by selective ^{15}N labelling of the molecules concerned.³²⁸

In adenosine (Table 104, note (b)) the primary site of protonation is evidently 1-N, as shown by the shielding changes, while in its 6-NH—CH₂Ph derivative some degree of protonation also at 3-N and 7-N is indicated.³²⁸ The binding of HgCl₂ and Zn(NO₃)₂ to adenosine is shown to occur at 1-N and 7-N (Table 104, note (a)), on the basis of the nitrogen shieldings;³⁵² the 1-N site seems to be preferred by Hg²⁺, and the 7-N binding site by Zn²⁺, as can be inferred from the shielding changes in these nitrogen atoms that occur on addition of the salts.

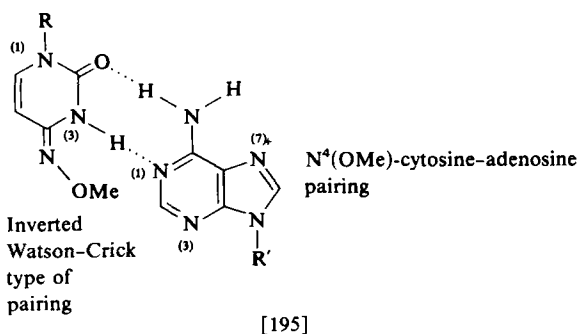
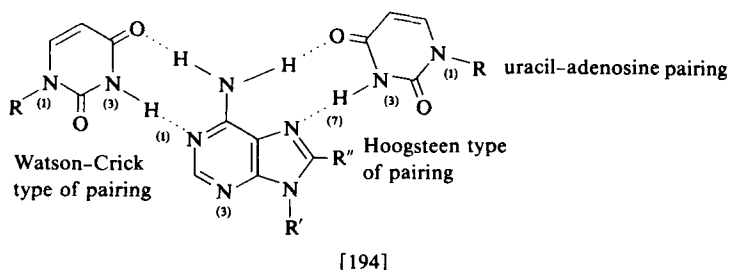
In guanosine, the nitrogen shieldings show 7-N as the preferred site of protonation, possibly with some contribution of the 3-N site (ref. 1, Table 126 therein) and the same is indicated for the binding of Hg²⁺ and Zn²⁺ to the nucleoside (Table 104, note (a)),³⁵² while Ba²⁺ is probably bound to the carbonyl oxygen rather than to nitrogen, since it does not significantly affect the guanosine nitrogen shieldings.

In inosine, the 7-N site is indicated for protonation and also for binding Zn²⁺ and Hg²⁺, as can be seen from the nitrogen shielding data in Table 104, note (h),³⁵³ and it has been suggested, on the basis of these results, that N-7 in inosine as well as in guanosine is the favoured binding site for "soft" or "intermediate" ions like Hg²⁺ and Zn²⁺, but not for "hard" ions like Ba²⁺.

Cytidine nitrogen shieldings (ref. 1, Table 126 therein) show 3-N as the primary site of protonation, and again the same site is indicated for Hg²⁺ and Zn²⁺ complexation (Table 104, note (a)),³⁵² while Ba²⁺ has little effect on the shieldings, and is probably bound to the carbonyl oxygen. The same site of protonation (3-N) is shown by the nitrogen shielding increase observed in 5-azacytidine (Table 104, note (k)), by about 65 ppm, on addition of CF₃COOH.³⁴⁹

Since hydrogen-bonding donation to pyridine-type nitrogen atoms should enhance the nitrogen shieldings concerned (Sections V.J, VI.R), while the donation of hydrogen bonds by amide- or lactam-type NH moieties should result in a decreased shielding in the latter (Sections V.J and VI.K), nitrogen NMR should theoretically constitute a convenient means of the detection of nucleoside association ("base pairing"), and actually there have been

some attempts^{121,243} (see also ref. 1, p. 93, and references therein) to locate the sites responsible for such association, on the basis of the nitrogen shieldings presented in Table 104, notes (c) and (d). The studies are concerned with adenosine derivatives and either 1-cyclohexyluracil²⁴³ or 1-Me-N⁴(OMe)-cytosine¹²¹ and the following types [194], [195] of pairing are considered:



but it is difficult to share the authors' opinion that the nitrogen shieldings (Table 104, notes (c, d)) provide any support for these structures. In the case of uracil-adenosine pairing, nitrogen shielding enhancements (of comparable magnitudes) are observed in the adenosine structure not only for 1-N and 7-N, but also for 3-N, and it is quite unlikely that the latter is an indirect effect of hydrogen bonding at 1-N and 7-N; the direct protonation effects on the nitrogen shieldings in nucleosides, including adenosine (Table 104, note (b)), are larger by at least an order of magnitude with respect to indirect effects. Actually, the data seem to indicate that also 3-N is involved in some kind of hydrogen bonding. All of this applies equally to the pairing of adenosine with the N⁴-cytosine derivative (Table 104, note (c)).

Ribonuclease T₁, an enzyme that is highly specific for guanylic acid residues, was shown to form a complex with guanosine-3'-monophosphate (GMP, see Table 104, note (e)) via the NH₂ moiety of the guanosine structure, on the basis of the decreased shielding of ¹⁵N in the latter moiety and a broadening of the ¹⁵N resonance signal;³⁵⁵ the ¹⁵N data exclude complexation via 7-N of GMP.

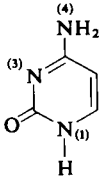
The nitrogen shieldings of nucleosides complexed with Pt(II) clearly show the binding sites, 7-N in guanosine, and 3-N in cytidine, since the relevant nitrogen nuclei experience a significant shielding effect in the complexes (Table 104, note (f)).²⁷⁶

There is a significant decrease in the nitrogen shieldings of 1-N and 7-N of the guanosine moiety (G^*) in the tetranucleotide $G^*-G-C-U$, compared with those for other nitrogen atoms, when the temperature is raised (Table 104, note (i)).³⁵⁵ This is assigned to the breaking of Watson-Crick type hydrogen bonding at 1-N, and possibly to the breaking of inter-strand hydrogen bonds at 7-N.

No significant changes in the nitrogen shieldings of adenosine-5'-monophosphate (AMP) are found upon the complexation of the latter with Mn^{2+} .³⁵⁶

It has already been noted, at the beginning of this section, that the nitrogen shielding patterns are characteristic of individual nucleoside structures. Thus they can be employed in the identification of such moieties in biopolymers, including DNA and RNA (Table 103). Nucleoside nitrogen shieldings are usually much smaller than those of the nitrogen atoms in peptide structures, and thus there is no overlap between the relevant spectral ranges in nitrogen NMR (Table 103, note (a); Table 72, note (c)).¹⁷⁸ The nitrogen shieldings in such biopolymers come close to those in monomeric nucleosides (Table 103, note (b)).³⁵⁷ With the exception of the nitrogen atoms involved in Watson-Crick type base pairing. The differentiation in the nitrogen shieldings in the tRNA structure of *Escherichia coli* (Table 103, note (c)), combined with $^1H/^15N$ double-resonance experiments,¹⁴³ allows one to make unambiguous assignments of proton resonance signals. Yeast tRNA (Table 103, note (d)) does not reveal any significant changes in the nitrogen shieldings upon denaturation and renaturation which take place upon heating and subsequent cooling respectively, but there are large changes in nuclear Overhauser effects, which result in the disappearance of some ^{15}N resonances. This seems to indicate that the lack of nitrogen shielding response to the change from double-helical structure to an un-ordered structure may result from the replacement of internucleoside hydrogen bonds with those between nucleoside moieties and water;³⁵⁸ another explanation may suggest that nitrogen shieldings are not sensitive to stacking and unstacking effects.³⁵⁸

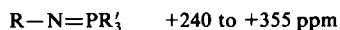
As far as parent heterocyclic systems of nucleosides are concerned, the ^{14}N spectra of cytosine (Table 50, note (i))²³⁸ show the deprotonation site at 3-N (pH = 4.6) and then at 1-N (pH = 12.3). Recent *ab initio* quantum-mechanical calculations (SCF perturbation method, gauge-invariant atomic orbitals) of cytosine [196] nitrogen shieldings give reasonable agreement with the experimental data, if one takes into account the rather small basis set employed and the diversity of nitrogenous moieties involved.²⁰

		Nitrogen shielding (ppm)	
		Calculated absolute shieldings ²⁰	Experimental (Table 50, in H ₂ O, pH = 8) referred to neat MeNO ₂ ²³⁸
	1-N	+183.18	+257
	3-N	+65.01	+191
	4-N	+243.67	+306
	cytosine [196]		

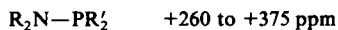
A comparison of the nitrogen shieldings in uracil and 1-*N*-cyclohexyl-uracil³⁵⁹ (Table 50, note (j)) indicates that the more shielded nitrogen nucleus in uracil is that in 1-*N*. The data show also that in a complex of uracil with Et₄N⁺F⁻, 1-NH is probably hydrogen bonded to the fluoride ion.³⁵⁹ The tautomeric equilibria and protonation sites of purine are reflected clearly in the ¹⁵N spectra,^{125,327} which are considered in Sections VI.Q and VI.R (Table 94, notes (e, f)); the same applies to adenine (Table 94, note (g); see Section VI.Q)³²⁸. The spectra show that adenine in DMSO is protonated by CF₃COOH at 1-*N* and 3-*N*, and the same is observed in the case of 7-*N*-ethyladenine. In contrast, 9-*N*-ethyladenine undergoes protonation essentially at 1-*N*, like adenosine. The sites of protonation are revealed by significant shielding effects on the nitrogen nuclei in the protonated pyridine-type nitrogen atoms concerned. As far as the 7-NH ⇌ 9-NH tautomerism is concerned, the nitrogen shielding data³²⁸ show the preponderance of the 9-NH tautomer (*ca.* 85%) in adenine, and even more so in the case of 6-*N*,6-*N*-dialkyl derivatives of adenine (Table 94, note (g)).

T. Cyclophosphazenes

Cyclophosphazene structures (Table 105) reveal nitrogen shieldings that are much higher than those in azine ring systems (Section VI.S). This is not surprising, since the nitrogen shieldings in phosphimine structures do not depart appreciably from those for the amino moieties in aminophosphines,

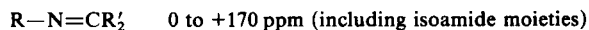


[197]

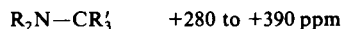


[198]

as shown in Table 25, and if ref. 1 (Table 30 therein), while there is a large difference in the nitrogen shieldings between amines and imines (Table 10),



[199]

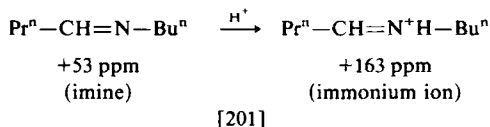


[200]

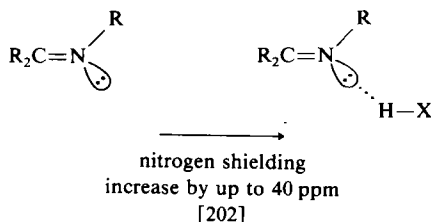
Actually, the spectral range of nitrogen shieldings for cyclophosphazenes is almost the same as for open-chain phosphimine structures. There is a significant influence on the phosphazene nitrogen shieldings of substituents located at the phosphorus atoms (Table 105). The highest shieldings are observed for the ring nitrogens if NR_2 or OR moieties are bound to P, and the lowest shieldings are found if the substituents at P are Cl, Br (but not F); this sequence seems to follow the decreasing back-donation of the lone-pair electrons from the substituents to the ring system, as in the case of substituted azines (Section VI.S). For cyclotetraphosphazenes the substituent effects on the ring nitrogen shieldings are reproduced roughly by the average excitation energy approximation method combined with CNDO/2 molecular orbital calculations.²²⁷ The data in Table 105 suggest that the ring nitrogen shieldings in cyclophosphazenes are affected significantly only by the substituents that are located at the nearest P atoms (Table 105, notes (d, e)).

U. Imines, nitrones, oximes and related ions

There is a close correspondence between the nitrogen shieldings in imino-moieties, $\text{R}_2\text{C}=\text{N}-\text{R}$, and in pyridine-type nitrogen atoms in azines and azoles (Tables 106, 108; see also Tables 85-99), and a large part of the considerations of the latter in Sections VI.Q and VI.R can be applied to imine nitrogen shieldings. The protonation (or *N*-alkylation) of an imine, which yields the corresponding immonium ion, results in a remarkable shielding effect on the nitrogen nucleus, for example (data from Table 108, note (a)):

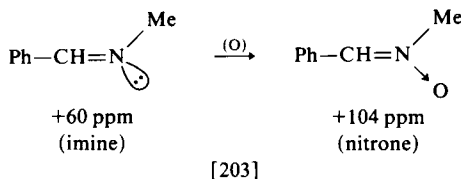


Numerous examples of this effect (see also Section V.H) can be found in Table 108. Smaller, but still large shielding enhancements are observed (see Table 108, note (a)) upon the involvement of the lone-pair electrons at an imino nitrogen atom in hydrogen bonding:



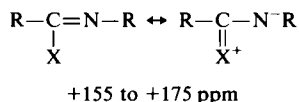
Such effects are also typical from the point of view of the general considera-

tions in Section V.J for this type of structure. The *N*-oxidation of an imine, which gives the corresponding nitron (imine *N*-oxide, see Table 111), also causes a clear increase in the nitrogen shielding:



Analogous *N*-oxidation effects are discussed in Section V.E.

The highest shieldings of imino nitrogen nuclei are found in the following structures (Tables 40, 106):

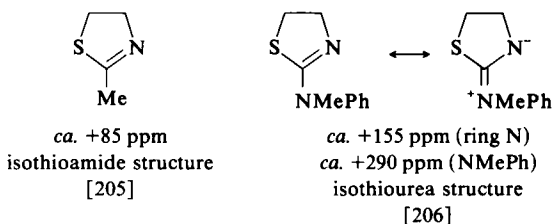


X = OR (isoamide structures)

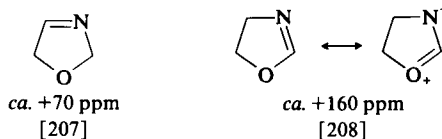
X = NR₂ (amidines)

[204]

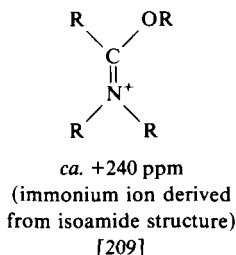
which are characterized by back-donation effects of the lone-pair electrons from X to the imino system. This enhanced shielding corresponds closely to those observed in substituted azine rings, and also azine *N*-oxides (Section VI.R), where such effects take place. One should notice that isothioamide structures, R—C(SR)=N—R (Table 106) are characterized by nitrogen shieldings that are within the normal range for imino moieties, but in the case of isothiourea derivatives the shieldings are increased markedly, owing to the back-donation effect of the additional nitrogen atom involved:



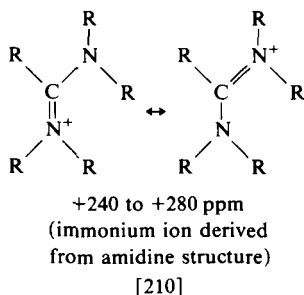
Another convincing example of the role of the lone-pair back-donation effects on imino nitrogen shieldings can be found in Table 106 (note (c)) and Table 108 (note (j)), for the following isomeric structures:



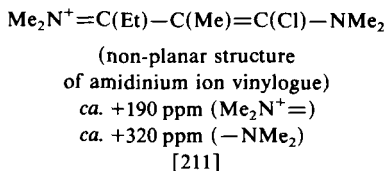
One cannot, however, assign the increased shielding by the back-donation effect simply to an increased electron charge density at N, and the subsequent increase in the diamagnetic term of the shielding constant, since analogous immonium cations (see Table 106, notes (d-g)) are characterized by still larger shieldings of their nitrogen nuclei, for example,



In cations of this type, the role of the back-donation effect is also evident from the nitrogen shieldings in immonium ions derived from amidine structures:

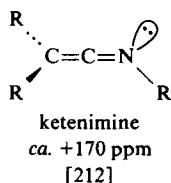


and their vinylogues (Table 108, notes (g, i, l)), since the nitrogen shieldings here are still larger than those in immonium ions derived from isoamide structures, and in symmetrically substituted amidinium ions the back-donation effect amounts to 50%, simply from symmetry reasons. If, however, there is any steric hindrance that forces a non-planar conformation of an amidinium-type ion, the back-donation is obstructed, and the nitrogen shieldings are split into values characteristic of normal immonium ions and enamines (Table 108, notes [g, i]):



There is still another kind of imino moiety, in addition to those in isoamide and amidine structures, which is characterized by unusually high shieldings

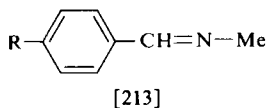
of the nitrogen nuclei; this occurs in ketenimines [212] (Table 107):



The rather high shieldings of the nitrogen nuclei in ketenimines were discussed in terms of resonance structures,³⁶⁰ and it was postulated that the delocalization of the lone-pair electrons from nitrogen to the $C=C=N$ system should be responsible for the shielding effect relative to simple imine structures; this should generate a partial positive charge on nitrogen, and according to the arguments presented should give rise to a shielding effect analogous to that observed in immonium ions relative to imines.³⁶⁰ However, the analogy seems to be stretched too far, since the formation of the immonium ion from an imine is concerned with an additional bond in the direction bisecting the $C-N-C$ angle. It seems to us that a simpler explanation is possible; the delocalization of the lone pair electrons should be favoured if the $C=N-R$ angles in ketenimines are larger than in simple imines, and thus the change would be in the direction of the linear structure of isocyanides, $R-N^+ \equiv C^-$. Actually, the nitrogen shieldings in ketenimines, +160 to +185 ppm (Table 107) approach those observed in isocyanides, +185 to +220 ppm (Table 81).

If the lone-pair electrons of an imino nitrogen atom are involved in complexation with metal atoms, the nitrogen shielding enhancement is also observed, and this effect can also be exploited in the identification of binding sites (see Table 108, notes (f, k, o)).

The transmission of conjugative effects of substituents R on the imino nitrogen atom in [213], is indicated clearly by the nitrogen shieldings presented in Table 108, note (c). Substituents that are characterized by lone-pair back-donation effects give rise to an increased shielding, and opposite effects are exerted by electron-withdrawing substituents.

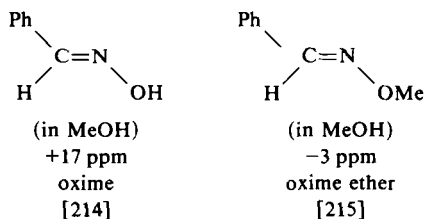


The sensitivity of imino nitrogen shieldings to N -protonation effects (the formation of immonium ions) provides an unambiguous proof that the imino groups in bacteriorhodopsin, in its dark-adapted form, are protonated (see Table 109). Bacteriorhodopsin is the single protein of the purple membrane of *Halobacterium halobium*, and contains the Schiff base (imine) derived

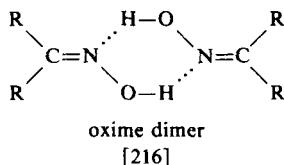
from the polyene aldehyde, retinal, which is attached to the ϵ -N atoms of lysine residues. The nitrogen shieldings obtained from the ^{15}N CP-MASS spectra of the protein (Table 109)^{187,361,362} and those of some model compounds (Table 109; see also Table 108, note (a)) show clearly that immonium rather than imino groups are present in the protein.

The nitrogen shieldings in the 4-N moiety of benzodiazepine structures presented in Table 102 are typical of imino groups. They show a clear effect of the presence of the Cl substituent at the *ortho* position in the neighbouring phenyl ring, and this was ascribed to direct interactions between the lone-pair electrons at the Cl and 4-N atoms involved.^{363,364} Triazolo-derivatives of the benzodiazepine structures (Table 102) were shown to undergo protonation at the triazole ring rather than at the 4-N imino moiety, as can be inferred from changes in the relevant shieldings on the addition of CF_3COOH .³³⁵

The *N*-hydroxy derivatives of imines and oximes, reveal nitrogen shieldings (Table 110) that are somewhat smaller than those in imines (Table 108). There is some differentiation of the shieldings between the corresponding *Z* and *E* isomers of oximes, but the differences depend significantly on the substituents attached to the oxime moiety (Table 110). The shieldings in oximes are usually higher than in the corresponding oxime ethers (Table 110, note (a); also ref. 1, Table 129 therein), for example

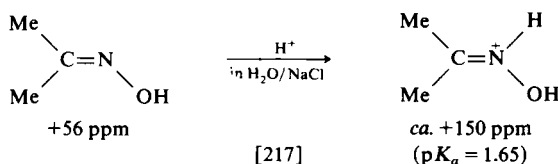


The difference can be attributed to the formation of strong hydrogen bonds in oxime dimers



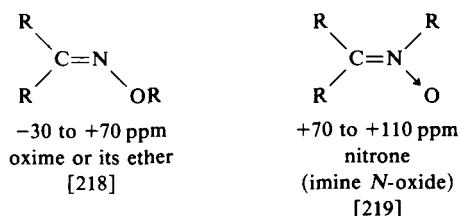
or analogous associates.²⁴⁷ Thus the direction of hydrogen-bonding effect is towards an increased shielding, as in the case of imines. The nitrogen shieldings in oximes decrease with increasing temperature (Table 9, note (a)); this is assigned to some loosening of the hydrogen bonds in the associates which are known to persist in the whole range of temperatures examined.²⁴⁷ The protonation of oximes results in significant enhancements of their nitrogen shieldings (Table 110, note (b)), which are analogous to

those observed in imines:



The values of the shieldings for the protonated forms as well as the corresponding $\text{p}K_a$ values²⁷⁸ are obtained from the analysis of the corresponding ^{15}N titration curves. Similar effects of protonation were observed for the oxime structures presented in Table 110, note (c). In the latter case there seems to be a linear correlation between the oxime nitrogen shieldings in the *E* isomers and the inductive constants σ_I for substituents R^1 , provided that $\text{R}^2 = \text{H}$, but actually this is based on only four experimental values of the shieldings.³⁶⁵

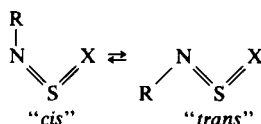
Oximes and their ethers are isomeric to nitrones (Table 111), and the relevant nitrogen shieldings differentiate clearly between the isomeric structures [218], [219] (Table 10):



These structures are also isomeric or tautomeric to *C*-nitroso compounds (Table 120), $\text{R}_3\text{C}-\text{N}=\text{O}$, whose nitrogen shieldings fall into the range -400 to -600 ppm. Such huge differences in the shieldings can be exploited in examinations of tautomeric equilibria that involve oxime and nitroso moieties (Sections V.K, VI.Z).

V. Sulphur–nitrogen compounds with sulphur–nitrogen multiple bonds

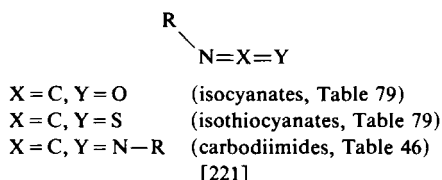
The bent structures of the type [220] are characterized by nitrogen shieldings that do not depart appreciably from those observed in imines



$\text{X} = \text{O}$ +25 to +80 ppm (Table 112)
(sulphinylamines)

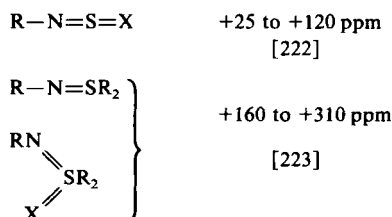
$\text{X} = \text{N}-\text{R}$ +60 to +120 ppm (Table 112)
(sulphodiimides)
[220]

(Section VI.U). One should notice that the singly bent structures [221] have much higher shieldings of their nitrogen nuclei.



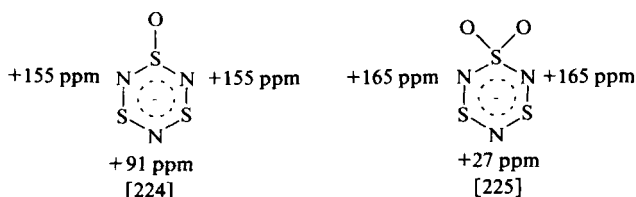
The nitrogen shieldings in alkyl sulphinylamines show typical effects of alkyl groups (Section V.F), with an exception for the reversed β -effect upon passing from $\text{R} = \text{Pr}^i$ to $\text{R} = \text{Bu}^t$; this has already been considered (see ref. 1, p. 96, and references therein) as an argument in favour of the *cis*-structure of the compounds as well as evidence against steric effects as a source of the β -effect; the latter seems to be actually quenched by such effects.

A survey of the data presented in Table 112 suggests that there is a clear-cut difference in the nitrogen shieldings between the $\text{N}=\text{S}$ moieties, which have only one additional atom bound to S, and those where a larger number of atoms are attached to S:



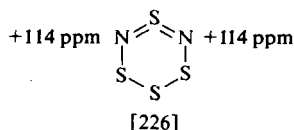
There are some exceptions from this rule for $\text{R}-\text{N}=\text{SCl}_2$ structures (Table 112). The rule holds also for cyclic structures containing $\text{S}=\text{N}$ moieties.

The oxidation of S_3N_3^- in acetonitrile by O_2 gives rise to a variety of products (Table 112, note (e)), whose formation can be followed by means of the ^{15}N spectra of the reaction mixture, using ^{15}N -labelled S_3N_3^- .³⁶⁶ Among the products, there are two anions, $\text{S}_3\text{N}_3\text{O}^-$ and $\text{S}_3\text{N}_3\text{O}_2^-$, which have the six-membered ring structure of S_3N_3^- (Table 112):

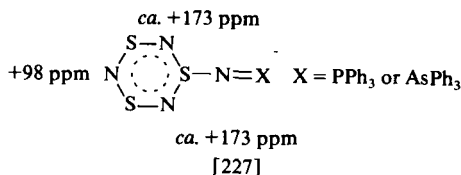


The relative shieldings in the oxo-anions seems also to follow the rule specified above; in each of the anions, there are two $\text{S}=\text{N}$ moieties that

belong partly to the $\text{N}=\text{SR}_2$ or $\text{N}=\text{SR}_3$ types, which are characterized by higher shieldings than the $\text{N}=\text{SR}$ type. The same applies to at least some of the sulphur nitrides studied (Table 112, note (c)),³⁶⁷ for example, the relatively low shielding in S_4N_2 [226], which supports the sulphodiimide-

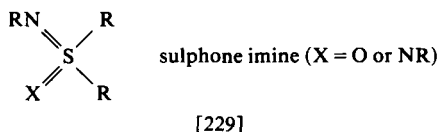
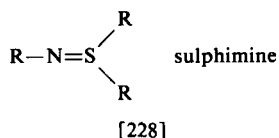


type structure shown above, as well as to the differentiation in the nitrogen shieldings in [227] (Table 112, note (c)):



where the lower shielding corresponds to the $\text{N}=\text{SR}$ type moiety, and the higher shielding to the two other $\text{S}=\text{N}$ moieties, which belong partly to the $\text{N}=\text{SR}_2$ type.

The sulphimine and sulphone imine structures [228] and [229] (Table 112, note (d)) reveal high shieldings of their nitrogen nuclei ($\text{N}=\text{SR}_2$ and $\text{N}=\text{SR}_3$ types of moieties are involved, respectively),³⁶⁸ and it is interesting to note that in the latter case the nitrogen shieldings are almost the same for $\text{X}=\text{O}$ and for $\text{X}=\text{NR}$.



W. Nitro groups, nitramines, nitrates and related structures

Nitro-group nitrogen shieldings span a range of about 100 ppm, from -30 to +65 ppm relative to neat nitromethane, if one takes into consideration *C*-nitro, *N*-nitro and *O*-nitro moieties (Tables 113, 113A, 114, 123; see also ref. 1, p. 97, and references therein). There seems to be a clear distinction

between the nitrogen shieldings of the following nitro moieties:

<i>O</i> -nitro groups (covalent nitrates, including HONO_2 and $\text{O}_2\text{N}-\text{O}-\text{NO}_2$)	+40 to +65 ppm
<i>N</i> -nitro groups (nitramines)	+20 to +35 ppm (NO_2) (<i>ca.</i> +200 ppm for amino nitrogen)
<i>C</i> -nitro groups	
aromatic nitro compounds and nitro-olefins (see also ref. 4, p. 203)	0 to +30 ppm
nitroalkanes (including nitromethane)	-30 to +7 ppm
nitroalkanes (excluding nitromethane)	-30 to -4 ppm

There are some exceptions from these rules; the aggregation of more than one NO_2 group at an alkane carbon atom results in a significant increase in the nitrogen shielding (see ref. 3, p. 234, and references therein):

$\text{CH}_2(\text{NO}_2)_2$	<i>ca.</i> +20 ppm
$\text{RCH}(\text{NO}_2)_2$	<i>ca.</i> +10 ppm
$\text{R}_2\text{C}(\text{NO}_2)_2$	<i>ca.</i> 0 ppm
$\text{CH}(\text{NO}_2)_3$	<i>ca.</i> +35 ppm
$\text{RC}(\text{NO}_2)_3$	<i>ca.</i> +25 ppm
$\text{C}(\text{NO}_2)_4$	<i>ca.</i> +47 ppm

Analogous effects are observed (ref. 3, p. 234) when halogens are attached to the carbon atom bound to NO_2 . The β -effect of alkyl groups (Section V.F) on the NO_2 nitrogen shieldings in nitroalkanes is quite evident from the data in Table 114, and ref. 1, Table 133 therein. The effect allows one to distinguish primary, secondary, and tertiary nitroalkanes (R s are alkyl groups):

MeNO_2	-2 to +7 ppm
$\text{R}-\text{CH}_2-\text{NO}_2$	-12 to -4 ppm
$\begin{array}{c} \text{R} \\ \diagdown \\ \text{CH}-\text{NO}_2 \\ \diagup \\ \text{R}' \end{array}$	-20 to -14 ppm
$\begin{array}{c} \text{R}'' \\ \\ \text{R}-\text{C}-\text{NO}_2 \\ \\ \text{R}' \end{array}$	-28 to -22 ppm

in spite of the fact that solvent effects on the NO_2 shielding can induce variations thereof within 6–9 ppm. Hydrogen-bonding effects seem to be small here, and the largest part of the range of solvent effects can be ascribed to those of medium polarity, as is shown by the solvaton-model calculations combined with INDO/S parameters (ref. 1, p. 98, and references therein); the highest shieldings of nitrogen nuclei in NO_2 groups are observed in non-polar solvents.

As far as nitro groups attached to aromatic rings are concerned, if the aromatic ring is of the benzene type, the range of the nitrogen shieldings is typically +9 to +20 ppm, and the aggregation of fluorine substituents extends the latter up to about +30 ppm; this provides a simple distinction between "aliphatic" and "aromatic" nitro groups. It has already been known (ref. 3, p. 238) that there is virtually no differentiation between the effects of *ortho*, *meta* and *para* substituents on the NO_2 shielding in nitrobenzene derivatives. This is corroborated by recent ^{15}N measurements (Table 114, note (b)). Moreover, both electron-donating substituents and electron acceptors seem to induce enhancements in the nitrogen shieldings of NO_2 . These effects are correlated with Taft's dual substituent parameters.³⁶⁹

Substituent position relative to NO_2 in nitrobenzene	Effect on NO_2 nitrogen shielding (in ppm) referred to that in unsubstituted nitrobenzene (solutions in DMSO)	Standard deviation) (ppm)
<i>para</i>	$6.0\sigma_1 + 1.0\sigma_{\text{R}}^0$	0.21
<i>meta</i>	$7.5\sigma_1 + 2.5\sigma_{\text{R}}^0$	0.31

It is argued³⁶⁹ that since the terms containing σ_1 dominate the effects, the π -polarization of the N–O bonds should be responsible for the substituent-induced changes in the shieldings; since the effects are comparable for both *para*- and *meta*-substituted series, and are even slightly higher in the latter, a through-space mechanism of transmission of the polarization was invoked. One should, however, be rather cautious with such interpretations of NO_2 nitrogen shielding changes that amount to a few parts per million, even if solutions in the same solvent are considered. Substituents can modify the solvation sphere of nitrobenzene, and the data in Table 114 show that solvent-solute interactions give rise to NO_2 nitrogen shielding variations of the same order of magnitude, including the case of nitrobenzene. *Ab initio* (STO-3G) molecular-orbital calculations of both the σ - and π -electron densities³⁶⁹ do not really reveal any correlations of the densities with the nitrogen shieldings in *para*- and *meta*-substituted nitrobenzenes, in spite of the claim that some correlation exists between the π -electron densities at the nitrogen atoms and the relevant shieldings; the data in Table 114,

note (b), show that both electron donors and electron acceptors as substituents induce enhanced shieldings in NO₂, while the calculations predict opposite effects in the two classes, as far as the σ and π densities are concerned, for example:

Substituent	Change in electron density induced by substituent			Change in NO ₂ nitrogen shielding (ppm)
	N(σ)	N(π)	N(total)	
<i>p</i> -NH ₂	+0.0055	-0.0068	-0.0013	+0.4
<i>p</i> -OH	+0.0023	-0.0031	-0.0008	+1.0 (OMe)
H	0	0	0	0
<i>p</i> -CN	-0.0060	+0.0055	-0.0005	+3.5
<i>p</i> -NO ₂	-0.0085	+0.0080	-0.005	+4.0

There is hardly any correlation between the electron densities calculated and the substituent effects on the NO₂ shieldings. Rather small effects on the nitrogen shieldings of NO₂ in 5-substituted-2-nitrofurans were observed upon changing substituents (Table 114, note (k)),³⁷⁰ within about 4 ppm, but these small effects seem to show a fairly linear correlation with the corresponding frequencies of the asymmetric stretching vibration of NO₂:

$$\text{nitrogen shielding} = 0.0786\nu_{\text{NO}_2}^{\text{as}} - 91.68$$

(ref. to MeNO₂)

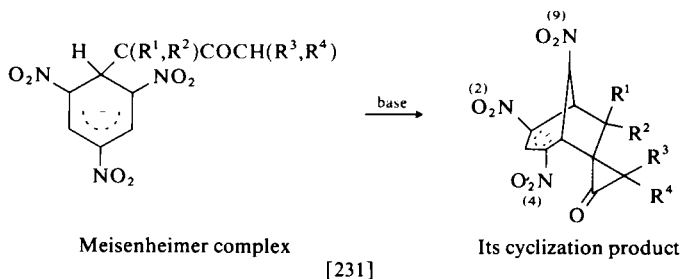
$$\text{standard deviation} = 0.60 \text{ ppm}$$

The correlation presented above is according to our own recalculation, since the originally reported values,³⁷⁰ $0.008\nu - 91.68$, and standard deviation 1.54 ppm, contain obvious printing errors.

The nitro groups in trinitrophenyl moieties (Table 114, note (f)) show a significant increase in their nitrogen shieldings on contact with myeloma protein M315, and this seems to indicate that the nitro groups are involved directly in binding such trinitrophenyl haptens to antibodies.³⁷¹

The nitrogen shieldings in the nitro groups of Meisenheimer complexes derived from sym-trinitrobenzene (Table 114, note (1)) are slightly lower than those in trinitrotoluene (Table 114, note (f)), and the difference between 2- (or 6-) nitro groups and 4-NO₂ is likely to result from the deviation from coplanarity in the case of 2-NO₂ and 6-NO₂; from this point of view, trinitrotoluene seems to be a better reference than trinitrobenzene, which was employed in ref. 372, where calculations of electron densities suggest that the nitrogen atoms in 2- (or 6-) NO₂ groups bear smaller electron charges than those in 4-NO₂, but that the difference is small. If we compare

the shieldings in the complexes with those in trinitrotoluene (Table 114, note (f)), changes in the shieldings are similar for 4-NO₂ and 2-(6-)NO₂. Thus the differentiation in the shieldings between 4-NO₂ and 2-(6-)NO₂ in the complexes is probably of steric origin. The base-catalysed cyclization of the Meisenheimer complexes of the type [231], generates an "aliphatic"

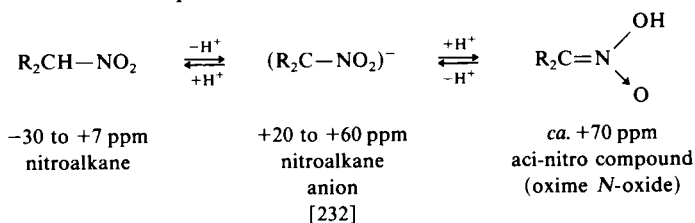


nitro group (9-NO₂) whose nitrogen shielding falls into the range characteristic of nitroalkanes (solutions in DMSO):³⁷³

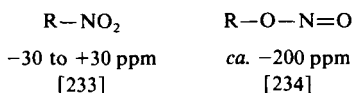
Substituents (other than H)	Nitrogen shielding (in ppm, referred to neat nitromethane)	
	2-(4-)NO ₂	9-NO ₂
R ² ·R ³ = (CH ₂) ₃	+16.4	-6.2
none	+16.1	-6.9
R ³ = COMe	+15.3; +17.7	-6.7
R ³ = COMe, R ⁴ = Me	+13.4; +16.0	-5.8
R ³ = CPh	+14.7; +17.3	-4.8

The ¹⁵N resonances of the nitro group in the nitration products of *N,N*-dimethylaniline²¹⁰ and its 2,4,6-trimethyl derivative²¹¹ show CIDNP effects that are considered in detail in Section IV.H, together with those for the ¹⁵NO₂ signals observed upon the rearrangement of *N*-nitro into *C*-nitro aniline derivatives.²¹²

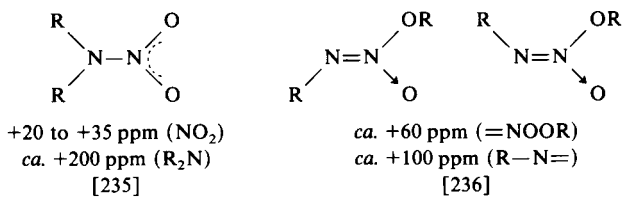
We recall (ref. 1, pp. 97-99, and references therein) that there is a significant difference between the isomeric (or tautomeric) structures of nitro and aci-nitro compounds:



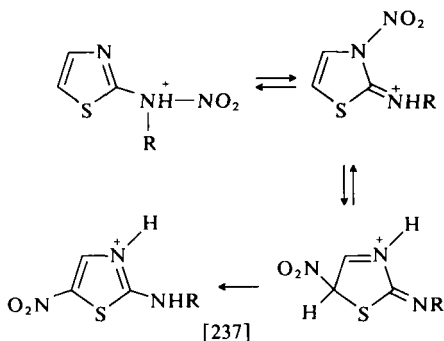
as far as the nitrogen shieldings are concerned. An even larger difference is observed between the isomeric structures of nitro compounds [233] (Table 114) and covalent nitrites [234] (Table 121):



The *N*-nitro moieties in nitramines [235] (Tables 113, 113A) are characterized by NO_2 nitrogen shieldings that are higher than those in most *C*-nitro compounds, and reveal a characteristic shielding in the amino part of the moiety, about +200 ppm; there is also a clear differentiation between the latter shieldings and those for the isomeric aci-nitramino type structures [236], (ref. 1, p. 97, and references therein):



If there is some π -electron conjugation between the *N*-nitro moiety and the remaining part of the molecule concerned, the NO_2 shieldings are decreased, and fall into the range characteristic of nitroarenes and nitroolefins (Table 113, note (d); Table 113A); a notable exception is *N*-nitropyrazole (Table 113, note (c)), where the NO_2 nitrogen shielding is the highest ever found in *N*-nitro moieties. Conjugated nitramines are known to undergo rearrangements into the isomeric *C*-nitro derivatives of amines, and nitrogen NMR is quite helpful in following the course of such rearrangements,³³² as is shown in Table 113 A, the data seem to exclude



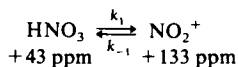
the possibility of NO_2 cleavage as the NO_2^+ ion (the nitrogen shielding in the latter is about +130 ppm, see Table 123), and any radical bond-fission mechanism (no CIDNP effects are observed), and the pathway [237] of the NO_2 migration is postulated on the basis of ^{15}N , ^{13}C , and proton spectra.³³² On the other hand, one should note that CIDNP effects on ^{15}N are observed in the acid-catalysed rearrangements of *N*-nitroaniline derivatives (Section IV.H) into the corresponding C-nitro derivatives,²¹² and these observations are rationalized in terms of radical pair formation; however, it is difficult to assess the actual contribution of such a mechanism to the overall process.

The binding of the NO_2 group to the imino moiety of nitroguanidine structures shown in Table 113 (note (d)) is indicated by the nitrogen shieldings, which rules out the alternative isomeric structures of *N*-nitrosoureas (Table 120).²⁸⁴

Covalent nitrates (nitric-acid esters) contain *O*-nitro moieties, which are characterized by the highest shieldings among the nitrogen nuclei in nitro groups, and there is a large difference between the shieldings in covalent nitrates [238] and in the nitrate ion [239] (Table 114):

$\text{R}-\text{O}-\text{NO}_2$	NO_3^-
ca. +40 ppm	ca. +4 ppm
[238]	[239]

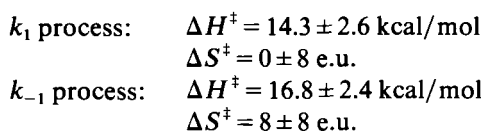
The nitrogen shieldings of nitric acid are very sensitive to solvent and concentration effects (Table 114, notes (a, p, q)); for dilute aqueous solutions they approach the NO_3^- shielding of about +4 ppm, and, on increasing the concentration of HNO_3 , they move towards the value of ca. +43 ppm, which can be attributed to the HONO_2 species. In solutions in H_2SO_4 , two ^{14}N signals were reported recently for the first time (Table 114, note (p)), one for HONO_2 at +43 ppm, and another for the nitronium ion, NO_2^+ , at +133 ppm.³⁷⁴ The latter assignment leaves no doubt in view of the data presented in Table 123, note (d). The ^{14}N data³⁷⁴ show that in 88% H_2SO_4 , about 50% of 0.5 M HNO_3 is converted into the NO_2^+ ions, and starting from 90% H_2SO_4 + 10% H_2O (w/w), the conversion is practically complete. This is in an excellent agreement with results obtained from Raman spectroscopy. The two ^{14}N signals observed for 0.5 M HNO_3 in H_2SO_4 show broadening in the intermediate range of H_2O content, and the lineshape analysis of the spectra yields the following parameters for the conversion [240]³⁷⁴



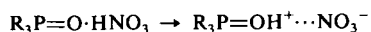
[240]

% H ₂ SO ₄ (w/w, in H ₂ O)	mol % of NO ₂ ⁺ in total HNO ₃	log <i>k</i> ₁ (s ⁻¹)	log <i>k</i> ₋₁ (s ⁻¹)	log <i>a</i> _w (<i>a</i> _w = activity of water)
81.0	0	—	—	—
86.2	12	2.26	3.11	-2.96
87.7	34	2.45	2.74	-3.15
88.6	54	2.48	2.41	-3.26
89.5	66	2.59	2.30	-3.36
91.2	92	3.44	2.18	-3.55
92.6	98	3.51	1.91	-3.72
96.7	100	—	—	—

In the case of 0.5 M HNO₃ in 88.6% H₂SO₄, the two ¹⁴N signals coalesce at 43.0°, and the lineshape analysis thereof gives the activation parameters for the conversion,



Investigations of HNO₃/tributylphosphate systems show that there is a minimum in the nitrogen shielding at a HNO₃/phosphate mol ratio of about 0.6 (Table 114, note (q)).³⁷⁵ Starting from low concentrations of HNO₃, the nitrogen shielding decreases, and this is explained in terms of dissociation of the following structures:



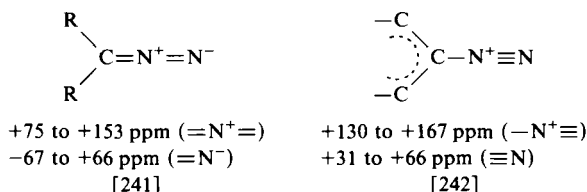
since the shielding moves in the direction of that for NO₃⁻. The subsequent rise in the nitrogen shielding reflects simply a movement in the direction of the shielding for neat HNO₃. Aqueous HNO₃ shows a rather significant dependence of its nitrogen shielding on temperature (Table 9, note (a)),²⁴⁷ and the relationship is not linear.

The nitrogen shielding in the nitrate ion, NO₃⁻, is typically *ca.* +4 ppm (from neat nitromethane), but it can be affected significantly by the presence of acids (Tables 6 and 114). There is an inflection point on the plot of NO₃⁻ nitrogen shielding in thallium nitrate against TlNO₃ concentration in liquid NH₃ (Table 114, note (o)); this occurs at 3.5:1 NH₃/TlNO₃ ratio, probably owing to a change from 2:1 to 3:1 solvates.²⁶³

The labelling of NO₃⁻ with ¹⁸O produces a clear and additive secondary isotope effect on the ¹⁵N shielding (Table 7, note (c)).²²⁶ Such effects can be exploited in following the fate of ¹⁸O labels in biological systems, using ¹⁵N NMR (Section V.A).

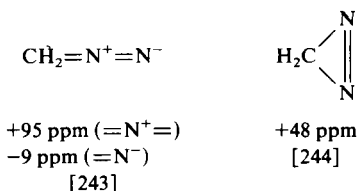
X. Diazo compounds, diazonium ions, diazotate ions and related structures

There is a similarity in the structures of diazo compounds [241] and those of aryldiazonium ions [242], since both contain linear CNN moieties:



The similarity is also reflected in the relevant nitrogen shieldings (Tables 115, 116). The central nitrogen atom shows a higher shielding of its nucleus, by about 100 ppm, compared with the terminal nitrogen atom.

Diazo [243] structures are isomeric to those of diazirine rings [244], and nitrogen NMR provides a simple means of distinguishing between such isomers (ref. 1, p. 100, and references therein):



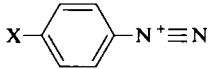
Variations in the nitrogen shieldings in diazo compounds that result from variations in the structure of substituents R have not so far been rationalized in terms of any simple rules (ref. 1, p. 101), and the only evident effect is the increased shielding of both the central and terminal nitrogen nuclei when the diazo moiety is conjugated with C=O or CN groups (Table 115).

As far as the nitrogen shieldings in aryldiazonium ions are concerned (Table 116), those for the central nitrogen atom reveal a neat, linear correlation with the σ^+ constants of *para* substituents,³²⁰ slope 3.83, $r = 0.979$ (Table 116, note (b)), but it turns out that the correlation comprises *meta* substituents as well³⁷⁶ (slope 3.86, $r = 0.990$) (Table 116, note (a)), provided that the NMe₂ substituent is excluded. Thus, it does not seem reasonable to consider the effects in terms of resonance structures,^{320,377} but direct polar interactions between the substituents and the diazonium moiety can be invoked,³⁷⁶ such as those discussed in Section VI.W for substituted nitrobenzenes. The situation is more complicated in the case of the nitrogen shieldings of the terminal nitrogen atoms of diazonium moieties (Table 116), since both electron-attracting and electron-donating substituents seem to decrease the nitrogen shielding, and the effects are much more pronounced for electron donors.^{320,376} A similar, but opposite effect has already been

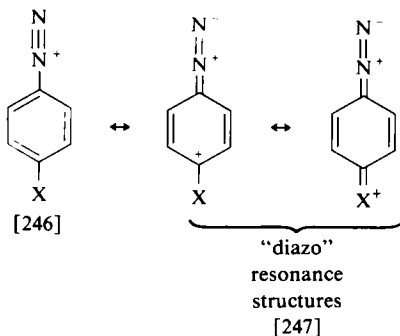
considered in the case of substituted nitrobenzenes and their nitrogen shieldings³⁶⁹ (Section VI.W, and discussion therein).

For *para*-substituted benzenediazonium tetrafluoroborates in sulfolane solutions the nitrogen shieldings of both the nitrogen atoms seem to increase non-linearly with the increasing (algebraically) polarographic half-wave potentials, and also with the decreasing wavelength of the corresponding UV absorption maxima.³⁷⁷ It is interesting to note that in the *p*-NMe₂ derivative, the exceptionally low shieldings (Table 116) correspond to the exceptionally large wavelength *ca.* 380 nm.³⁷⁷ This indicates the role of excitation energies in the general equations for nitrogen shieldings (Section II), in addition to other factors. This can also explain the deterioration of correlations between the nitrogen shieldings in substituted benzenediazonium ions and the σ^+ constants when the NMe₂ derivatives are included. It therefore seems that simple theories can hardly substitute for quantum-mechanical calculations in explanations of the nitrogen shieldings of aryldiazonium ions.

Some specific effects on the nitrogen shieldings of benzene diazonium ions [245] were noticed on addition of a crown ether:³²⁰

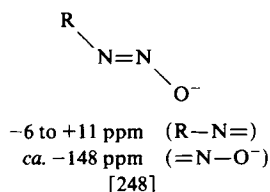
 (in dimethylformamide) [245]	Change in nitrogen shielding (ppm) on addition of 1 equivalent of 18-crown-6 ether	
	$-\text{N}^+\equiv$	$\equiv\text{N}$
X = OMe	+4.5	-1.5
X = Bu ⁿ	+4.5	-2.3
X = H	+5.7	-3.2

Attempts have been made³²⁰ to explain these changes in terms of the increasing contribution of the "diazonium" resonance structure [246] to the electron distribution in the ions complexed with the crown ether:



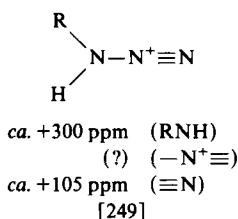
It is difficult to accept this, in view of the shielding decrease observed for the terminal nitrogen atoms; diazonium ions are characterized by higher shieldings in both central and terminal nitrogen atoms relative to the respective atoms in diazo compounds.

The CIDNP effects observed in the ^{15}N spectra of benzenediazonium ions (Table 8) under conditions of their cleavage in weakly alkaline aqueous solutions are considered in Section IV.H.²⁰⁹ These studies provide information about the nitrogen shieldings in diazotate anions Table 116, note (f) [248]:



where R = aryl. Only two such ions were examined (R = Ph or *p*-Cl-phenyl), but the data seem to indicate that the shielding in the R—N moiety is sensitive to substituent effects while that in the N—O moiety is not. There is a large difference in the nitrogen shieldings between diazotate ions and diazonium ions, which makes their spectral distinction quite straightforward.

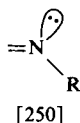
One should note that protonated azides have structures of aminodiazonium ions [249], (Table 77, note (f)):³¹⁷



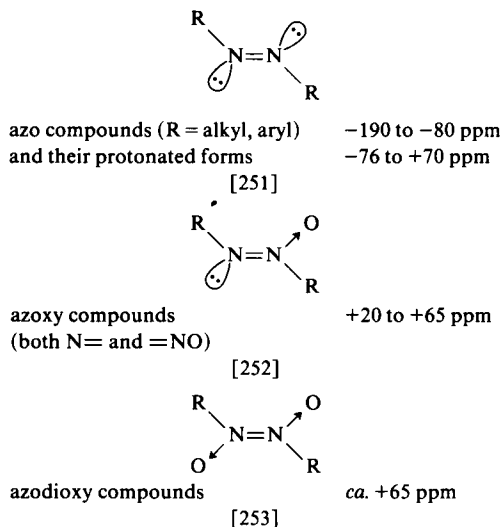
and the nitrogen shieldings in their terminal (≡N) atoms are appreciably higher than those in arenediazonium ions.

Y. Azo, azoxy and azodioxy compounds, diazene, triazene, and tetrazene structures

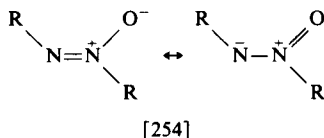
Azo bridges that are contained between two carbon atoms show a considerable deshielding of their nitrogen nuclei (Table 117) compared with most nitrogen-containing structures (Table 10). The electronic structure at azo-type nitrogen atoms [250]



resemble those at pyridine-type (Sections VI.Q, VI.R) and imino-type (Section VI.U) nitrogen atoms, and their respective nitrogen shieldings respond in an algebraic increase upon any involvement of the lone-pair electrons into some kind of bonding, such as that due to *N*-oxidation, *N*-protonation or *N*-complexation with metals (Sections V.E, V.H, V.J). In the case of azo compounds, all such effects are quite formidable (Table 117; see also ref. 1, Table 136 therein):



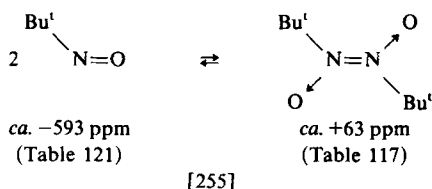
In azoxy compounds there is only a slight difference in the nitrogen shieldings between the *N*-oxide moiety and the other nitrogen atom (Table 117, notes (c, f)). This means that a significant enhancement of the nitrogen shieldings of both the nitrogens in an azo compound takes place on *N*-oxidation to the corresponding azoxy compound. It is simply another example of the lone-pair back-donation effect (see Section V.E), which in this case may be depicted as



which is analogous to those observed in the nitrogen shieldings in the mono-*N*-oxides of pyrazine and pyridazine (Section VI.R). In the latter cases, the *N*-oxidation results not only in a substantial increase in the nitrogen shielding in the N atom being oxidized, but also in the other nitrogen atoms present, compared with the corresponding atoms in the parent azine rings; this is not the case if the mono-*N*-oxide of pyrimidine

is considered with reference to pyrimidine. A question arises on the assignment of the nitrogen shieldings in an azoxy compound to the $R-N=$ and $=NO-R$ moieties there. Hydrogen bonding and protonation effects on the shieldings (Table 117, note (c)) are not quite conclusive, since the assignment of the higher shielding to $=NO-R$ requires an assumption that the oxygen atom is involved predominantly in hydrogen bonding and protonation.³⁷⁸ However, such an assignment is supported by a consideration of azimine structures and their nitrogen shieldings, in comparison with the parent azo-structures (ref. 1, p. 102, and references therein). Thus one may assume that the higher shielding represents the *N*-oxide moiety in an azoxy compound, at least till some evidence to the contrary is found.

Azodioxy structures (Table 117, note (k)) are dimeric forms of the corresponding nitroso compounds (Table 121, note (a)), and can occur in equilibria with the latter; there is a huge difference between their nitrogen shieldings, for example [255],



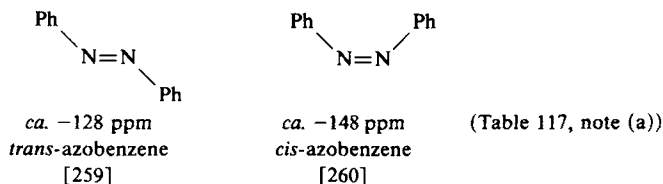
This difference provides a simple means of recognition of components of such equilibria. It is interesting to note that the shieldings in azodioxy structures are only slightly higher than those in azoxy compounds.

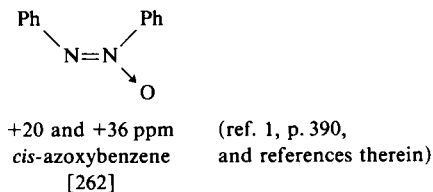
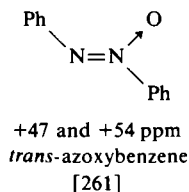
The range of nitrogen shieldings in azo bridges is extended remarkably if one considers elements other than carbon attached to the $N=N$ bridge, as indicated by the data in ref. 1 (Table 136 therein), and Table 118; for examples,

$\text{Me}_2\text{N}-\text{N}=\text{N}-\text{Ph}$	-72 and +20 ppm ($\text{N}=\text{N}$)	[256]
$\text{Me}_2\text{N}-\text{N}=\text{N}-\text{NMe}_2$	-25 ppm ($\text{N}=\text{N}$)	[257]
$\text{Me}_3\text{Si}-\text{N}=\text{N}-\text{SiMe}_3$	-618 ppm	[258]

If such structures are included, the range of the nitrogen shieldings in $-N=N-$ moieties extends from about +40 to about -620 ppm.

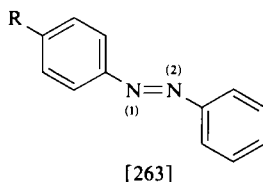
Azo compounds and their *N*-oxides can exist as geometrical isomers, and the differences in the nitrogen shieldings within such isomeric pairs are quite pronounced:



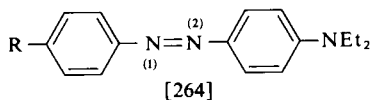


(additional data can be found in ref. 1, Table 136 therein), and it seems that as a rule the *cis*-structures exhibit smaller shieldings of the nitrogen nuclei than the corresponding *trans*-structures. The differences amount to about 20 ppm; their origin probably lies in the non-planarity of the *cis*-structures owing to steric-hindrance effects.

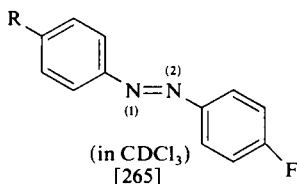
The large body of nitrogen shielding data for 4-monosubstituted *trans*-azobenzenes [263] (Table 117, notes (a, b)), indicates that electron-attracting



substituents, R, induce a decrease in the shielding in 2-N, and electron-donating substituents R give rise to enhancements of the 2-N shieldings.³⁷⁹ However, the 1-N shielding is invariably increased by both kinds of substituents R. The effects (referenced to the nitrogen shielding in *trans*-azobenzene) can be used for predicting, with an accuracy of about ± 3 ppm, the shieldings in 4,4'-disubstituted *trans*-azobenzenes (Table 117, notes (a, b)).³⁷⁹ These results explain the rather poor correlation of the 1-N shieldings with the Hammett constants σ_p of substituents R in structures [264] (Table 117, note (e)) and a reasonable correlation in the case of the



2-N shieldings.³⁸⁰ Analogous effects are reported for 4'-substituted 4-fluoroazobenzenes [265],³⁸¹

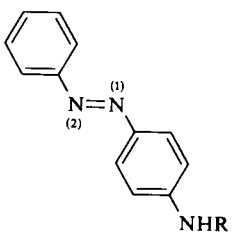


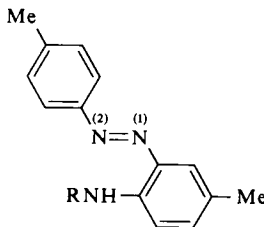
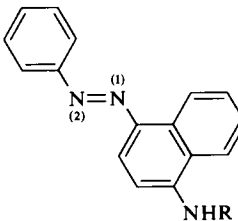
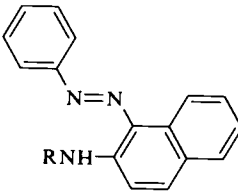
Substituent R	Nitrogen shielding (in ppm), referred to neat nitromethane	
	2-N	1-N
H	-123.8	-126.1
NMe ₂	-92.0	-115.2
OMe	-109.5	-119.7
Me	-117.4	-123.6
F	-121.1	-121.1
NO ₂	-139.1	-118.6

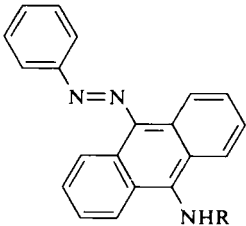
One should note that the assignments in all of the data for substituted azobenzenes leave no doubt, since they are established by means of ¹⁵N labelling.³⁷⁹⁻³⁸¹

Thus there are again some complications, as in the case of substituted nitrobenzenes (Section VI.W) and benzenediazonium ions (Section VI.X), in explaining substituent effects on the nitrogen shieldings in terms of single parameters characterizing the substituents involved; one would probably have to employ dual parameter relationships such as those used for substituted nitrobenzenes.

Nitrogen shieldings are useful in investigations of azo-hydrazone tautomerism (ref. 1, Table 137 therein) since there are large differences in the shieldings between the tautomeric structures (see Tables 39, 117). Recent measurements of a number of amino- and acetamido derivatives of azoarenes show that the compounds exist essentially as azo compounds (experimental details are the same as those specified in Table 117, notes (a, b));²⁶⁰

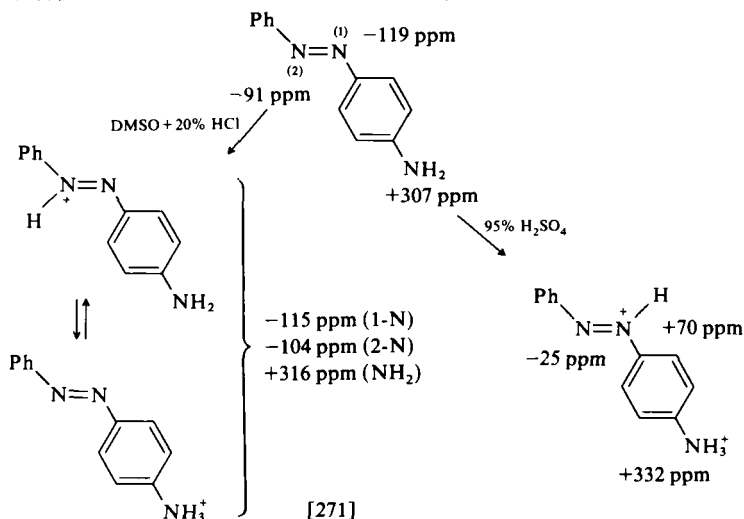
Structure	Solvent	Nitrogen shielding in (ppm, at 300 K) referred to neat nitromethane		
		1-N	2-N	other
				
R = H	CDCl ₃	-118.0	-101.7	+318.4 (NH ₂)
R = COMe)	DMSO-d ₆	-124.3	-118.1	+235.3 (NHCOMe)
[266]				

Structure	Solvent	Nitrogen shielding in (ppm, at 300 K) referred to neat nitromethane		
		1-N	2-N	other
				
R = H	CDCl ₃	-115.0	-97.3	+322.7 (NH ₂)
R = COMe	CDCl ₃	-106.4	-110.9	+255.8 (NHCOMe)
[267]				
				
R = H	acetone-d ₆	-114.5	-93.1	(?) (NH ₂)
	CDCl ₃	-117.8	-101.3	(?) (NH ₂)
	DMSO-d ₆	-112.8	-86.4	(?) (NH ₂)
R = COMe	DMSO-d ₆	-123.2	-123.4	(?) (NHCOMe)
[268]				
				
R = H	CDCl ₃	-118.9	-72.9	+301.9 (NH ₂)
	DMSO-d ₆	-114.8	-65.9	(?) (NH ₂)
	acetone-d ₆	-116.1	-67.6	(?) (NH ₂)
R = COMe	CDCl ₃	-129.3	-94.1	(?) (NHCOMe)
[269]				

		Nitrogen shielding in (ppm, at 300 K) referred to neat nitromethane		
Structure	Solvent	1-N	2-N	other
				
R = H	DMSO-d ₆	-117.4	-77.2	(?) (NH ₂)
R = COMe	DMSO-d ₆	-144.0	-151.9	(?) (NHCOMe)
[270]				

These shieldings show some variation with temperature,²⁶⁰ but they are so remote from those characteristic of hydrazone structures (Table 39) that there is hardly any indication of the presence of any significant amount of hydrazone tautomers of such azo dyes. The presence of an azo moiety in the product of a mild oxidation of dehydro-1-ascroic acid bis(phenylhydrazine) (Table 117, note (g); see also Section VI.H, and Table 39, note (b)) is shown clearly by the nitrogen shieldings.²⁷⁹

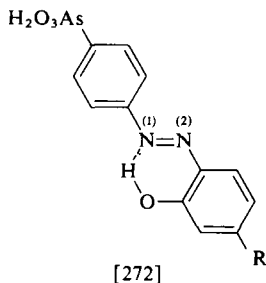
The scheme [271] of protonation of 4-aminoazobenzene in weak and strong acid solutions is postulated on the basis of nitrogen shieldings (Table 117, note (d)), NOE data and ¹⁵N-¹³C couplings:³⁸²



However, in our opinion, the evidence is still non-conclusive in some parts. In the case of solutions in DMSO + 20% HCl, the existence of the 2-N protonated species was postulated on the basis of the inverted 2- ^{15}N signal (there is no ambiguity about the assignment, since a selectively labelled sample is also examined); nevertheless, the 2-N nucleus becomes deshielded relative to that in a neutral solution, and this is just contrary to what one can expect for the protonation at this site. Actually, the shieldings of both 1-N and 2-N under these conditions seem to reflect a change in the amino substituent, from an electron donor (NH_2) to an electron-deficient group (NH_3^+), in view of the considerations of substituent effects in the present section. In the dication that is present in 95% H_2SO_4 , the ^{15}N - ^1H coupling pattern evidently shows the presence of an NH_3^+ moiety, but the protonation at 1-N is suggested only by the larger shielding effect on 1-N, compared with that for 2-N, relative to the neutral molecule in DMSO.

Large algebraic increases in the nitrogen shieldings in aromatic azo compounds are observed when one of the nitrogen atoms in the azo bridge undergoes complexation with Pd (Table 117, note (h)).³⁸³ Such effects are larger by an order of magnitude in nitrogen atoms involved directly in the complexation, as compared with other nitrogens.

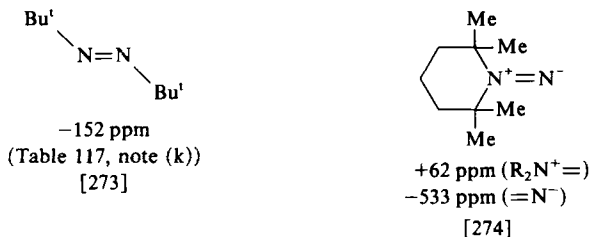
The rather substantial difference in the nitrogen shieldings between the two $-\text{N}=\text{N}-$ atoms in arsanilazo-*N*-acetyltyrosine, and an analogous moiety in arsanilazocarboxypeptidase A (Table 117, note (i)) suggests that 1-N in such structures is internally hydrogen-bonded [272].³⁸⁴



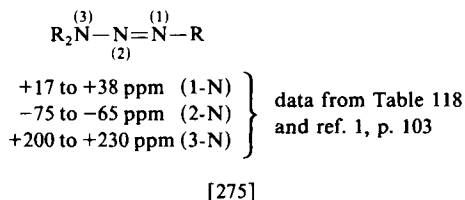
However, the formation of the phenolate ion seems to exert only little effect on the shieldings, if aqueous solutions are considered. This apparent anomaly can be explained in terms of a replacement of the hydrogen-bonding effect on 1-N with that of the strong electron-donor substituent, $-\text{O}^-$, in the phenolate ion.³⁸⁴ The latter effect is consistent with considerations of substituent effects on the nitrogen shieldings in *para*-substituted azobenzenes. The nitrogen shieldings in the systems considered show that azo rather than hydrazone-type structures are present there. In arsanilazocarboxypeptidase A, the complexation with Zn takes place essentially via 1-N, as indicated by the large algebraic increase in the 1-N shielding

(Table 117, note (i)); the experimental difference of about 20 ppm for 1-N between aqueous solutions at pH = 7.0 and 8.8 reflects only a part of the Zn complexation effect at 1-N, since the complexation destroys the internal hydrogen bonding. Thus the Zn binding to 1-N actually exerts a shielding effect of about 50 ppm on the nitrogen nucleus involved. This is corroborated by the fact that the addition of the enzyme inhibitor β -phenylpropionate or Gly-Tyr (Table 117, note (i)), which are likely to bind Zn, results in a considerable deshielding of 1-N.

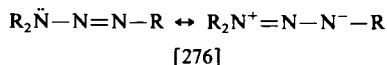
The structures of azo compounds, which may be termed 1,2-diazenes [273], are isomeric to aminonitrene ("1,1-diazene") [274] systems, and the nitrogen shielding data for a representative of the latter (Table 118, note (a)) show an essential differentiation between the isomers:



As far as triazene structures are concerned (Table 118), one should consider separately the aminoazo and iminoazo structures. Triazenes of the aminoazo type [275],

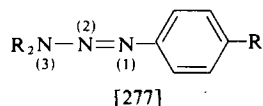


reveal nitrogen shieldings that in the case of 1-N are much higher than in azo compounds, and in the case of 3-N are much lower than in enamines. This is obviously a manifestation of the lone-pair back-donation effect [276]



which was considered in Sections V.E, V.G, VI.B, VI.R, VI.T, VI.U and the present section, for a variety of molecular structures. The present example is particularly instructive since it encompasses both deshielding and shielding effects of the back-donation. The same applies to the acetamidoazo structures of triazenes shown in Table 118 (note (d)), where the nitrogen shieldings in the amide moieties are smaller than in amides, and the

shieldings in the 1-N atoms are higher than those in C-bound azo bridges. Effects of substituents R in structures [277] (Table 118, notes (c, d)) on the 1-N, 2-N and 3-N shielding are fairly simple, since in each case electron



donors act in the opposite direction relative to electron acceptors; for 2-N and 3-N, electron acceptors decrease the shieldings, and they enhance the shielding in 1-N, while electron-donating groups R act in the opposite ways respectively. It is therefore not surprising that the shieldings correlate linearly with the Hammett constants of substituents (shielding data in Table 118, note (c)).³⁸⁵ In the case of acetamidoazo types of triazenes (Table 118, note (d)), the nitrogen and carbon shieldings have been subjected to factor analysis in terms of principal components.³⁸⁶ It turns out that the substituents should be divided into two classes: halogens and non-halogens; one principal component is sufficient to describe the effects of a halogen substituent, while two principal components are required in order to describe the effects of any substituent of the non-halogen class. Among these components, only one of the two components describing the non-halogen class revealed a relationship to any simple molecular property, electron charge density in this case.³⁸⁶ One should be cautious, however, in assigning too much significance to such analyses of nitrogen shieldings, since, in the structures considered, the effects of substituents on the nitrogen shieldings show at least some trends that reflect the electron-donor and electron-acceptor properties of the substituents, and this includes all the three kinds of nitrogen atoms present in such structures. This is rather exceptional in view of the complicated patterns of substituent effects on nitrogen shieldings observed in nitrobenzenes (Section VI.W), benzenediazonium salts (Section VI.X), and azobenzenes (this section). It is very unlikely that the latter effects could be fitted into any simple scheme of linear combinations of parameters (principal components) characterizing the substituents from the point of view of their effects on at least a large part of carbon and nitrogen shieldings in the systems considered.

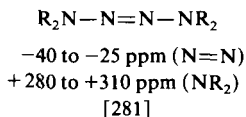
The role of the back-donation of the lone electron pair from the NR₂ moiety of aminoazo triazenes in the nitrogen shielding in the latter moiety is corroborated by the linear correlation between NMe₂ nitrogen shieldings in a variety of structures (*N*-nitrosamines, *N*-nitramines, triazenes, hydrazones, and hydrazines) and the corresponding barriers to the rotation of the NMe₂ group around the N—N bond in such structures. One should remember, however, that such correlations can be observed only within a set of such structures which feature the same NR₂ groups; otherwise,

$$\begin{array}{c} \text{R}_2\text{C}=\text{N}-\text{N}=\text{N}-\text{R} \\ \quad \quad \quad (2) \\ \quad \quad \quad (3) \quad \quad (1) \end{array}$$

-87 to -25 ppm (1-N)
 -122 to -40 ppm (2-N)
 +55 to +92 ppm (3-N)
 [278]

$$\text{R}_2\text{C}=\text{N}^{(2)}-\text{N}^{(3)}=\text{N}^{(1)}-\text{C}_6\text{H}_4-\text{X}$$

[279]



There is also an interesting aspect of the nitrogen shielding data for azobenzenes (Table 118, notes (a-c)) from the point of view of the use of relaxation reagents such as $\text{Cr}(\text{acac})_3$. The addition of the latter induced changes of up to about 2 ppm in the shieldings, and probably a large part of the variations should be ascribed to changes in the bulk magnetic susceptibility of the samples doped with the reagent (Section III).

Z. Nitroso compounds, nitrosamines and nitrites

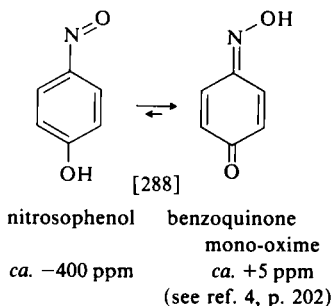
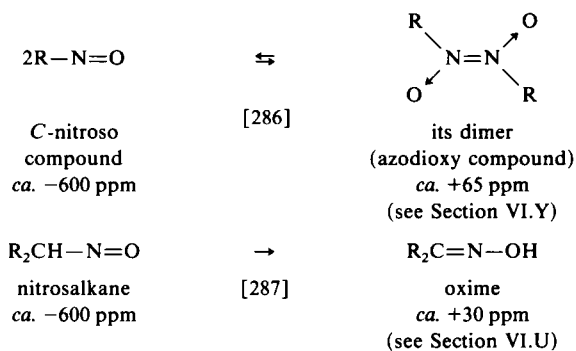
The nitrogen nuclei in *C*-nitroso moieties are strongly deshielded with respect to those in any nitrogenous moiety with the exception of some azo bridges bound to heteroatoms like Si (Section VI.Y), and the smallest algebraical shieldings are observed for nitrosoalkanes (Table 121). One should notice that the results of ^{15}N and high-precision ^{14}N measurements presented in Table 121 show, in some cases, appreciable differences with respect to those from wide-line NMR techniques, quoted in ref. 1 (Table 140 and references therein). If there is an aggregation of F or CF_3 substituents at the α -C atom of a nitrosoalkane, the nitrogen shielding increases appreciably, by about 150 ppm; this is ascribed to increased excitation energies of $n \rightarrow \pi^*$ transitions,³⁸⁷ in accord with some correlation of the nitrogen shieldings in $\text{X}-\text{N}=\text{O}$ structures with the corresponding low-wavelength absorption bands in their electronic spectra. Nitrosoarenes are characterized by nitrogen shieldings that are higher by about 100 ppm than those in nitroalkanes, but there seems to be almost no effect of fluorine substituents (Table 121, notes (c, d)). The largest algebraic shieldings in the nitroso class are found in *N*-nitroso moieties (nitrosamines, nitrosamides, and related structures, Tables 119, 120), and in the *O*-nitroso moieties of covalent nitrites (Table 121); the *S*-nitroso groups of covalent thionitrite structures (Table 121) have nitrogen shieldings that fall between those for nitrosoarenes and nitrosoamines.

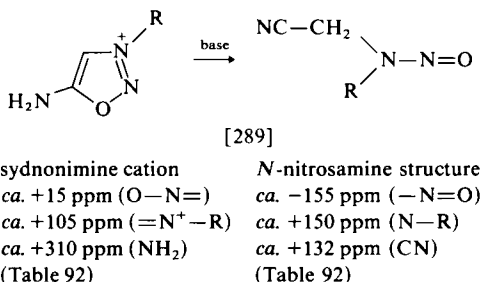
$\begin{array}{c} \text{R} \\ \diagdown \\ \text{N}=\text{O} \end{array}$	
R = alkyl (nitrosoalkane)	-603 to -590 ppm
R = alkyl with F or CF_3 substituents at α -C	-485 to -425 ppm
R = aryl (nitrosoarene)	ca. -500 ppm
$\begin{array}{c} \text{RS} \\ \diagdown \\ \text{N}=\text{O} \\ \text{(thionitrite)} \\ \text{[283]} \end{array}$	
	ca. -400 ppm

$\begin{array}{c} \text{R}_2\text{N} \\ \diagdown \\ \text{N}=\text{O} \end{array}$ (nitrosamines, nitrosamides) [284]	-200 to -155 ppm ($-\text{N}=\text{O}$) +95 to +156 ppm (R_2N)
$\begin{array}{c} \text{RO} \\ \diagdown \\ \text{N}=\text{O} \end{array}$ (covalent nitrites, including HONO) [285]	-207 to -180 ppm

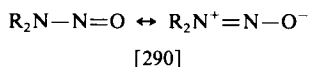
Thus it is fairly easy to distinguish individual types of nitroso derivatives by means of NO nitrogen shieldings, and this includes some nitroso-type moieties in inorganic molecules and ions (Table 123).

The large difference between the nitrogen shieldings in nitroso groups and those in most other nitrogen-containing moieties facilitates their spectral distinction, and this includes molecules that are isomeric, tautomeric or related in any way to nitroso-type structures, [286]–[289]:





The rather low shieldings of the amino nitrogen atoms in *N*-nitrosamines (Table 119) can be explained in terms of the delocalization of their lone-pair electrons into the nitroso moiety, since the nitrogen shielding of NMe₂ in Me₂N—N=O falls neatly into a linear correlation between NMe₂ nitrogen shieldings in a number of structures and the corresponding barriers to rotation around the N—N bonds (ref. 1, p. 106, and references therein):



This is another example of the lone-pair back-donation effect on nitrogen shieldings (Section V.E), which in the case of the lone-pair donor results in a decrease in the shielding. The restricted rotation around the N—N bonds in *N*-nitrosamines is also revealed in nitrogen NMR spectra, since separate signals of the geometrical isomers involved are often observed (Table 119). In the case of *trans*-1,4,5,8-tetranitroso-1,4,5,8-tetraazadecalin (Table 119, note (c)),³⁸⁸ a comparison of the NO nitrogen shieldings for individual isomers suggests that the highest algebraic shieldings should be assigned to the nitroso groups that have, in the vicinity of their nitrogen atoms, the oxygen atoms of other nitroso groups. In *N*-nitrosodecahydroquinolines and some related structures (Table 119, note (d))³⁸⁹ the largest deviations of the nitrogen shieldings, from those observed in *N*-nitrosopiperidine, occur when either substituents or the conformation of the rings force the nitroso moiety into a position that precludes or hampers the delocalization of the lone-pair electrons from the amino nitrogen atom to N=O. There are also typical effects of alkyl substituents (Section V.F) on the shielding in the amino nitrogen atom. A difference of 2.1 ppm is observed between the nitrogen shieldings of the ¹⁵N labelled N=O group in *cis* and *trans* isomers of *N*-nitroso-2(3',7'-dimethyl-2',6'-octadienyl)aminoethanol.³⁹⁰

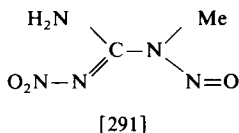
There have been a wealth of nitrogen shielding data reported on *N*-nitroso derivatives of urea and thiourea (Table 120). In the case of nitrosation of thiourea derivatives with NaNO₂ in 0.1 M HCl, the ¹⁵N spectra indicate clearly the formation of *N*-nitroso structures (Table 120, note (g)),³⁹¹ but

in 1 M HCl in EtOH at -10°C , the first stage involves the formation of an *S*-nitroso (thionitrite) moiety (Table 121, note (e)), as indicated by the ^{15}N spectrum, and this intermediate is subsequently transformed into derivatives of urea on hydrolysis. The nitrogen nuclei in the nitroso groups of *N*-nitroso-urea and *N*-nitrosothiourea derivatives (Table 120) are somewhat more deshielded than those in *N*-nitrosamines (Table 119).

The nitrite ion, NO_2^- , in neutral aqueous solutions is characterized by a nitrogen shielding of about -228 ppm (Table 121), but the latter value is sensitive to the presence of acids, since the shielding then moves in the direction of that for $\text{HO}-\text{N}=\text{O}$ (Table 122). A comprehensive study of the ^{15}N spectra of NaNO_2 in a variety of acidified solutions reveals the presence of three species, NO_2^- , $\text{HO}-\text{N}=\text{O}$, and NO_3^- (Table 122),³⁹² but there are additional signals whose origin is not certain. One of the latter, that at about -32 ppm (Table 122), is assigned to ClNO , while the resonance at $+25$ ppm is ascribed to BrNO ,³⁹² but this is in obvious disagreement with the relevant data in Table 123 (note (1)) for the latter molecules.

The nitrogen shielding in NO_2^- reveals a clear and additive secondary isotope effect upon introduction of ^{18}O (Table 7);^{226,227} such effects can be exploited in following the fate of ^{18}O tracers in biological samples (Section V.A).

The nitrogen shieldings presented in Table 120, note (i), indicate the localizations of the nitroso and nitro moieties in the *N*-nitroso-*N'*-nitro derivative of *N*-methylguanidine [291]²⁸⁴ since there are values characteristic of a nitrosamine moiety, $+125$ and -187 ppm, and also that of a guanidino NH_2 group, $+286$ ppm.

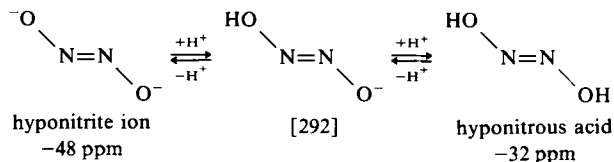


AA. Nitrogen oxides, nitrogen-oxygen ions, and related species

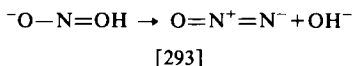
Nitrogen oxides and related inorganic molecules (Table 123) often contain moieties that are analogous to those found in organic molecules, such as nitro, nitroso and azo groups. The relevant shieldings of the nitrogen nuclei in such moieties do not differ appreciably from those in the corresponding organic molecular structures. This applies to the NO_2 moieties in N_2O_3 , N_2O_4 , ClNO_2 and BrNO_2 , as well as to the NO moieties in N_2O_3 , ClNO , and BrNO (Table 123). Molecular nitric (HONO_2) and nitrous (HONO) acids have nitrogen shieldings that are very close to those of alkyl nitrates and alkyl nitrites respectively (Tables 123, 122, 121 and 114). The structures of hyponitrous acid, $\text{H}_2\text{N}_2\text{O}_2$, and the corresponding hyponitrite ion (Table 123), contain azo-type $\text{N}=\text{N}$ moieties, and the nitrogen shieldings are

similar to those observed for azo bridges that link atoms bearing lone-pair electrons (tetrazenes, *N*-oxides of azo compounds, (Section VI.Y).

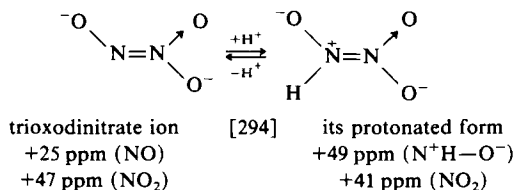
The protonation of the hyponitrite ion, $\text{N}_2\text{O}_2^{2-}$, results in a relatively weak shielding effect on the nitrogen nuclei (Table 123, note (g)),²³⁴ and this indicates that *O*-protonation takes place [292]:



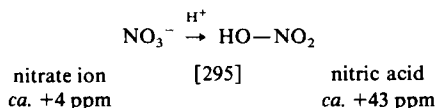
The data show that the diprotonation is practically complete at pH = 5.²³⁴ Using doubly ^{15}N -labelled hyponitrite, it has been shown that both labels are present in N_2O that is formed upon the decomposition of hyponitrite; which therefore must proceed according to the scheme [293], in accord with the *O*-protonation pathway.



In the trioxodinitrate ion, ONNO_2^{2-} (Table 123, note (h)), the nitrogen shieldings suggest that *N*-protonation takes place [294],²³⁵ since there is a large shielding effect on the NO nitrogen nucleus, and the corresponding ^{15}N signal becomes inverted in the protonated form of the ion, owing to the nuclear Overhauser effect upon proton decoupling; the assignments leave no doubt, since they were verified by selective ^{15}N labelling of the ion.²³⁵ These assignments are the reverse of those quoted in ref. 1 (Table 8 and reference therein).

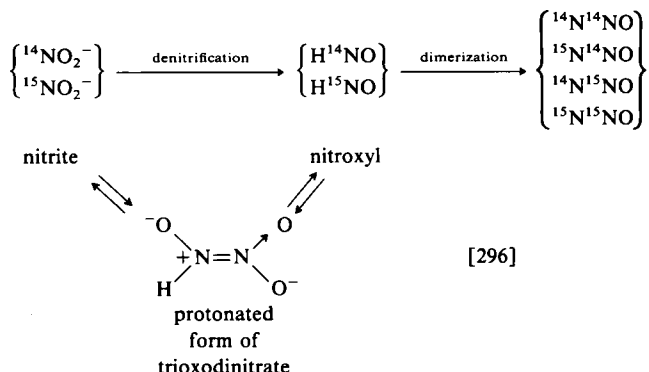


The localization of the protonation sites in the examples quoted above is quite convincing, but one should exercise some caution in the interpretation of large shielding effects on the nitrogen nuclei in nitrogen-oxygen ions in terms of *N*-protonation, since *O*-protonation can in some cases lead to such effects (Table 123) [295],



The observation of the formation of the nitronium ions, NO_2^+ , in solutions of HNO_3 in H_2SO_4 was considered in Section VI.W; separate ^{14}N signals are observed for the HONO_2 and NO_2^+ species (Table 123, note (f)), and quantitative analysis is possible.³⁷⁴

The pathway of reduction of nitrogen in NO_2^- by some denitrifying bacteria has been elucidated using ^{15}N labelled nitrite and ^{15}N NMR spectra.³⁹³ It has been shown that the key intermediate in the formation of N_2O from NO_2^- is probably nitroxyl, HNO , while the trioxodinitrate ion, HN_2O_3^- , is not an intermediate. The scheme [296] for the transformation is suggested;³⁹³



the arguments are based on the fact that ^{15}N isotope scrambling, in the N_2O formed, is observed in all cases, even when doubly ^{15}N -labelled trioxodinitrate is added to the medium thus the $\text{N}=\text{N}$ bond of the latter is not retained in the product, N_2O .

Calculations of the nitrogen shieldings in N_2O , based on experimental values of spin-rotation constants (Section V.B),⁵⁶ give reasonable results for the terminal nitrogen atom in N_2O , but not for the central atom; a thorough analysis of the discrepancy suggests that in the latter case, the value of the constant is in error.

The nitrogen shieldings in the nitrate, NO_3^- , and nitrite, NO_2^- , ions were considered in Sections VI.W and VI.Z respectively.

BB. Dinitrogen, its complexes, and related structures

Reliable values of the nitrogen shielding in N_2 are now available (Table 124, notes (a, b)) with respect to that in neat liquid nitromethane. However, the value for gaseous N_2 , extrapolated to the zero-pressure limit (+74.70 ppm, Table 124),⁵⁶ contains bulk-susceptibility effects, and a correction for the latter (Section III) brings the N_2 nitrogen shielding to +73.9 ppm relative to neat nitromethane. Attempts have been made to calculate absolute shieldings of nitrogen nuclei in a number of gaseous compounds, including

N_2 , on the basis of experimental values of the corresponding spin-rotational coupling constants (Section V.B), but there is a disagreement between the experimental and calculated values for N_2 and for the central nitrogen in N_2O . It is likely that the experimental errors in the spin-rotation constants involved are actually much larger than those reported in the literature.⁵⁶ The nitrogen shielding in gaseous N_2 , in the zero-pressure limit, depends linearly on the temperature of the gas, with a slope of $-0.85 (\pm 0.10) \times 10^{-3}$ ppm/deg.⁵² This effect is assigned to the centrifugal distortion of the molecule upon raising the temperature, and the effects of vibrational averaging are assessed as negligible, at least within 220–380 K.

Nitrogen shieldings can be employed in distinguishing complexes of molecular N_2 from other complexes that may be involved in the reductive degradation of N_2 to ammonia³⁹⁴ (Tables 124, 125). In complexes of N_2 with metals, the nitrogen nucleus in the atom bound to the metal seems to be more shielded (ref. 1, p. 108, and references therein). This is corroborated by the changes [297] in the nitrogen shieldings (Tables 124, 125) upon coordination of $AlMe_3$ to the other nitrogen atom in N_2 .³⁹⁴

$OsCl_2(N_\alpha = N_\beta)(PMe_2Ph)_3$	+118 ppm (N_α)
	+64 ppm (N_β)
$OsCl_2(N_\alpha = N_\beta-AlMe_3)(PMe_2Ph)_3$	+104 ppm (N_α)
	+140 ppm (N_β , signal broadened)

[297]

There is a quite remarkable difference between the nitrogen shieldings in singly bent and doubly bent diazenido complexes derived from N_2 (Table 125; see also ref. 1, Table 143 therein).³⁹⁴ The complex of N_2 with tantalum shown in Table 124 (note (e)) contains a linear $Ta=N-N-Ta$ moiety with the longest (1.298 Å) N—N bond ever observed for dinitrogen bridging complexes.³⁹⁵ Its nitrogen shielding is also different from those of other types of N_2 complexes (Tables 124, 125). The ^{15}N spectra of reaction mixtures where $^{15}N_2$ is reduced to ammonia by the enzyme nitrogenase, fail to reveal any formation of complexes of N_2 with the enzyme.³⁶⁵

Motionally averaged anisotropy of the nitrogen shielding in N_2 adsorbed on mordenites suggests that adsorbed N_2 molecules have restricted rotational freedom when the ratio Si/Al in the mordenite is less than 4.70, since N_2 is adsorbed, under such circumstances, into the side-pocket type adsorption sites rather than into the main channels of the zeolite.³⁹⁶

CC. Metal complexes containing nitrogenous ligands and some free radicals

A large part of the nitrogen shielding data on metal complexes, where nitrogenous ligands are involved, has already been considered in the preceding sections: in particular, those concerned with individual structural types

of nitrogenous compounds and ions. However even these are given some attention in the present section, with appropriate references to other parts of the review. An account has appeared²¹⁸ of applications, mostly prior to 1980, of nitrogen NMR to the fields of inorganic organometallic and bioinorganic chemistry. Since 1980 considerable advances in the application of nitrogen NMR to these and related areas of chemistry have been made.

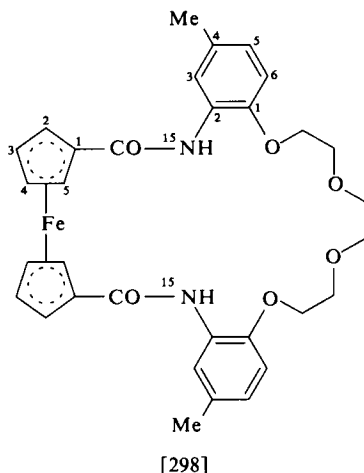
Nitrosyl complexes (Table 126) reveal a huge range of nitrogen shieldings, from about +75 to -740 ppm relative to the neat nitromethane reference. The magnitude of the spectral range is concerned with the fact that nitrosyl moieties, $M-NO$, where M is a metal, can assume a wide range of geometries, from linear ($M-N-O$ angle of about 180°) to strongly bent ($M-N-O$ angle smaller than 160°). Actually the nitrogen shieldings of nitrosyl groups offer a sensitive indicator of the degree of bending of $M-NO$ structures (Table 126):^{387,397} the largest shieldings are found in linear structures, while the largest deshieldings are observed in strongly bent $M-NO$ moieties. The ^{14}N resonance signals of molybdenum-bound nitrosyls are sharp enough to reveal $^{14}N-^{95}Mo$ couplings (Table 126, note (c)).³⁹⁸

A study of $^{13}C/^{12}C$ isotope effects on the ^{15}N shielding of some diamagnetic cyano complexes has been reported. The ^{15}N resonances of the ^{13}C labelled compounds are the more highly shielded by amounts varying from 0.06 ppm to 0.10 ppm (Section VI.P, Table 7, and Table 83).³⁹⁹

By keeping to a consideration of diamagnetic metal complexes, one's attention naturally turns to those containing larger nitrogenous ligand systems. Natural-abundance ^{15}N NMR spectra have been reported for aqueous solutions of *trans*-1,2-diaminocyclohexane- N,N,N',N' -tetraacetate with $Cd(II)$, $Hg(II)$, $Ag(I)$ and $Pb(II)$ (Table 129, note (d)).²⁷³ Values of $^1J(M-^{15}N)$ have been measured for those cases where M is ^{111}Cd , ^{113}Cd , ^{199}Hg and ^{207}Pb . The coordination shifts are small and in all cases result in nitrogen deshielding. Different values of $^1J(M-^{15}N)$ for these molecules reveal the presence of square and dynamically folded trigonal bipyramidal isomeric nitrogen donor sets in solution.

The ^{15}N NMR spectra of the macrocycle [298] containing the ferrocene unit, and some of its complexes with lithium, calcium and potassium ions have been reported:⁴⁰⁰ ^{15}N coordination shifts are observed in the presence of the calcium and lithium ions, but not when the potassium ion is present. It is concluded that the calcium and lithium ions are bound more strongly than potassium. The binding most probably occurs via the four oxygen atoms and, possibly, the ferrous ion.

Coronands, cryptands and some of their complexes with alkali, alkaline earth, $Ag(I)$ and $Tl(I)$ ions have been the subject of a ^{15}N NMR study.²⁶⁷ Complexation results in nitrogen deshielding, the extent of which depends upon the ionic character of the metal-nitrogen bond and on the charge residing on the metal. An increase in the polarizability of the metal ion



produces an increase in the nitrogen shielding. $^1J(\text{M}-^{15}\text{N})$ values are reported for some of the thallium and silver cryptates (Tables 17, 97).

From a comparable study, the value of $^1J(^{113}\text{Cd}-^{15}\text{N})$, for the pyridine adduct of cadmium-*meso*-tetraphenylporphyrin, is found to be +150.1 Hz.⁴⁰¹

Binding of $\text{Hg}(\text{II})$, $\text{Zn}(\text{II})$ and $\text{Ba}(\text{II})$ to the nucleosides adenosine, cytidine and guanosine in DMSO has been investigated by means of ^{15}N NMR.³⁵² The observed nitrogen shielding changes provide a means of monitoring the metal-nucleoside binding sites. As shown by increases in the nitrogen shielding, mercury binds preferentially to the well-established protonation sites of the three nucleosides. The same conclusion applies to the binding of zinc to cytidine and guanosine, whereas zinc binding to adenosine appears to favour a different nitrogen atom.

The absence of noticeable nitrogen shielding changes upon addition of barium nitrate implies that barium does not bind to any of the nitrogen atoms in these nucleosides.

In a similar ^{15}N study on the nucleoside inosine it is shown that protonation occurs preferentially at N7. $\text{Zn}(\text{II})$ and $\text{Hg}(\text{II})$ also favour N7 as a binding site in DMSO solution (Table 104).³⁵³

From a study of the binding sites of pyruvate kinase, it appears that the ammonium ion approaches to within 7.0 Å of manganese in the enzyme- $\text{Mn}(\text{II})$ -ammonium complex, whereas in the corresponding enzyme- $\text{Mn}(\text{II})$ -ammonium-phosphoenolpyruvate complex the relevant distance is 4.4 Å.⁴⁰²

Complexation of 1-methylimidazole by $\text{Zn}(\text{II})$ and $\text{Cd}(\text{II})$ in aqueous solution has been followed by means of ^{15}N NMR.⁴⁰³ A large increase in the shielding of the pyridine-type nitrogen nucleus occurs on complexation,

whereas the pyrrole-type nitrogen experiences a concomitant shielding decrease (Table 89).

In comparison with the nitrogen shielding of some unbound α -amino acids, coordination to Co(III) produces an increase of between 24 and 42 ppm.⁴⁰⁴ In contrast, the nitrogen shielding of some β -amino acids is less markedly influenced by binding to Co(III) (Table 65).⁴⁰⁴

¹⁵N NMR data have been presented for the three isomers of bis(aspartato)cobaltate(III).⁴⁰⁵ The results are discussed in terms of the coordination shifts and by a comparison with those for some analogous Co(III) and Rh(III) complexes.

In the case of some glycinate and ethylenediamine Co(III) complexes, the nitrogen coordination shifts range in magnitude from 19 to 62 ppm. The extent of the nitrogen shielding increase is rather dependent upon the ligand *trans* influence (Table 65).⁴⁰⁶

A number of reports have appeared of ¹⁵N NMR studies on complexes of Pt(II) (Tables 127, 128).^{407,415} These include a study of *cis*-diammine-chloroplatinum(II),^{407,411} and its hydrolysis and oligomerization complexes,⁴¹¹ and a study of the binding of acetamide to *cis*-[Pt(NH₃)₂(H₂O)₂]²⁺ and in the corresponding complex ion where ethylenediamine has replaced the two ammonia molecules.⁴⁰⁸

In the case of some Pt(II) Schiff's-base complexes, changes in the value of ¹*J*(¹⁹⁵Pt-¹⁵N) are interpreted in terms of a variation in the strength of the platinum-nitrogen bond.⁴⁰⁹

An investigation of [PtCl₂(*t*-butyl-N=CH-CH=N-*t*-butyl)(η^2 -Styrene)] reveals that it contains five-coordinate platinum in solution, while *trans*[[PtCl₂(P*bu*tyl₃)]₂((*t*-butyl-N=CH-CH=N-*t*-butyl)] is binuclear and *trans*[PtCl₂(*t*-butyl-N=CH-CH=N-*t*-butyl)(P*bu*tyl₃)] is four-coordinate with only one nitrogen atom of the diimine ligand coordinated at -50°C in CD₂Cl₂.⁴¹⁰

¹⁵N NMR studies of thiocyanato metal complexes reveal clearly whether the thiocyanate is nitrogen- or sulphur-bonded to the metal. Several linkage isomers of [Pt(NCS)_{*n*}(SCN)_{4-*n*}]²⁻ are shown to exist in CH₂Cl₂ solution.⁴¹⁴ Well resolved ¹⁹⁵Pt-¹⁴N couplings are observed in the ¹⁹⁵Pt NMR spectra of Pt(II) and Pt(IV) amine complexes at elevated temperatures.⁴¹² This results from a decrease in the ¹⁴N quadrupolar relaxation rate at higher temperatures. The ¹⁹⁵Pt-¹⁴N couplings observed are sensitive to the nature of the *trans* influence of some nitrite Pt(II) and Pt(IV) complexes it has been revealed that the value of ¹*J*(¹⁹⁵Pt-¹⁵N) is linearly dependent on the number of nitrite ligands present in the complexes of both platinum oxidation states.⁴¹³ ¹⁵N NMR has been useful in the characterization of some new Pt(II) and Pt(IV) antitumour drugs and in the study of the interaction of inosine and 5-adenosine monophosphate with *cis*-platin.⁴¹⁵

In a study of Pa(II) complexes containing a tripodal ligand, the ^{15}N shielding difference, of over 100 ppm, between the *S*- and *N*-bonded forms of thiocyanate is used to demonstrate that an equilibrium exists in solution between the two potential linkage isomers (Table 79).³¹⁹

A multinuclear NMR study on $\text{Hg(II)}\text{-Hg(CN)}_2\text{-D}_2\text{O}$ in perchlorate media reveals that $[\text{Hg}_2(\text{CN})_2]^{2+}$ predominates over a wide range of concentrations and values of the Hg to CN ratio (Table 83).⁴¹⁶ The ^{15}N T_1 value for this ion is estimated to be 11.0 s. Another multinuclear NMR study, involving ^{15}N , is that on a complex formed from an arenediazonium salt and $\text{IrCl(CO)(PPh}_3)_2$ (Table 129).⁴¹⁷

^{14}N NMR measurements have been undertaken in order to determine the effect of pressure on the exchange rates of ammonia⁴¹⁸ and acetonitrile^{419,420} on various paramagnetic transition metal ions.

The pseudo-first-order rate constant for the departure of a particular ammonia molecule from the inner sphere of $[\text{Ni(NH}_3)_6]^{2+}$ is found at 298 K to be $7.0 \times 10^4 \text{ s}^{-1}$ with $\Delta H^\ddagger = 57.3 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = 40.2 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta V^\ddagger = 5.9 \text{ cm}^3 \text{ mol}^{-1}$.⁴¹⁸ For the exchange of acetonitrile on iron(II) perchlorate at 298 K, the rate constant is $6.6 \times 10^5 \text{ s}^{-1}$, $\Delta H^\ddagger = 41.4 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = 5.3 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta V^\ddagger = 3.0 \text{ cm}^3 \text{ mol}^{-1}$;⁴²⁰ the corresponding parameters for acetonitrile exchange with manganese(II) perchlorate at 298 K are $1.36 \times 10^7 \text{ s}^{-1}$, 29.6 kJ mol^{-1} , $-8.9 \text{ J K}^{-1} \text{ mol}^{-1}$ and $-7.0 \text{ cm}^3 \text{ mol}^{-1}$ respectively.⁴²⁰

In the case of acetonitrile exchange with Co(II) and Ni(II) , the volumes of activation, in the range 0–160 MPa, are $6.3 \text{ cm}^3 \text{ mol}^{-1}$, for diffusion by rotation perpendicular to the molecular C_{3v} axis, $7.3 \text{ cm}^3 \text{ mol}^{-1}$ for solvent exchange with $[\text{Ni(CH}_3\text{CN)}_6]^{2+}$ and $6.7 \text{ cm}^3 \text{ mol}^{-1}$ for solvent exchange with $[\text{Co(CH}_3\text{CN)}_6]^{2+}$.⁴¹⁹

^{14}N Knight shift data for lithium–methylamine solutions permit the determination of unpaired electron spin densities at the nitrogen nucleus. The total electron density on the nitrogen is reported to be about half that found in lithium and sodium–ammonia solutions. The orbital containing the excess electron in ammonia and methylamine solutions with alkali metals is found to have a larger electron density at the nitrogen and carbon nuclei and a node close to the protons.⁴²¹

A ^{15}N NMR investigation⁴²² of the copper(II) complex of poly(L-lysine) reveals that the side-chain amino groups of the polymer have a far greater tendency than the amide groups to bind to copper. This conclusion is based on measurements taken at a variety of pH values.

In a ^{15}N NMR study of $\text{Xe[N(SO}_2\text{F)}_2]_2$ the observed $^1J(^{129}\text{Xe-}^{15}\text{N})$ data demonstrate the presence of two equivalent Xe–N bonds, thus supporting the proposed structure (Table 55).²⁹¹

Saturation transfer ESR measurements have permitted a study of the rotational motion of the ^{15}N nitroxide spin label, 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl, over a range of temperatures.⁴²³

^{14}N ENDOR data have been reported for the nitrobenzene radical anion in dimethoxyethane solution,¹⁵⁷ for bis(acetylacetonate)oxovanadium(IV) and some of its adducts,¹⁶⁰ oxovanadium(IV) complexes with imidazole,¹⁵⁹ carnosine and histidine,¹⁵⁹ for oxovanadium(IV) porphyrin in solid solution,¹⁵⁵ and for copper(II)-doped L-alanine.⁴²⁴ In the latter two cases the ^{14}N quadrupole interaction tensors are evaluated. Finally, mention should be made of ^{14}N and ^1H ENDOR and TRIPLE resonance data for liquid solutions of bacteriochlorophyll-a anion radicals,¹⁵³ for flavin and thiaflavin radical cations,¹⁵⁴ and for some azaaromatic radicals produced by sodium reduction in liquid ammonia,⁴²⁵ and of some ^{14}N and ^1H ENDOR results for nitrosylhaemoglobin.¹⁵⁸

VII. CORRELATION OF NITROGEN SPIN-SPIN COUPLINGS WITH MOLECULAR STRUCTURE

Various aspects of spin-spin coupling interactions involving nitrogen and other nuclei have previously been covered in detail.¹ In general the coupling data are obtained as a consequence of interactions involving the ^{15}N isotope. Rapid quadrupolar relaxation usually precludes the possibility of obtaining spin-spin coupling information from measurements involving the ^{14}N nucleus.

In those instances when ^{14}N spin-coupling results are available, to a nucleus X, they are converted to ^{15}N couplings by means of the relationship

$$J(^{15}\text{N}-\text{X}) = -1.4027 J(^{14}\text{N}-\text{X}) \quad (30)$$

Consequently the spin-coupling data presented here are given in terms of couplings involving the ^{15}N isotope. During the period under consideration a review⁴²⁶ has appeared covering the literature dealt with in our previous account.¹ For ease of accession we present the tabular couplings $n_J(^{15}\text{N}-\text{X})$ in terms of the number n of intervening bonds between ^{15}N and the coupled nucleus X.

A. $^1J(^{15}\text{N}-^1\text{H})$

One-bond ^{15}N couplings to ^1H are negative, and as shown in Table 130 can vary from about 40 to around 110 Hz in magnitude.

In general there is a correlation between the amount of s character in the N-H bond and the magnitude of the corresponding spin-spin coupling. Such a correlation is anticipated from the dominating influence of the contact interaction to couplings involving hydrogen. However, exceptions to this simple concept are known, such as ketimines (ref. 1, p. 112).

In the case of some amino diazonium ions a study of $^1J(^{15}\text{N}-^1\text{H})$ implies a range of 37.0 to 40.1% s character.³¹⁷ A similar study on some organometal amines results in a variation of % s character from 18.3 to 23.1.⁴²⁷ Further details of related calculations are to be found in Section II.

Deuterium isotope effects on the value of $^1J(^{15}\text{N}-^1\text{H})$ for the ammonium ion are additive, and amount to 0.21 Hz for the trideuteriated species (Table 135).²²⁹

Calculations based on the solvaton model indicate an increase in the magnitude of $^1J(^{15}\text{N}-^1\text{H})$ as the dielectric constant of the medium increases.⁴²⁸ Experimental observations (Table 150) support this result. However, in many cases the choice of solvent is such that not only may a change in dielectric occur, but also the possibility of hydrogen bond formation with the solvent must be considered.⁴²⁹⁻⁴³¹

The effects of stereospecificity on the value of $^1J(^{15}\text{N}-^1\text{H})$ have been noted. In the case of formamide the N-H coupling *cis* to the carbonyl group is about 2 Hz smaller in magnitude than the corresponding *trans* coupling (Table 130).^{145,432-434} In some cyclic amides (lactams) with medium-sized rings, which assume the *cis* conformation of the amide group, the magnitude of $^1J(^{15}\text{N}-^1\text{H})$ is smaller than in those taking the *trans* conformation, with the exception of 2-pyrrolidone. In this case the *cis* coupling is comparable in magnitude to the *trans* couplings found for the other amides studied (Table 130).⁴³¹ This is explained on the basis of a discussion of ring strain relating to the CNC angle.⁴³¹ It is interesting to note that the values of $^1J(^{15}\text{N}-^1\text{H})$ in some secondary amides and the corresponding iminium salts are essentially the same (Table 130).¹¹⁸

The lineshape analysis of ^{15}N spectra including N-H multiplets has been used to study proton exchange rates in some amides (Section IV.I).^{214,215}

$^1J(^{15}\text{N}-^1\text{H})$ values for some polyfluorinated anilines are essentially the same as in the corresponding non-fluorinated anilines (Table 130).⁴³⁵

Tautomeric equilibria may be studied by means of $^1J(^{15}\text{N}-^1\text{H})$ data, for example phenylhydrazone,⁴³⁶ some Schiff's bases,⁴³⁷ some 9-hydrazono-6,7,8,9-tetrahydro-4-oxo-4*H*-pyrido-[1,2- α]pyrimidines,²⁵⁴ some substituted thiadiazoles³³¹ and nucleic-acid base pairs in tRNA.^{438,439} In the case of dithizone the value of $^1J(^{15}\text{N}-^1\text{H})$ indicates the presence of a single species in solution rather than the widely accepted view of equilibria between thiol and thione forms.⁴⁴⁰

Structural studies involving the use of $^1J(^{15}\text{N}-^1\text{H})$ data include evidence for the site of protonation of 4-aminoazobenzene,³⁸² structural information on some iridium complexes with aryldiazonium ions,⁴¹⁷ actinomycin D,²⁴² *cyclo* (Pro-Phe-Gly-Phe-Gly)_{*n*}, where *n* = 1 or 2,⁴⁴¹ 5-azacyclidine,³⁴⁹ some G.U base pairs,^{147,659} base pairing in the ribotetranucleotide GGCUp,³³⁵ and neosaxitoxin and gonyautoxin-II.²⁸⁵ In some substituted anilines a correlation is reported between $^1J(^{15}\text{N}-^1\text{N})$ and nitrogen shielding.⁴⁴²

B. ${}^2J({}^{15}\text{N}-{}^1\text{H})$

In general two-bond ${}^{15}\text{N}-\text{C}-{}^1\text{H}$ couplings across a saturated carbon atom are rather small in magnitude and usually bear a positive sign.¹ Some calculated data are to be found in Section II.B. If the intervening carbon atom is tricoordinate the situation is different. Couplings across carbonyl-type carbon atoms are usually large in magnitude (Table 131). In imino-type moieties the value of ${}^2J({}^{15}\text{N}-{}^1\text{H})$ depends critically on the electronic environment of the nitrogen atom involved. If the nitrogen has a lone pair of electrons the coupling is expected to be large and negative. The effective removal of the lone-pair, for example by protonation or *N*-oxide formation, leads to a significant reduction in the magnitude of ${}^2J({}^{15}\text{N}-{}^1\text{H})$ and can result in the coupling becoming small and positive in sign. The *cis* orientation of the lone-pair and the C-H bond results in the largest values of ${}^2J({}^{15}\text{N}-{}^1\text{H})$ across tricoordinate carbon atoms; such information is of considerable diagnostic value (Table 131).¹²⁰

${}^2J({}^{15}\text{N}-{}^1\text{H})$ data have been used to assist in nitrogen shielding assignments for N-heterocycles,^{25,26,182,345} and in the case of quinazoline have led to a reversal of the nitrogen shielding assignments—N1 is more shielded than N3 (Table 98),^{25,345} which is in agreement with the results of some INDO/S-SOS shielding calculations.²⁵ In the case of the incorporation of glycine in *Eubacterium limosum*, the site of attachment of the glycine nitrogen is shown to be 5,6-dimethylbenzimidazole by means of ${}^2J({}^{15}\text{N}-{}^1\text{H})$ doublet splitting.⁴⁴³ A further application of two-bond N-H couplings is in the assignment of the purine nitrogen signals.³²⁷ Some small substituent effects are reported for values of ${}^2J({}^{15}\text{N}-{}^1\text{H})$ in some pyridines.¹¹⁷

N-protonation, in general, leads to a significant reduction in the value of ${}^2J({}^{15}\text{N}-{}^1\text{H})$ (Table 131).¹²⁵ Coupling across an oxygen atom, or a saturated nitrogen atom, results in small values of ${}^2J({}^{15}\text{N}-{}^1\text{H})$ (Table 131).^{365,436} Coupling across a silicon atom in SiH_3NCS , and related compounds, leads to values of ${}^2J({}^{15}\text{N}-{}^1\text{H})$ of the order of -4 Hz.⁴⁴⁴

C. ${}^3J({}^{15}\text{N}-{}^1\text{H})$

As is usual with three-bond couplings, the magnitude of ${}^3J({}^{15}\text{N}-\text{C}-\text{C}-{}^1\text{H})$ depends on the dihedral angle ϕ between the N-C and C-H bonds, maximum values being expected when ϕ is 0° (*cis* form) and 180° (*trans* form), and a minimum ${}^3J({}^{15}\text{N}-{}^1\text{H})$ is anticipated when ϕ is about 90° .¹

In general, the magnitude of ${}^3J({}^{15}\text{N}-{}^1\text{H})$ is larger than that of ${}^2J({}^{15}\text{N}-{}^1\text{H})$.^{267,268} The sign of ${}^3J({}^{15}\text{N}-{}^1\text{H})$ is usually negative, in agreement with theoretical predictions (Section II.B).¹⁸ Values that are small in magnitude may be of either sign, as demonstrated by isothiazole and 2-thiazole carboxaldehyde,⁴⁴⁵ which have small positive values of ${}^3J({}^{15}\text{N}-{}^1\text{H})$; more frequently negative signs are found.

The largest negative values of $^3J(^{15}\text{N}-^1\text{H})$, of around -10 Hz, are found between the pyrrole-type nitrogen atom (N4) and the proton attached to C-3 in some pyrazoles (Table 132).⁹¹

A Karplus-type relationship between ϕ and $^3J(^{15}\text{N}-^1\text{H})$ has been employed in many structural investigations, including those on some cyclo-dipeptides,⁴⁴⁶ angiotensin,²³⁷ Tyr-Gly-Gly-Phe, Tyr-Gly-Gly-Phe-Leu⁴⁴⁷ and 5-azacytidine³⁴⁹. In the case of Tyr-Gly-Gly-Phe-Leu, a 2-5 β_{II} type turn is proposed in place of the previously suggested 2-5 β_{I} bend.⁴⁴⁷

D. $^{15}\text{N}-^1\text{H}$ couplings across more than three bonds

As shown in Tables 133 and 134, $^{15}\text{N}-^1\text{H}$ couplings across more than three bonds are usually small and positive. An exception to this general rule is provided by $^5J(^{15}\text{N}-^1\text{H})$ for nitrobenzene, where a value of -0.3 Hz is obtained (table 134).¹

E. $^1J(^{15}\text{N}-^{13}\text{C})$

One-bond $^{15}\text{N}-^{13}\text{C}$ couplings are usually negative in sign, the values reported to date cover the range from -77.5 Hz to $+9.3$ Hz for an azo compound. The sign of the $^1J(^{15}\text{N}-^{13}\text{C})$ value for the azo compounds considered is not determined experimentally, but is based on a calculation that assumes the dominance of the contact contribution to the coupling.

The large negative value due to 2,4,6-trimethylbenzonitrile *N*-oxide has not been exceeded.¹ However, comparable values are found for some nitrile *N*-oxides (fulminates) (Table 136).⁴⁴⁸ The introduction of a neighbouring silicon atom leads to a substantial reduction in the value of $^1J(^{15}\text{N}-^{13}\text{C})$.

Owing to the possibility of lone-pair effects and of non-contact contributions, it is, in general, not possible to estimate the *s* character of N-C bonds from the corresponding spin-spin couplings. However, reports have appeared in which estimates of this kind are made.^{32,449-452} Another large coupling is -46.3 Hz reported for $^1J(^{15}\text{N}-^{13}\text{C})$ in SiH_3NCO ,⁴⁴⁴ it is interesting to speculate that this might be larger if the silicon atom was suitably replaced.

A number of theoretical calculations of various N-C couplings have appeared, some including the effects of solvation on the values of the couplings. These are considered in more detail in Section II.B.

Normally the absolute magnitude of one-bond nitrogen-carbon couplings is larger than those across more bonds. However, exceptions to this general observation are to be found in *trans*-azobenzenes,³⁷⁹ some aminosugar derivatives,⁴⁵³ some pyrimidines⁴⁵⁴ and some substituted phenazines,⁴⁵⁵ where the value of $^1J(^{15}\text{N}-^{13}\text{C})$ is around 2 Hz.

Owing to the change of sign occurring in the observed range of $^1J(^{15}\text{N}-^{13}\text{C})$ values (Table 136), it is possible for the coupling to take the value of

zero. Thus the apparent absence of $^1J(^{15}\text{N}-^{13}\text{C})$ data does not necessarily imply that the corresponding bond is non-existent. However, examples exist where the observation of $^1J(^{15}\text{N}-^{13}\text{C})$ is taken to imply the presence of a bond between the coupled nuclei.^{286,456,457}

Other reports in which the observation of $^1J(^{15}\text{N}-^{13}\text{C})$ data are used to establish bond formation include those on the incorporation of L-[guanido- $^{13}\text{C},^{15}\text{N}_2$]arginine and DL-[guanido- $^{13}\text{C},2-^{15}\text{N}$]arginine into streptothricin F¹,⁴⁵⁸ the incorporation of DL-[3- $^{13}\text{C},2-^{15}\text{N}$]lysine into streptothricin F¹,⁴⁵⁹ and that on the structure determination of neosaxitoxin and gonyautoxin-II²⁸⁵.

The uses of $^1J(^{15}\text{N}-^{13}\text{C})$ values in structural investigations are numerous. The large value of $^1J(^{15}\text{N}-^{13}\text{C})$ found³³⁶ for the exocyclic NH_2 group of *N*-methylsydnimine hydrochloride implies that the NH_2 group is planar and the nitrogen lone-pair is delocalized into the conjugated system involving the ring π electrons. A similar situation is reported for 2-phenylamino-2-thiazoline.⁴⁶⁰ The enhancement of the value of $^1J(^{15}\text{N}-^{13}\text{C})$, due to the effective removal of the lone-pair electrons, may also occur through protonation as observed in the case of 4-aminoazobenzene,³⁸² the increase being from <0.6 Hz to 3.7 Hz on protonation of the azo-bridge nitrogen atom. Comparable data are given for some imines and their salts.⁴⁶¹ A similar situation arises if the lone pair of electrons occupy an atomic orbital on the nitrogen atom that is essentially p in character, as demonstrated by studies on some nitramines.⁴⁶² An increase in the double-bond character of the N-C bond also leads to an increase in the value of $^1J(^{15}\text{N}-^{13}\text{C})$, as noted for some secondary amide and iminium salts.¹¹⁸ In contrast, steric inhibition of nitrogen lone-pair delocalization in some *N,N*-dimethylaniline derivatives leads to smaller values of $^1J(^{15}\text{N}-^{13}\text{C})$.⁸⁷ Comparable data are known for pyridine-type and pyrrole-type nitrogen atoms involved in N-C couplings in imidazoles³²⁶ and in some substituted thiadiazoles.³³¹ Nitrogen-carbon couplings have been used to assist in the carbon assignments of the ^{13}C spectra of some azo dyes.⁴⁶³ In the case of some carbocyclic phenyl imine phosphonates the effect of *gauche* interactions on $^1J(^{15}\text{N}-^{13}\text{C})$ is found to be consistent with that on $^1J(^{31}\text{P}-^{13}\text{C})$.⁴⁶⁴

Studies on diamagnetic metal cyano complexes have yielded a correlation between the value of $^1J(^{15}\text{N}-^{13}\text{C})$ and the N-C force constant.³²³

F. $^{15}\text{N}-^{13}\text{C}$ couplings across more than one bond

Two-bond $^{15}\text{N}-^{13}\text{C}$ couplings are usually smaller in saturated systems than those across one bond, and can be of either sign (Table 137). It is shown that $^2J(^{15}\text{N}-^{13}\text{C})$ data across a saturated carbon are of little use in conformational analyses of peptides.⁴⁴⁶ If the coupling is across an unsaturated carbon atom the magnitude of $^2J(^{15}\text{N}-^{13}\text{C})$ increases; for example,

across a carbonyl carbon atom a value of $^2J(^{15}\text{N}-^{13}\text{C})$ of 12.0 Hz has been reported for some thiadiazoles³³¹ and 7.3 Hz for a similar coupling in some aminosugar derivatives⁴⁵³.

In unsaturated systems the presence of a nitrogen lone-pair with significant s character can influence both the sign and magnitude of $^2J(^{15}\text{N}-^{13}\text{C})$. A critical dependence is that of the lone-pair, being either *cis* or *trans*, to the ^{13}C nucleus involved in the coupling in $\text{N}=\text{C}-\text{C}$ fragments. The *cis* arrangement produces couplings in the range of -7 to -11 Hz, whereas *trans* structures lead to positive couplings usually between 1 and 3 Hz in magnitude. Examples of this phenomenon are afforded by some pyrazolone derivatives,⁴⁵² an ethanoneoxime,⁴⁵⁰ some azodyes,⁴⁶³ *N*-methylsydnone and some related structures,³³⁶ some pyrazoles,⁴⁶⁵ some phenazines,⁴⁵⁵ some imines,⁴⁶¹ some phenylhydrazones,⁴⁶⁶ and some imidazoles. A *trans* two-bond $^{15}\text{N}-^{13}\text{C}$ coupling across a nitrogen atom in *cis*-azobenzene has a value of $+10$ Hz.^{467,468} In general, $^2J(^{15}\text{N}-^{13}\text{C})$ values across nitrogen also show a *cis-trans* effect; an example is provided by some substituted nitrosoureas and some *N*-nitrosothioureas,⁴³⁰ this has been used to demonstrate the onset of ring rotation in some substituted azobenzenes.⁴⁶⁹ Effective removal of the lone-pair electrons, by protonation, leads to a significant reduction in the magnitude of the *cis* $^2J(^{15}\text{N}-^{13}\text{C})$ interaction. This has been demonstrated for some imines⁴⁶¹ and 4-aminoazobenzene.³⁸² Lone-pair removal by complex formation has produced a significant decrease in the value of $^2J(^{15}\text{N}-^{13}\text{C})$ for a pyrimidine-tetrone-5-oxime.⁴⁵⁴

Theoretical studies dealing with the effects of lone-pairs with s character on $^2J(^{15}\text{N}-^{13}\text{C})$ are covered in Section II.B.

Three-bond $^{15}\text{N}-^{13}\text{C}$ couplings are usually negative in sign, as demonstrated by the data in Table 138. In general, values of $^3J(^{15}\text{N}-^{13}\text{C})$ for saturated systems depend on the dihedral angles between the C-C and N-C bonds in N-C-C-C fragments.

The maximum magnitudes of $^3J(^{15}\text{N}-^{13}\text{C})$ are expected for dihedral angles of 0° and 180° and minimum values for about 90° . Examples are provided by some α -nitrogen and γ -carbon couplings in amino acids and peptides^{114,470} for some tetraaryl-3,7-diazabicyclo[3.3.1]nonanes, where the boat conformation is deduced from $^3J(^{15}\text{N}-^{13}\text{C})$ data.⁴⁷¹

In cases where electron lone-pair effects tend to lead to small $^1J(^{15}\text{N}-^{13}\text{C})$ and $^2J(^{15}\text{N}-^{13}\text{C})$ values, $^3J(^{15}\text{N}-^{13}\text{C})$ may be the largest $^{15}\text{N}-^{13}\text{C}$ coupling observed. Examples are provided by some substituted *trans*-azobenzenes^{379,467,468} and some substituted phenazines.⁴⁵⁵

Couplings across more than three bonds between ^{15}N and ^{13}C reflect the rather small gyromagnetic ratios of these two nuclei, in that they are usually less than 1 Hz in magnitude. In very rare instances they may exceed 1 Hz in magnitude; see Tables 139 and 140 for four- and five-bond $^{15}\text{N}-^{13}\text{C}$ couplings respectively. As such, they are of little diagnostic value.

G. ^{15}N - ^{15}N couplings

Most reports on ^{15}N - ^{15}N couplings relate to *one-bond interactions*. As expected from theoretical considerations (Section II.B), the values of $^1J(^{15}\text{N}-^{15}\text{N})$ interactions depend critically upon lone-pair orientation effects. Usually $^1J(^{15}\text{N}-^{15}\text{N})$ data are negative in sign, as shown by Table 141.

The largest magnitudes are observed for *N*-nitrosamines (Table 141), and the smallest in molecular nitrogen and some of its metal complexes, and hydrazines (ref. 1 and Table 152 therein). Significant differences are observed for the $^1J(^{15}\text{N}-^{15}\text{N})$ data between metal complexes of diazenido ligands and those of molecular nitrogen (Table 141),⁴⁷² which is indicative of the mode of coordination. The values found for the diazenido complexes are similar to those observed for azo compounds.

Lone-pair s-character effects are apparent in azide $^1J(^{15}\text{N}-^{15}\text{N})$ data. The N_α - N_β coupling is often more than twice the magnitude of the N_β - N_γ interaction. Some nitramines have values of $^1J(^{15}\text{N}-^{15}\text{N})$ of around 5 Hz, whereas values of 12 Hz are also found for this coupling, this variation being due to the dependence of the coupling on the lone-pair s character. The sign of $^1J(^{15}\text{N}-^{15}\text{N})$ in 1-phenylpyrazole is measured as being positive. The tautomeric equilibria of some phenylhydrazones have been studied by $^1J(^{15}\text{N}-^{15}\text{N})$ data.⁴³⁶

Two-bond ^{15}N - ^{15}N couplings across a carbon atom can be reasonably large when the intervening carbon is an unsaturated one (Table 142). Lone-pair effects can be significant in determining the magnitude of the couplings. These can give rise to *cis-trans* effects, as noted in the case of $^2J(^{15}\text{N}-^{13}\text{C})$ couplings (Table 142). Couplings across another nitrogen atom are similar in character to those across an unsaturated carbon atom. The effect of pH on $^2J(^{15}\text{N}-^{13}\text{C})$ values, due to protonation involving lone-pair electrons, is very noticeable (Table 142).

$^2J(^{15}\text{N}-^{15}\text{N})$ interactions across sulphur are about 3 Hz in some cyclophosphadithiatriazenes and some S-N ring compounds.³⁶⁷ When phosphorus is the intervening atom, as in some phosphazones, the value of $^2J(\text{N}-\text{N})$ is about 2 Hz.⁴⁷³

Some three-bond ^{15}N - ^{15}N couplings have been reported (Table 143). The largest value reported is 5 Hz in a platinum diimine complex.⁴¹⁰

H. ^{31}P - ^{15}N couplings

One bond ^{31}P - ^{15}N couplings cover a large range of both positive and negative values (Table 146). Lone-pair effects are particularly noticeable in determining the change of sign of $^1J(^{31}\text{P}-^{15}\text{N})$ in passing from trivalent to pentavalent phosphorus compounds, as discussed in Section II.B. However, a change in sign of $^1J(^{31}\text{P}-^{15}\text{N})$ is also possible, depending on the nature of the bond, for pentavalent phosphorus as demonstrated by the example

of some geminally disubstituted cyclotriphosphazenes.^{474,475} In the case of some phospho-3,5-dithia-2,4,6-triazenes, $^1J(^{31}\text{P}-^{15}\text{N})$ values of around 40–50 Hz are reported.

Although the contact interaction tends to dominate the value of $^1J(^{31}\text{P}-^{15}\text{N})$, the orbital contribution can also be significant, more particularly for trivalent phosphorus compounds.^{49,92}

In the case of some dioxaphosphorinanes, the magnitudes of $^1J(^{31}\text{P}-^{15}\text{N})$ observed are indicative of the equatorial bonds being shorter than the axial P–N bonds.⁴⁷⁶ Such coupling data are also used as a probe for the assignment of absolute configuration of some phosphordimethylamidates⁴⁷⁷ and related compounds⁴⁷⁸. The magnitude of $^1J(^{31}\text{P}-^{15}\text{N})$ for some aminophosphines is reported to be very dependent on the number and size of the alkyl substituents on the nitrogen atom.³⁶ $^1J(^{31}\text{P}-^{15}\text{N})$ data have been used to identify a new bisphosphorylated compound produced when an excess of chlorine is reacted with hexamethylphosphotriamide.⁴⁴²

In the case of trivalent phosphorus compounds the orientation of the lone-pair electrons is shown to have a large influence on the magnitude of $^1J(^{31}\text{P}-^{15}\text{N})$, *exo* couplings being approximately twice the size of *endo* couplings (Table 146).^{479,480}

Some $^{31}\text{P}-^{15}\text{N}$ couplings across two and three bonds are shown in Tables 147 and 148 to be normally small. However, when the coupled nuclei occupy *trans* positions across a platinum atom $^2J(^{31}\text{P}-^{15}\text{N})$ interactions can be as large as 52.5 Hz. Similar compounds in which the coupled nuclei are in *cis* positions show $^2J(^{31}\text{P}-^{15}\text{N})$ values of around 1 Hz. Thus the value of the spin-coupling interaction is indicative of the relative positions of the ligands complexed to platinum (Table 147).²⁹⁷

I. $^{19}\text{F}-^{15}\text{N}$ couplings

Normally $^1J(^{19}\text{F}-^{15}\text{N})$ values are large in magnitude and positive in sign, as shown in Table 144. However, as discussed in Section II.B, lone-pair effects can be significant. The largest value of $^1J(^{19}\text{F}-^{15}\text{N})$ so far reported relates to $\text{FN}\equiv\text{N}^+$, where the coupled nitrogen atom has a lone-pair with high *s* character.⁹⁹

Lone-pair effects on $^2J(^{19}\text{F}-^{15}\text{N})$ are also very noticeable (Table 145). For example the *cis* $^2J(^{19}\text{F}-^{15}\text{N})$ interaction in $\text{FN}=\text{NF}$ results in 51.9 Hz, whereas the value of the *trans* coupling is 102.4 Hz.⁹⁹

J. $^{195}\text{Pt}-^{15}\text{N}$ couplings

One bond $^{195}\text{Pt}-^{15}\text{N}$ couplings are usually large in magnitude and positive in sign. The arrangement of the ligands in square-planar platinum complexes has a large influence on the value of $^1J(^{195}\text{Pt}-^{15}\text{N})$ (Table 149).⁴¹¹ In the

case of nitrite complexes, the size of the coupling is found to be linearly dependent on the number of nitrite ligands for both di- and tetravalent platinum complexes.⁴¹³ In general, the value of $^1J(^{195}\text{Pt}-^{15}\text{N})$ is reduced when the ligand containing the coupled nitrogen nucleus is *trans* to a ligand that has a large *trans* influence, since the $^{195}\text{Pt}-^{15}\text{N}$ bond can be weakened in this case.^{276,415} Structural investigations involving the use of $^1J(^{195}\text{Pt}-^{15}\text{N})$ data include those on the binding interactions of *cis*-diamminodichloroplatinum(II) with amines and nucleosides,²⁷⁶ that on the coordination of amides to *cis*-diamminodiaquoplatinum(II),⁴⁰⁸ and a study of the donor and acceptor properties of nitrogenous ligands.⁴¹⁰

Some $^{195}\text{Pt}-^{15}\text{N}$ couplings across two and three bonds can also be significant in magnitude (Table 150). The only value of $^2J(^{195}\text{Pt}-^{15}\text{N})$ so far reported is that for tetracyanoplatinum(IV),³⁹⁹ which is 61.2 Hz. three-bond couplings have also been reported (Table 150).

K. Some miscellaneous couplings involving ^{15}N

Various miscellaneous ^{15}N couplings are available (Tables 151-163). The signs of the $^1J(^{15}\text{N}-^{11}\text{B})$ data given in Table 151 are all negative. For some trimethylamine adducts of some mixed boron trihalides the magnitude of $^1J(^{15}\text{N}-^{11}\text{B})$ closely follows the order of the B-N bond strength.¹²⁴ This is a reflection of the degree of delocalization of the nitrogen lone-pair electrons. In $\text{SiCN}(\text{Me})_3$ the value of $^2J(^{29}\text{Si}-^{15}\text{N})$ is reported to be 1.6 Hz.^{444,481}

Table 152 contains some $^1J(^{27}\text{Al}-^{15}\text{N})$ data, while some $^1J(^{57}\text{Fe}-^{15}\text{N})$ results are given in Table 153 for some porphyrin complexes.

The results of some $^1J(^{59}\text{Co}-^{15}\text{N})$ measurements are given in Table 154; in the case of a nitroso complex the coupling to the nitroso nitrogen is about 9 Hz.³⁹⁷ In general it is assumed that ^{15}N couplings to heavy nuclei are contact-dominated.⁴⁸²

Table 155 contains some $^1J(^{71}\text{Ga}-^{15}\text{N})$ results, and some $^1J(^{195}\text{Mo}-^{15}\text{N})$ data are presented in Table 156. In the latter case, couplings in excess of 60 Hz are reported. $^1J(^{103}\text{Rh}-^{15}\text{N})$ values given in Table 157 show a variation from 4.5 to 30 Hz. The results of $^1J(^{113}\text{Cd}-^{15}\text{N})$ measurements for a selection of cadmium complexes are given in Table 158. In the case of the pyridine adduct of cadmium *meso*-tetraphenylporphyrin, the sign of $^1J(^{113}\text{Cd}-^{15}\text{N})$ has been determined to be positive. From solid-state NMR measurements on this compound, $^1J(^{113}\text{Cd}-^{15}\text{N})$ is found to be about 150 Hz.⁴⁸³

Both positive and negative signs are reported for the $^1J(^{119}\text{Sn}-^{15}\text{N})$ data given in Table 159. The values range from -41.4 Hz to +175.0 Hz. It seems likely that s-electron lone-pair effects are largely responsible for this range of coupling results. The first example of a directly bonded $^{195}\text{Xe}-^{15}\text{N}$ coupling was for $\text{FXeN}(\text{SO}_2\text{F})_2$, which gave a value of 305 Hz.²⁹⁰ The results given in Table 160 are more recent, and a value of 307 Hz for this coupling is now reported.²⁹²

Table 161 contains some $^1J(^{199}\text{Hg}-^{15}\text{N})$ data, the values reported lie between 300 and 400 Hz in magnitude.²⁷³ Some $^1J(^{207}\text{Pb}-^{15}\text{N})$ results are to be found in Table 162. A significant dependence on the position of the ligands is noted, axial couplings being much smaller than equatorial.

Some direct dipolar couplings involving ^{15}N are reported in Table 163. Such data are useful for determining the structures of oriented molecules. Other examples include a study of *p*-bromo- and *p*-nitroaniline,¹⁷² pyrazine and pyrimidine¹⁷¹. Both magnitudes and signs are available from studies on nematic phases.

L. Some notes on measurements of nitrogen couplings

The low ^{15}N sensitivity of natural abundance samples makes the direct determination of spin-spin couplings involving ^{15}N a somewhat difficult task. Sensitivity enhancement by means of the INEPT technique has been used to determine a number of N-H couplings. Examples of this may be found for some pyridines and pyrimidines,¹²³ some *N*-alkylformamides⁴³³ and *cyclo*-(Pro-Phe-Gly-Phe-Gly)_{*n*}, where *n* = 1,2.⁴⁴¹ The INEPT procedure has also been employed to determine the sign and magnitude of $^1J(^{15}\text{N}-^{11}\text{B})$ in tris(methylamino)borane.¹²⁶ Selective population transfer (SPT) is less general than INEPT in that it tends to concentrate on one ^{15}N resonance at a time. An application of SPT is to be found in a study of $^{15}\text{N}-^1\text{H}$ and $^{15}\text{N}-^{13}\text{C}$ couplings in some secondary amide and iminium salts,¹¹⁸ also for the determination of $^1J(^{15}\text{N}-^{15}\text{N})$ in a pyrazole derivative,⁹¹ and for the ^{15}N satellites in ^{13}C NMR spectra⁴⁸⁴. Thus the natural abundance levels of ^{15}N and ^{13}C can be used to obtain $^{15}\text{N}-^{13}\text{C}$ coupling data.

Another technique is AISEFT (abundant-isotope-signals elimination by Fourier transformation), which has been used to produce $^1J(^{15}\text{N}-^1\text{H})$ data for some simple amides.⁴³¹

Two-dimensional procedures are now becoming widely applied in NMR spectroscopy. Examples relating to ^{15}N couplings have been reported in a number of cases, a selection being the observation of ^{15}N satellites in the ^1H NMR study of formamide,¹⁴⁵ the determination of natural-abundance long-range $^{15}\text{N}-^1\text{H}$ couplings by polarization-enhanced two-dimensional NMR,¹¹⁹ and a multiquantum $^{15}\text{N}-^1\text{H}$ two-dimensional correlation NMR study of G-C base pairs to produce natural-abundance coupling data¹⁴⁷.

Finally mention should be made of the indirect determination of $^{14}\text{N}-^{13}\text{C}$ couplings by measurements of $T_{1\rho}$.⁴⁸⁵

VIII. RELAXATION PHENOMENA

The quadrupolar mechanism is usually dominant for ^{14}N nuclear relaxation, whereas ^{15}N , which has $I = \frac{1}{2}$, usually has its relaxation controlled by

one of the less efficient processes. Thus ^{15}N signals are normally much narrower than those found in ^{14}N NMR spectra.

A. ^{14}N relaxation

The extreme narrowing condition

$$(2\pi\nu\tau_c)^2 \ll 1 \quad (31)$$

is usually obeyed in low-viscosity solutions, where ν is the resonance frequency of the nucleus of interest and τ_c the corresponding correlation time. Within this confine, the relation between the quadrupole coupling χ of a ^{14}N nucleus and its relaxation time T_Q is given by,

$$1/T_Q = \frac{3}{8}(1 + \frac{1}{3}\eta^2)\chi^2\tau_c \quad (32)$$

where χ (in frequency units) depends upon the nuclear quadrupole moment eQ and the electric-field gradient eq at the nucleus, as shown by equation (33):

$$\chi = eqeQ/h \quad (33)$$

In equation (32) η describes the deviation of the electric-field gradient from axial symmetry. It is clear from equation (33) that quadrupolar relaxation requires the presence of an electric-field gradient at the ^{14}N nucleus in order to be operative. Thus ^{14}N relaxation provides a means of monitoring variations in this gradient due to molecular motions.

By assuming that the width of the ^{14}N signal of cyanide ion in aqueous solution results entirely from quadrupole relaxation, it is possible to obtain an estimate of τ_c from equation (32). This approach has been employed to demonstrate that the ^{13}C relaxation of cyanide ion is not controlled by chemical shielding anisotropy effects,⁴⁸⁶ as had been previously proposed.⁴⁸⁷ Additionally, it appears that the ^{15}N relaxation of this ion, in low to moderately strong magnetic fields, is also not dominated by the chemical shielding anisotropy process.⁴⁸⁶

In some nitrile oxides the replacement of a carbon atom, adjacent to the CNO function, by a silicon atom results in nitrogen deshielding and a sharpening of the ^{14}N signal accompanied by a sharp triplet in the ^{13}C spectrum of the CNO carbon due to scalar ^{14}N - ^{13}C coupling. This appears to arise from the presence of an enhanced electron density on the CNO carbon atom, thus leading to a reduction in the electric-field gradient at the ^{14}N nucleus, upon the introduction of the adjacent silicon atom.⁴⁴⁸

An external electric field may be used to produce ^{14}N signal splittings. The field causes the alignment of polar molecules such that any resulting signal splitting depends upon the degree of alignment, the component of the electric field gradient at the nucleus in a direction parallel to the nuclear

electric dipole moment, and on the magnitude of the ^{14}N quadrupole moment. This technique has been used to determine the complete ^{14}N quadrupole coupling tensors of neat liquid nitrobenzene and of *m*-dinitrobenzene dissolved in benzene.⁴⁹⁰ The major component of the tensor lies along the N-C, bond and the value of η is reported to be 0.55. By measuring the electric field induced ^{14}N splitting of nitrobenzene in solutions with benzene and acetamide, it is found that any solvent effect on the splitting is negligible.⁴⁸⁹

The ^{14}N relaxation of acetonitrile has been studied in carbon tetrachloride⁴⁸⁸ and in some n-alkanes.⁴⁹¹ In carbon tetrachloride the acetonitrile clusters that occur in the neat liquid remain at molar fractions as low as 0.2. Even at 0.02 molar, some important interactions persist between the acetonitrile molecules.⁴⁸⁸ In n-alkane solutions the correlation time, for reorientation of the acetonitrile major axis, is directly proportional to the solvent viscosity and inversely proportional to the temperature. It is found that the magnitude of Kivelson's kappa parameter decreases, and the activation energy of the acetonitrile reorientation increases, as the solvent molecules become larger.⁴⁹¹

Values of χ for the ^{14}N nuclei of 2-pyrrolidone, δ -valerolactam and ϵ -caprolactam, in water and carbon tetrachloride solutions, have been determined.⁴⁹³ The coupling is found to be independent of ring size. It is further demonstrated that ^{14}N quadrupole relaxation is a valuable aid towards a total analysis of the anisotropic motion of 2-pyrrolidone.

^{14}N relaxation data have been combined with measured anisotropic reorientation rates in order to estimate the ^{14}N quadrupole coupling of pyridine-*N*-oxide in carbon tetrachloride.⁴⁹⁴ The solution results indicate a small decrease in the value of the quadrupole coupling from that obtained by solid-state measurements.

^{13}C $T_{1\rho}$ measurements have been used to provide ^{14}N spin-lattice relaxation and $^1J(^{14}\text{N}-^{13}\text{C})$ data for isobutylamine, diethylamine, pyrrolidine, piperidine and triethylamine as neat liquids.⁴⁹² The ^{14}N spin-spin relaxation times are estimated from the ^{14}N signal widths and found to be very close to the values obtained for the spin-lattice relaxation results. The shortest ^{14}N relaxation times are found for piperidine and the longest for diethylamine.

Quadrupole relaxation data can provide information on the structure of electrolyte solutions. From the quadrupolar relaxation measurements one may obtain the square of the electric-field gradient at the nucleus, equation (32). This has an r^{-8} and an r^{-6} distance dependence for ion-solvent and ion-ion interactions respectively. Thus information on the first coordination shell is obtainable. In addition, the square of the electric-field gradient is a sensitive probe of the symmetry of this gradient at the relaxing nucleus. Thus it provides information on higher particle correlations. ^{14}N relaxation

rates for solutions of RbI in formamide and in *N*-methylformamide assist in indicating the presence of higher ion associates.⁴⁹⁶

¹⁴N, ³⁵Cl and ⁸¹Br NMR line widths of various chlorides, bromides and perchlorates of 4-substituted pyridinium and related cations have been estimated as functions of concentration in aqueous solutions. The results are interpreted by assuming the presence of contact ion pair formation.⁴⁹⁷

The binary phase diagram of hexadecyltrimethylammonium fluoride (TAF) in water has been determined as a result of ¹⁴N and ²H NMR studies.⁴⁹⁵ A hexagonal liquid-crystalline phase occurs between 40% and 60% TAF which is stable from 300 to 400 K. Between 328 and 383 K a cubic liquid-crystalline phase appears in the region between 74% and 85% TAF. Liquid crystals have been used as the media in determinations of χ for the ¹⁴N nuclei of nitromethane¹⁶⁸ and the methylammonium ion.⁴⁹⁹ Poly- γ -benzyl-L-glutamate in methylene chloride has been employed to orient nitromethane. The resulting value of χ for the ¹⁴N nucleus is 1679 ± 139 kHz.¹⁶⁸ For the methylammonium ion in a lyotropic nematic phase of methylammonium decyl sulphate, the ¹⁴N value of χ is reported to be 1106.7 ± 1.5 kHz.⁴⁹⁹

A ¹⁴N NMR study of the azide ion in two lyotropic liquid crystals reveals that the ratio of the quadrupole splittings of the signals of the central to terminal ¹⁴N nuclei is about 0.5; which is the ratio of their corresponding χ values.¹⁶⁷ In contrast with earlier, less reliable, measurements the average ratio of the spin-lattice relaxation times, for the terminal to central ¹⁴N nuclei of the azide ion in aqueous solution, is found to be 0.25 ± 0.01 .

¹⁴N quadrupolar relaxation has been used in studies on the headgroup structure of lipids. In the case of the choline headgroup of sphingomyelin, the ¹⁴N quadrupole splitting indicates that the orientational order in the liquid-crystalline phase is not the same as that of its counterpart in dipalmitoyl-L- α -phosphatidylcholine.¹⁶² Relaxation-time measurements suggest that there are also dynamic differences between the choline headgroups in the two cases studied.¹⁶²

A quadrupole echo FT method has provided ¹⁴N NMR spectra for a variety of lipid bilayer systems.¹⁶⁵ In the liquid-crystalline phase the ¹⁴N NMR spectra of lecithins are characterized by sharp signals with quadrupole splittings of about 10 kHz. The bilayer normal represents the axis of motional averaging of the ¹⁴N quadrupolar tensor. In the rigid lattice the value of χ for ¹⁴N in the lecithin bilayer is around 130 kHz.¹⁶⁵

¹⁴N quadrupole splittings have been employed in a study of the effects of a variety of ions, drugs, antibiotics and proteins on phospholipid bilayer structure. In all cases the addition of the impurity molecule results in a decrease in the phospholipid ¹⁴N quadrupole splitting. The largest decrease is reported on addition of the tricyclic antidepressant drug, desipromine, the reduction being by a factor of two at fifty mole percentage levels. It is

thus deduced that the most ordered state of the lecithin bilayer headgroup is that found in the pure bilayer itself.¹⁶⁵

¹⁴N data on the phosphocholine headgroup have been used in a study of the lipid solvation of cytochrome C oxidase. The anisotropy of the segmented motions is characterized by the residual ¹⁴N quadrupole splitting.²⁰⁰

Owing to the relatively high symmetry of the ¹⁴N environment of the trimethylammonium group, and to the rather low degree of ordering experienced relative to that of thermotropic liquid crystals, the choline ¹⁴N signals of dipalmitoylphosphatidylcholine (DPPC) and egg-yolk phosphatidylcholine (EPC) in simple bilayer vesicles show small quadrupole splittings.²⁰⁰

From a study of the ¹⁴N spin-lattice and spin-spin relaxation times, it is concluded that the activation energies for the rapid local motion of N-C_β bonds are 36 and 31 kJ mol⁻¹ respectively for DPPC and EPC. These results indicate that the trimethylammonium group is bound in the polar surface. As the temperature is raised, the vesicle radius tends to decrease prior to a phase transition. ¹⁴N NMR data have also been used in a comparison study of the headgroup conformation and dynamics of synthetic analogues of DPPC.¹⁶³

Measurements of ¹⁴N relaxation data and ¹⁴N-¹³C couplings of phosphatidylcholine (PC) show that these parameters are solvent-dependent.⁵⁰⁰ It appears that this dependence arises not so much owing to phospholipid-solvent interactions, but rather as a consequence of the relative amounts of PC aggregation in a given medium.

Quantum-mechanically derived expressions have been reported for the quadrupolar relaxation rates of ¹⁴N and ²H in lipid bilayers.⁵⁰¹ Predictions are made for the ¹⁴N relaxation phenomena of DPPC which remain to be verified by detailed experimental studies.

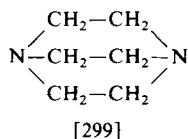
Light-scattering and ¹⁴N relaxation data reveal that microemulsions containing hexadecyltrimethylammonium bromide, hexanol, water and n-decane can be described by a model with fairly small spherical reversed micelles.⁵⁰²

A number of reports have appeared of solid-state ¹⁴N relaxation measurements. The ¹⁴N and ²H quadrupole coupling tensors have been determined for sodium nitroprusside by NMR techniques.⁵⁰³ The ¹⁴N coupling tensors are found to be almost axially symmetric, with their unique axes parallel to the bond directions of the respective CN and NO groups.

The angular variation of the proton-enhanced ¹⁴N NMR spectra of a single crystal of L-serine monohydrate has been investigated to yield 1.069 MHz and 0.214 for χ and η , respectively, of the NH₃⁺ nitrogen nucleus.⁵⁰⁴

Values of χ and η have been obtained for a number of quaternary ammonium salts from ^{14}N NMR powder patterns.¹⁹⁹ The values of χ are comparable to those often found for ^2H , while η takes on a variety of values between zero and unity. In some cases the parameters appear to be related entirely to lattice effects, while for others a combination of lattice and intramolecular effects is thought likely.

Within the rotational diffusion model, applied to the disordered solid I phase of triethylenediamine [299], the correlation times indicate that reorientation of the C_3 axis is more hindered than is reorientation about this axis.⁵⁰⁵



The ^{14}N spin-lattice relaxation times of the cubic phases of NaCN and KCN,⁵⁰⁸ and of RbCN and CsCN in the solid I phase,¹⁷⁰ increase as the temperature is raised. The corresponding activation energies are $1.40 \pm 0.10 \text{ kcal mol}^{-1}$ and $0.78 \pm 0.05 \text{ kcal mol}^{-1}$ for NaCN and KCN,⁵⁰⁸ while a value of $0.68 \pm 0.05 \text{ kcal mol}^{-1}$ is reported for both RbCN and CsCN.¹⁷⁰ At 300 K the rotational correlation times for the cyanide ion are obtained as 0.356 ps for NaCN, 0.161 ps for KCN, 0.152 ps for RbCN and 0.150 ps for CsCN. These results are comparable to those measured for HCN and CH_3CN in the liquid state.^{509,510}

In contrast with a previous report,⁵¹¹ the cubic-phase rotational correlation time for the cyanide ion is found to be shorter for KCN than for NaCN at any temperature reported. Additionally, the value of this correlation time for NaCN is more than two orders of magnitude smaller than that reported earlier. The currently reported decrease in rotational correlation time with increasing cation size, and deformability, appears to be reasonable.

The temperature dependences of the ^{14}N quadrupole splittings and relaxation times have been studied for the paraelectric, incommensurate and ferroelectric phases of ammonium fluoroberyllate.⁵⁰⁷ The results indicate that the incommensurate modulation has some soliton character close to the phase-transition point and that the ^{14}N relaxation within this phase is determined by phasons with a finite energy gap.

Solid-state NMR studies of both $^{14}\text{N}_2$ and $^{15}\text{N}_2$ have been reported.^{194-197,506} In hexagonal close-packed (h.c.p.) N_2 , self-diffusion is a thermally activated process with an activation enthalpy of $1030 \pm 25 \text{ kcal}$. Below 4.2 K an amorphous broadening of the NMR signal of $^{15}\text{N}_2$ is attributed to the onset of a partial orientational ordering, which is much more pronounced than that observed for the h.c.p. form of $^{14}\text{N}_2$.

Comparison may be made with gaseous-phase results, where $^{14}\text{N}_2$ relaxation is controlled by the quadrupolar process.⁵¹²

In a N_2 -argon solid mixture the low-temperature NMR results show that the N_2 molecules adopt random, frozen-in, orientations.¹⁹⁷ Any residual motion occurs at frequencies of less than 10^{-2} Hz.

The ^{14}N spectrum of a single crystal normally consists of two signals for each magnetically inequivalent nitrogen position. The separation $\Delta\nu_Q$ between a quadrupole split pair of lines is given by

$$\Delta\nu_Q = \frac{3\chi}{4} [(3 \cos^2 \beta - 1) + \eta \sin^2 \beta \cos 2\alpha] \quad (34)$$

where α and β are the Euler angles describing the orientation of the quadrupole coupling tensor in the applied magnetic field.

The ^{14}N spectrum of a single crystal of glycine is shown in Fig. 2.²⁰⁴ The two inequivalent nitrogen locations per unit cell give rise to the four signals whose widths are about 600 Hz, which is fairly typical of those observed for ammonium groups. The value of χ is reported to be 1.18 ± 0.01 MHz, and that of η is 0.54 ± 0.01 .²⁰⁴ The z -component of the electric-field gradient lies approximately along the N-C bond and the x -component is almost perpendicular to the CCN plane.²⁰⁴

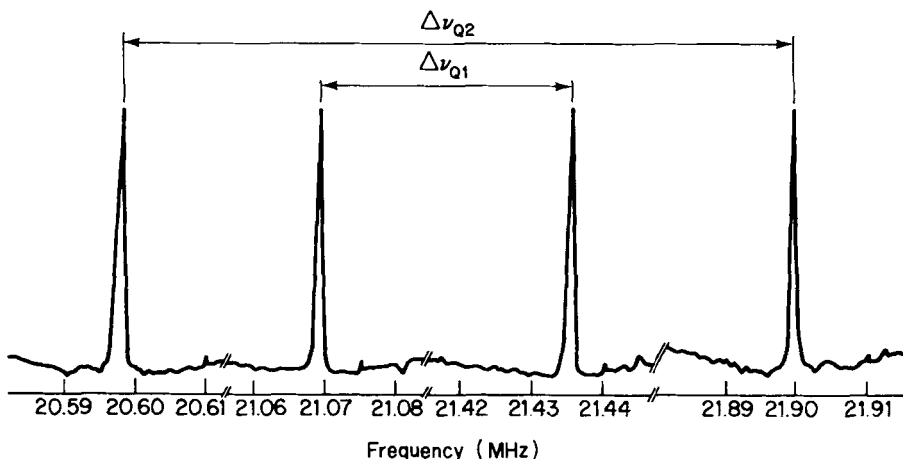


FIG. 2

Measurement of the ^{14}N and ^7Li quadrupole splittings in single crystals of Li_3N , as a function of orientation with respect to the applied magnetic field, provides an estimate of the electric-field gradients experienced by these nuclei. The results obtained are interpreted in favour of ionic bonding, which is in contrast with conclusions based upon NMR data for polycrystalline Li_3N .¹⁹²

The resonances of carbon atoms directly bonded to ^{14}N , in polycrystalline samples, are often broadened and split into asymmetric doublets. This arises from a perturbation of the ^{14}N - ^{13}C dipolar interaction by the ^{14}N quadrupole interaction.^{202,203,205,206,513-526} The factors that influence the ^{13}C signal shapes are the sign, magnitude and asymmetry of the ^{14}N quadrupole coupling tensor, as well as the C-N separation, the magnitude of the applied magnetic field and the orientation of the internuclear vector in the principal-axis system of the electric-field gradient. The identification of the asymmetric doublet splitting is useful for the assignment of solid-state ^{13}C NMR signals of biologically important molecules. Additionally, a study of the splitting can lead to a determination of the sign and magnitude of χ for the bonded ^{14}N nucleus. The availability of the sign of χ is significant, since this is not provided by the usual ^{14}N NMR and NQR investigations.

In order to be able to obtain a satisfactory estimate of the electric-field gradient at a ^{14}N nucleus, from a measured value of χ , it is important to have a reliable estimate of the Sternheimer antishielding factor $|1 - \gamma_\infty|$. For the disordered phase of ammonium chloride two independent methods, based on ^{14}N and ^{15}N relaxation data, provide values of 20 and 16 for $|1 - \gamma_\infty|$.⁵¹⁵ These results are in contrast with the values of 2995 and 0.6 that have been calculated for the $^{14}\text{N}^+$ and $^{14}\text{N}^{3+}$ ions respectively.⁵²⁰ Consequently, there appears to be some room for improvement before experimental determinations of χ can lead to dependable estimates of ^{14}N electric-field gradients.

An alternative approach to this problem is to use molecular-orbital (MO) procedures to independently calculate the electric-field gradients. *Ab initio* calculations, using basis sets of various qualities, have been reported for the electric field gradients at nitrogen nuclei in a variety of molecules.^{517-519,521,522} It seems that, in general, relatively small MO basis sets such as STO-4G are able to provide satisfactory agreement between calculated and observed values of χ for ^{14}N .⁵²¹ No direct correlation is found between χ and the usual electronic distribution indices such as those included in a Mulliken population analysis.⁵²¹

In other *ab initio* MO calculations use of the STO-3G basis set produces poor agreement with the experimental values of χ for the ^{14}N nuclei in imidazole, whereas the split valence shell, 4-31G, basis set gives results in good agreement with the measured data.⁵²² Calculations of double zeta quality satisfactorily account for the values of χ for the ^{14}N nuclei in some azoles and azines.⁵¹⁷ A 6-31G basis set is successful in reproducing the ^{14}N and ^2H electric-field gradients in the dimers $\text{HCN}\cdots\text{HCN}$, $\text{HCN}\cdots\text{HF}$ and $\text{CH}_3\text{CN}\cdots\text{HF}$.⁵¹⁸ In a double zeta quality *ab initio* calculation of χ , for trimeric imidazole, the changes observed in the three principal ^{14}N tensor components, when imidazole passes from the gas to the solid state, are well accounted for.⁵¹⁹

A discussion of the calculation of electric-field gradients by several semi-empirical MO techniques has appeared.⁵²³ In general, CNDO/2 and INDO calculations produce poor agreement with experiment. The results of MINDO/3 parameterized calculations are often closer to the measured data, but the effects of lone-pair electrons are not reliably predicted. Estimates of χ for various ^{14}N environments by the MNDO procedure are usually too high.

Although the semi-empirical MO techniques are not satisfactory in predicting values of χ , they are not, in general, inferior to *ab initio* calculations using the STO-3G basis set. A significant improvement is noted when the 4-31G basis set is employed.⁵²³

Notwithstanding the poor performance of most semi-empirical MO calculations in predicting absolute nitrogen electric-field gradients, the Townes and Dailey model incorporating INDO data provides a satisfactory account of the relative NMR linewidths for a number of ^{14}N nuclei in a given molecule.⁵²⁴ This approach has been further demonstrated as a suitable aid to ^{14}N signal assignment by means of some studies on a series of polyazine *N*-oxides.³⁴⁶

The interplay of theory and experiment has been considered in a discussion of a relationship between χ and η . The importance of the effects of hydrogen bonding on these two parameters is stressed.⁵²⁷

Charge densities, obtained from an analysis of X-ray diffraction structure factors, have been used to provide estimates of χ and η for the two ^{14}N sites in a single crystal of imidazole. A direct estimate of χ and η from the structure factors has also been obtained.⁵²⁶ In neither case do the calculated results indicate the known significant difference between the two nitrogen sites. It is not clear whether the poor results demonstrate a real limitation of the X-ray diffraction data.

The lowest photoexcited triplet state of acridine- d_9 has been studied by high-resolution ODMR and ODNQR spectroscopies.⁵²⁸ For the ^{14}N nucleus values of $\chi = -4.36$ MHz and $\eta = 0.22$ are reported as well as a rough estimation of the in-plane components of the ^{14}N hyperfine tensor.

Although germane to the present review, but not strictly within its remit, some references to estimations of η by ^{14}N NQR and microwave spectroscopies, are included. Microwave ^{14}N data have appeared for 2,2-difluoroethylamine,⁵²⁵ the $\text{N}_2 \cdots \text{HF}$ dimer⁵²⁹ and the $\text{CH}_3\text{CN} \cdots \text{HF}$ dimer.⁵³⁰ ^{14}N NQR and spin-lattice relaxation data have been reported for solid tetramethylpyrazine between liquid-helium and room temperatures.⁵³¹ Below 150 K the ^{14}N relaxation time is governed by methyl-group reorientation. The activation energy and pre-exponential factor for the correlation time are 6.0 kJ mol^{-1} and $2 \times 10^{-13} \text{ s}$ respectively. Above 130 K, torsional lattice vibrations control the ^{14}N relaxation time.⁵³¹

^{14}N NQR measurements of χ are available for the twisted nitro groups of 1-nitro; 1,5-dinitro-, 1,8-dinitro-, 2-nitronaphthalene, 9-nitroanthracene and *p*-fluoronitrobenzene,⁵³² *p*-nitrotoluene,⁵³³ sodium nitrite in the crystalline form as well as in its incommensurate⁵³⁴ and ferroelectric phases,⁵³⁵⁻⁵³⁷ some *N*-acetyl amino acids,⁵³⁸ alloxan monohydrate,⁵³⁹ hexamethylenetetramine^{540,546} and some guanidine compounds,⁵⁴⁰ some hydrogen-bonded complexes of 1,4-diazabicyclo[2.2.2]octane with phenols and thiourea,^{541,577} RDX, HMX⁵⁴² and TNT,⁵⁴³ some molecular complexes of urea,^{544,545} 4-methoxyaniline,^{546,547} hydrazine monohydrate,⁵⁴⁸ some symmetric hydrazide derivatives,⁵⁴⁹ some hydrazine derivatives,⁵⁵⁰ some amidinium salts,⁵⁵¹ thermochromic and photochromic *N*-salicylideneanilines,⁵⁵² substituted anilines⁵⁵³ and sulphanilamides⁵⁵⁴ with *in vitro* activities, acetamide⁵⁵⁵ and chloroacetamide,⁵⁵⁵ 1,2-diphenylhydrazine,⁵⁵⁶ some nicotonic-acid derivatives,⁵⁵⁷ a series of carbazoles,⁵⁵⁸ methylamine,⁵⁵⁹ anthranilic acid,⁵⁶⁰ some weakly paramagnetic organic dye cations,⁵⁶¹ β -octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine,⁵⁶² tetracyanobenzene and its molecular complexes,⁵⁶³ some substituted pyridines⁵⁶⁴ and carcinostatic phosphamides,⁵⁶⁵ 1-methylcytosine hemihydroiodide hemihydrate,⁵⁶⁶ H_3BNH_3 ,⁵⁶⁷ some methylbenzonitriles,⁵⁶⁸ *N*-piperidine,⁵⁶⁹ 2-mercaptobenzothiazole,⁵⁷⁰ isatin,⁵⁷¹ isatoic anhydride,⁵⁷² some pyridine-halogen complexes,⁵⁷³ other types of pyridine complexes⁵⁷⁴ a lipid bilayer embedded in a crystalline matrix,⁵⁷⁵ the intercalated bilayer compound $\text{C}_{10}\text{H}_2\text{NH}_3\text{Cl}$,⁵⁷⁴ the smectic phase of IBPBAC,⁵⁷⁵ some heterocyclic compounds,⁵⁷⁶ $\text{KCu}(\text{CN})_2$,^{578,579} dichloro(4*H*-1,2,4-triazole) $\text{Cu}(\text{II})$,⁵⁸⁰ and the corresponding dibromo compound in a study of magnetic phase transitions,⁵⁸¹ dichloro(dimethylnitrosamine) $\text{Cu}(\text{II})$,⁵⁸² dichloro(*N*-nitrosopiperidine)- $\text{Cu}(\text{II})$,⁵⁸³ some metal anthranilate complexes,⁵⁸⁴ chloroglycylglycinato-(imidazole) $\text{Cd}(\text{II})$,⁵⁸⁴ some palladium(II) thiocyanate complexes,⁵⁸⁵ $\text{K}_2\text{SrCu}(\text{NO}_2)_6$,⁵⁸⁶ $\text{K}_2\text{BaCu}(\text{NO}_2)_6$,⁵⁸⁶ $\text{CsPbCu}(\text{NO}_2)_6$,⁵⁸⁶ $\text{Cs}_2(\text{TCNQ})_3$,⁵⁸⁷ some metal complexes of hexamethylenetetramine,⁵⁸⁸ some cyanate complexes,⁵⁸⁹ metal complexes of *N*-heterocycles,⁵⁹⁰ some cyanides,⁵⁹¹ and for a selection of organic molecules that have been studied in order to determine electron distributions.⁵⁹²

Finally, mention should be made of the use of ^{14}N NQR data to verify the crystal structure of both the α and β phases of 3d-acetonitrile,⁵⁹³ of ^{14}N and ^2H quadrupole double-resonance studies of four salts of cytosine,⁵⁹⁴ adenine dihydrobromide⁵⁹⁴ and fifteen substituted imidazoles,⁵⁹⁵ of a theoretical analysis of contributions to nitrogen NQR spectra effects due to level crossing and thermal mixing,⁵⁹⁶ of a study of adiabatic demagnetization and two-frequency methods in ^{14}N NQR,⁵⁹⁷ and of a study of the spin-lattice relaxation of quasi-steady states in ^{14}N NQR by means of multipulse experiments on sodium nitrite.⁵⁹⁸

B. ^{15}N relaxation

^{15}N nuclear relaxation is usually due to one, or more, of the less efficient relaxation mechanisms; namely those arising from dipole-dipole, spin-rotation, chemical shielding anisotropy and scalar coupling interactions. If the ^{15}N nucleus in question is directly bonded to one or more protons then dipole-dipole interactions normally dominate.

Use has been made of this observation in a study of the amino acids in *Neurospora Crassa* as a probe of intracellular environment.⁶⁰¹ ^{15}N spin-lattice relaxation and NOE measurements have been performed for intracellular glutamine, alanine and arginine in the intact mycelia. The NOE data reveal that the ^{15}N - ^1H dipolar mechanism predominates over the ^{15}N relaxation. Consequently, the relaxation times are related to the microviscosities of the various nitrogen environments. However, there are non-dipolar contributions to some of the ^{15}N relaxation results which have to be taken into account.

^{15}N relaxation results have been reported for diazabicyclo[2.2.2]octane (DABCO), and hexamethylenetetramine (HMTA) in aqueous solution.⁴⁵ Analysis of the relaxation data reveals that more than fifty per cent of the total ^{15}N dipolar relaxation rate for DABCO arises from hydrogen-bonded water protons, while for HMTA the contribution is about twenty per cent. This suggests the presence of weaker hydrogen bonds in the case of HMTA. Protonation of both DABCO and HMTA leads to more rapid ^{15}N relaxation.

The ^{15}N and ^{13}C dipolar relaxation rates of poly(vinylamine) and poly(iminoethylene) provide information on the relative motions of the nitrogen-containing groups and the polymer backbones.⁵⁹⁹ The results for poly(vinylamine) are consistent with relatively unhindered rotation of the ammonium group. The rotation rate is reduced at neutral pH, indicating the presence of hydrogen bonding between alternate NH_3^+ and NH_2 groups. In poly(iminoethylene) the motion of the NH groups is more restricted with respect to the polymer-backbone methylene groups.

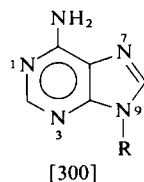
The anisotropic motion of 2-pyrrolidone has been similarly analysed by means of dipole-controlled ^{15}N and ^{13}C relaxation data.⁶⁰⁰ The dipolar relaxation processes are found to be dominated by the anisotropic reorientation of the dimer.

In some ^{15}N -enriched enkephalin derivatives the dipole-dipole-dominated ^{15}N relaxation data are interpreted in terms of molecular motion.⁶⁰² The occurrence of concerted motion is noted for linked N-C nuclei along the peptide backbone. In addition, an overall isotropic motion model, with internal libration, gives the best account of the ^{15}N NOE and relaxation measurements.

The fact that dipole-dipole interactions are relatively inefficient in producing ^{15}N relaxation, even when protons are directly attached, often leads to

long ^{15}N spin-lattice relaxation times. In order to make efficient use of FT NMR instrumentation, paramagnetic relaxation reagents may be used. However, such reagents may also induce ^{15}N shielding changes, and thus are not always suitable for use when ^{15}N shielding results are required. A reliable alternative approach to the problem of long spin-lattice relaxation times is to increase the viscosity of the solutions used. This has the effect of increasing the rotational correlation time and thus increasing the spin-lattice relaxation rate.⁷ Glycerol appears to be a suitable solvent for decreasing the spin-lattice relaxation times of ^{15}N nuclei in molecules that are water soluble, and a saturated mixture of toluene and polystyrene appears to suffice for molecules that are soluble in organic media.¹³⁵

The base-stacked Mn^{2+} -AMP complex in solution exhibits ^{15}N relaxation data that are controlled by electron-nucleus dipole-dipole interactions.³⁵⁶ The Mn^{2+} -nitrogen distances have been estimated from the ^{15}N spin-lattice relaxation measurements, and shown to indicate a direct inner-sphere coordination of Mn to N_1 , N_7 and to the amino nitrogen of the aminopurine fragment [300] of AMP:



The N-1 and N-3 resonances of some neomycin B derivatives are based on ^{15}N spin-lattice relaxation experiments in which $\text{Gd}[2.2.1]\text{cryptate}$ is used as a spin-labelling reagent in aqueous and DMSO solutions.²⁷⁴ The influence of exchange phenomena on ^{15}N relaxation rates have been studied for some linear peptides by means of a cross-polarization INEPT sequence. The antisymmetric relaxation times are shown to depend on both proton-exchange and proton-relaxation mechanisms.¹²⁸

In the solid state the tunnelling motion of ammonium ions results in an increased efficiency of ^{15}N - ^1H dipole-dipole relaxation.⁶⁰⁴ In some thorium carbonitrides the ^{15}N and ^{13}C relaxation rates are reported to contain strong paramagnetic orbital contributions.⁶⁰³ This interpretation is consistent with the absence of metalloid 2s electrons at the Fermi level, as predicted by band calculations. A theory of solid echoes, following a two-pulse r.f. sequence, has been applied to solid $^{15}\text{N}_2$.¹⁹⁵ Dipolar interactions between different molecules produce a damping of the solid echoes which depends upon the angle and the axis of rotation of the nuclear spins by the second pulse. It has been demonstrated that stimulated echoes, formed in ordered crystals of $^{15}\text{N}_2$, can be used to detect slow rotational motions.¹⁹⁶ In the gaseous phase the relaxation of $^{15}\text{N}_2$ appears to be fully controlled by the spin-rotation interaction process.⁵¹²

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TABLES 1-163

Note: Shieldings are expressed throughout in ppm.

A complete list of tables is given on p. 755.

Table 1

Comparison of some calculated values of nitrogen nuclear shieldings (σ) and chemical shifts (δ) with respect to nitromethane, and some experimental results

Compound	1 Centre σ	σ P BB	σ P AB	Total σ	1 Centre δ	Total δ	Exp δ
CH_3NO_2	-87.79	-23.40	-21.21	-132.4	0.0	0.0	0.0
N_2	-64.61	-4.33	-5.42	-74.36	-23.18	-58.04	-70.2 ± 1.5
CH_3CN	-16.47	-10.97	-15.62	-43.06	-71.32	-89.34	-135.8 ± 0.06
* NNO	8.28	-6.50	-9.05	-7.27	-96.07	-125.13	-232.3 ± 0.1
CH_3NC	68.45	-10.94	-24.94	32.57	-156.24	-164.97	-218.0 ± 0.5
* NNO	43.77	-15.35	-21.09	7.33	-131.56	-139.73	-148.0 ± 0.1
NH_4^+	133.72	0.0	-7.96	125.76	-221.51	-258.16	-353.5 ± 0.5
NH_3	99.51	0.0	-10.39	89.12	-187.3	-221.52	-381.9 ± 0.1

TABLE 2

Comparison of some INDO/S-SOS calculated nitrogen shieldings of some
N-heterocycles with experimental data

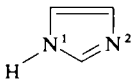
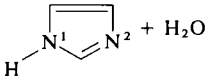
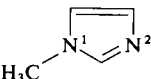
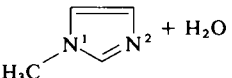
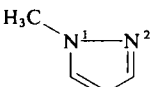
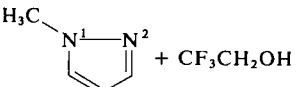
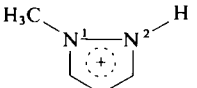
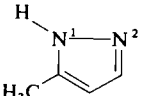
System	Shielding source	N-1	N-2	Average
	Calc. Expt.	172.42	111.89	142.16 172.6
	Calc. Expt.	177.40	114.78	146.09 177.2
	Calc. Expt.	158.91 206.0	158.91 206.0	
	Calc. Expt.	174.83 221.3	117.73 125.5	
	Calc. Expt.	172.96 217.7	128.45 134.7	
	Calc. Expt.	170.76 217.0	166.45 196.0	
	Calc. Expt.	165.40 204.5	165.40 204.5	
	Calc. Expt.	166.31 180.8	114.15 76.5	
	Calc. Expt.	169.05 182.2	124.64 94.4	
	Calc. Expt.	177.90 186.4	168.93 146.4	
	Calc. Expt.	146.83 134.3	148.12 139.8	

TABLE 2—*cont.*

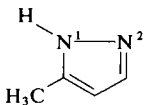
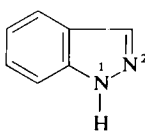
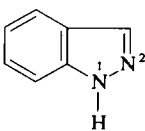
System	Shielding source	N-1	N-2	Average
 $+ \text{CF}_3\text{CH}_2\text{OH}$	Calc. Expt.	155.14 145.7	156.88 148.3	
	Calc. Expt.	192.13 200.6	80.58 65.1	
 $+ \text{CF}_3\text{CH}_2\text{OH}$	Calc. Expt.	195.04 207.2	102.68 90.8	

TABLE 3

Comparison of some calculated and experimental $^1J(^{31}\text{P}-^{15}\text{N})$ data

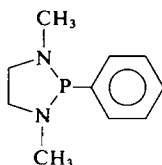
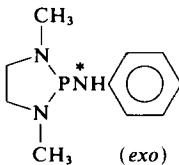
Compound	Contact term	Orbital term	Dipolar term	Total calc.	Expt.
$\text{F}_2\text{P}^{\oplus}\text{PF}_3$	67.866	10.393	-0.676	77.58	+93.8
F_2PNH_2	66.041	7.004	-0.410	72.63	73.0
$\text{Cl}_2\text{PN}(\text{CH}_3)_2$	76.201	7.343	-0.536	83.01	89.4
$[(\text{C}_2\text{H}_5)_2\text{N}]_3\text{P}$	60.166	5.675	-0.283	65.56	59.1
	48.715	4.833	-0.681	52.87	49.8
 (<i>exo</i>)	62.572	13.070	-0.429	75.21	+84.2

TABLE 3—*cont.*

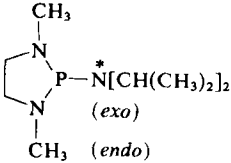
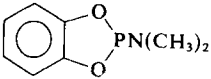
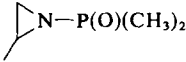
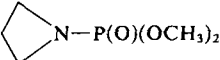
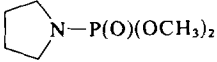
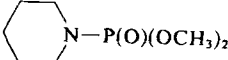
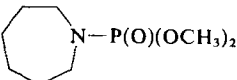
Compound	Contact term	Orbital term	Dipolar term	Total calc.	Expt.
	63.260 36.832	11.474 11.583	-0.325 -0.655	74.41 47.76	96.0 51.0
	68.622	12.411	-0.317	80.72	89.0
$F_2PN=\ddot{P}F_3$	-35.918	4.056	-0.637	-32.50	-53.2
$[(CH_3)_2N]_3PO$	-19.229	2.464	-1.664	-18.43	-26.9
	-23.667	7.086	-0.195	-16.78	10.0
	-31.002	7.491	-0.218	-23.73	20.9
	-65.549	8.646	-0.261	-57.16	41.2
	-69.667	8.367	-0.235	-61.54	39.1
	-67.671	8.372	-0.229	-59.53	42.7

Table 4

Conversion schemes, and consequences thereof, for shielding constants (σ) referred to different reference signals

No.	Observed shielding relative to secondary reference $(\sigma_{\text{sample}} - \sigma_{\text{ref.II}})_{\text{observed}}$	Observed shielding of secondary reference relative to primary reference $(\sigma_{\text{ref.II}} - \sigma_{\text{ref.I}})_{\text{observed}}$	Correction which should be added to the algebraical sum of the two shieldings in the second and third columns in order to obtain true ("intrinsic") value of $(\sigma_{\text{sample}} - \sigma_{\text{ref.I}})$
I	true	true	none
II _a	apparent (field perpendicular to sample tube)	true	$(\chi_{\text{ref.II}} - \chi_{\text{sample}})/6$
II _b	apparent (field parallel to sample tube)	true	$-(\chi_{\text{ref.II}} - \chi_{\text{sample}})/3$
III _a	true	apparent (field perpendicular to sample tube)	$(\chi_{\text{ref.I}} - \chi_{\text{ref.II}})/6$

III _b	true	apparent (field parallel to sample tube)	$-(\chi_{\text{ref.I}} - \chi_{\text{ref.II}})/3$
IV _a	apparent (field perpendicular to sample tube)	apparent (field perpendicular to sample tube)	$(\chi_{\text{ref.I}} - \chi_{\text{sample}})/6$
IV _b	apparent (field parallel to sample tube)	apparent (field parallel to sample tube)	$-(\chi_{\text{ref.I}} - \chi_{\text{sample}})/3$
IV _c	apparent (field perpendicular to sample tube)	apparent (field parallel to sample tube)	$(3\chi_{\text{ref.II}} - \chi_{\text{sample}} - 2\chi_{\text{ref.I}})/6$
IV _d	apparent (field parallel to sample tube)	apparent (field perpendicular to sample tube)	$-(3\chi_{\text{ref.II}} - 2\chi_{\text{sample}} - \chi_{\text{ref.I}})/6$

ref. I = primary reference (external neat nitromethane is used in the present work)

ref. II = any secondary reference actually employed

true = true difference between shielding constants

apparent = apparent difference between shielding constants, as estimated from the positions of the resonance signals involved, under conditions of concentric cylindrical tubes

Table 4 (continued)

χ = volume magnetic susceptibility, expressed in the SI system (see Table 5)

$$\text{master equation : } (\sigma_{\chi} - \sigma_Y)_{\text{true}} = (\sigma_X - \sigma_Y)_{\text{observed}} - \left(\frac{1}{3} - \alpha\right) (\chi_Y - \chi_X)$$

where $\alpha = 0$ for magnetic field (B_0) parallel to concentric cylindrical sample tubes,

$\alpha = 1/2$ for B_0 perpendicular to concentric cylindrical sample tubes,

$\alpha = 1/3$ for spherical sample containers; form of equation is consistent

with volume susceptibility values expressed in the SI system (Table 5).

Table 5

Volume bulk magnetic susceptibilities at 30°C
(expressed in the SI system = $4\pi \times$ CGS system)

Substance (neat liquid, if not stated otherwise)	Volume susceptibility (ppm)
C(NO ₂) ₄	-4.499
MeNO ₂	-4.863
acetone	-5.730
MeCN	-6.509
MeOH	-6.572
Et ₂ O	-6.560
MeCOOH	-6.900
n-hexane	-7.012
MeNH ₂ (liquid under pressure)	-7.087
EtOH	-7.150
Bu ⁿ NH ₂	-7.427
dioxane	-7.427
pyridine	-7.502
(Pr ⁱ) ₂ NH	-7.515
benzene	-7.653
HNO ₃ (70 % w/w in H ₂ O)	-7.766
DMSO	-7.766
N-Me-piperidine	-7.779
cyclohexane	-7.829
cis-2,6-Me ₂ -piperidine	-7.980
CCl ₄	-8.595
CS ₂	-8.708
HNO ₃ (1 M in H ₂ O)	-8.985
H ₂ O	-8.998
CH ₂ Cl ₂	-9.010
NH ₄ NO ₃ (satd. in H ₂ O)	-9.073
H ₂ SO ₄ (100 %)	-9.085
NaNO ₃ (satd. in H ₂ O)	-9.161
CHCl ₃	-9.173
NH ₄ Cl (satd. in H ₂ O)	-9.664
CH ₂ Br ₂	-11.712

Data from ref. 1, Table 5 therein, and references therein,
recalculated from the CGS system used there.

Table 6

Nitrogen shieldings used as conversion factors for various reference substances^a

Standard	Solution or state	Nitrogen shielding referred to neat liquid nitromethane		
		true	apparent	
			external field perpendicular to cylindrical sample axis	external field parallel to cylindrical sample axis external field at the magic angle (54°44') relative to cylindrical sample axis
MeNO ₂	neat liquid	0.0000		
NaNO ₃	satd. in H ₂ O (7.93 M)	+3.7	(+3.0) ^b	(+5.1) ^b
	0.30 M in H ₂ O	+3.5	(+2.8) ^b	(+4.9) ^b
KNO ₃	0.30 M in H ₂ O	+3.5	(+2.8) ^b	(+4.9) ^b
HNO ₃	1.0 M in H ₂ O	+4.4	(+3.7) ^b	+6.2; (+5.9) ^b
	7.0 M in H ₂ O	+12.6		
	10.0 M in H ₂ O	+18.2		
	15.7 M in H ₂ O (70% w/w)	+31.3		

MeNO ₂	0.30 M in DMSO	-2.0 ^c
	0.30 M in H ₂ O	-2.0 ^c
	0.30 M in 11.7 M HCl	-1.9 ^c
	0.30 M in Me ₂ NCHO	-0.7 ^c
	0.30 M in MeCN	+0.2 ^c
	0.30 M in acetone	+0.8 ^c
	0.30 M in dioxane	+1.8 ^c
	0.30 M in MeOH	+2.0 ^c
	0.30 M in EtOH	+2.7 ^c
	0.30 M in CH ₂ Cl ₂	+3.2 ^c
	0.30 M in CH ₂ Br ₂	+3.4 ^c
	0.30 M in CHCl ₃	+3.8 ^c
	0.30 M in Et ₂ O	+3.9 ^c
	0.30 M in benzene	+4.4 ^c
	0.30 M in CCl ₄	+7.1 ^c

NH₄NO₃ solid

satd. in H ₂ O	+359.6 (NH ₄ ⁺)	(+358.9) ^b	(+361.0) ^b
	+4.0 (NO ₃ ⁻)	(+3.3) ^b	(+5.4) ^b

+358.4^d (NH₄⁺)
+5.0^d (NO₃⁻)

Table 6 (continued)

	4 M in 2 M HNO ₃	+359.1 (NH ₄ ⁺)	(+358.4) ^b	(+360.5) ^b
		+5.6 (NO ₃ ⁻)	(+4.9) ^b	(+7.0) ^b
	5 M in 2 M HNO ₃	+359.0 (NH ₄ ⁺)	(+358.3) ^b	(+360.4) ^b
		+4.6 (NO ₃ ⁻)	(+3.9) ^b	(+6.0) ^b
	5 M in 2 M HCl	+358.0 (NH ₄ ⁺)		
		+5.2 (NO ₃ ⁻)		
	4.5 M in 3 M HCl	+357.1 (NH ₄ ⁺)		
		+6.3 (NO ₃ ⁻)		
	satd. in DMSO	+358.1 ^e (NH ₄ ⁺)		
		+3.3 ^e (NO ₃ ⁻)		
NH ₄ Cl	solid			+341.0 ^d
	satd. in H ₂ O	+352.9	(+352.1) ^b	(+354.7) ^b
	satd. in 2 M HCl	+352.5		
	1 M in 10 M HCl	+349.9		
(NH ₄) ₂ SO ₄	solid			+355.7 ^d
NH ₃	neat liquid	+381.9	+380.2 ^f	
C(NO ₂) ₄	neat liquid	+46.6		

$\text{Me}_4\text{N}^+\text{Cl}^-$	satd. in H_2O (6.03 M)	+336.7		
	0.30 M in H_2O	+337.7	(+337.0) ^b	(+339.1) ^b
	2 M in H_2O			+339.0
$\text{Me}_4\text{N}^+\text{I}^-$	0.30 M in H_2O	+337.3		
	satd. in DMSO	+337.0 ^e		
NaNO_2	satd. in H_2O (7.56 M)	-228.9		
	0.30 M in H_2O	-227.6		
$\text{K}^+(\text{NCO})^-$	satd. in H_2O	+302.6		
PhNO_2	neat liquid	+9.6		+9.9 ^g
	2 M in Me_2SO_4		+9.3 ^h	
MeCN	neat liquid	+135.8 ⁱ		+136.4 ⁱ ; (+136.3) ^b
	0.30 M in MeNO_2	+137.8 ⁱ		
KCN	satd. in H_2O (8.5 M)	+102.5		
	0.30 M in H_2O	+106.1		
N_2	gaseous	(+75.5) ^b	+74.7 ^j	(+77.1) ^b

Table 6 (continued)

Me ₂ NCHO	neat liquid	+277.0 ^k		
H ₂ NCHO	neat liquid		+267.8 ^k	+268.6 ^l
	in DMSO		+264.7 ^m	

(a) Unless stated otherwise, data from ref. 1, Table 6 therein, and references therein; "true" values were determined from high precision ¹⁴N measurements (differential saturation technique, full lineshape fitting procedure), using concentric spherical sample/standard containers in order to eliminate bulk susceptibility effects; measurements were carried out at 4.3342 MHz, +30°C.

(b) Values calculated using magnetic susceptibility values from Table 5.

(c) See ref. 1, Table 133 therein, and references therein.

(d) See Table 30, notes (a) and (b).

(e) Data from ref. 1530, experimental details as in note (a).

(f) Data from ref. 109, and references therein.

(g) Data from ref. 1149.

(h) See Table 9, note (a).

(i) See ref. 1, Table 108 therein, and references therein.

(j) See Table 124, note (a).

(k) See ref. 1, Table 57 therein, and references therein.

(l) See ref. 1, Table 60 therein, and references therein.

(m) See ref. 1, Table 61 therein, and reference therein; the value reported in the present Table was converted from the original reference (NaNO₃/H₂O) using a value of +3.0 ppm for the latter (see data in the present Table) in order to conform with conversion scheme IV_a (Table 4).

Table 7

Isotope effects on nitrogen shielding

Molecule	Solvent	Approximate shielding referred to external neat nitromethane	Difference in nitrogen shielding between isotopomers	Notes
			$\sigma(^{13}\text{C}^{15}\text{N}) - \sigma(^{12}\text{C}^{15}\text{N})$	
$\text{CN}^- (\text{K}^+)$	H_2O	+106.1	+0.075 $\pm$ 0.005	(a)
$\text{Ni}(\text{CN})_4^{2-}$	H_2O	+90.2	+0.066 $\pm$ 0.010	(a)
$\text{Pd}(\text{CN})_4^{2-}$	H_2O	+99.3	+0.101 $\pm$ 0.025	(a)
$\text{Pt}(\text{CN})_4^{2-}$	H_2O	+109.6	+0.077 $\pm$ 0.010	(a)
$\text{Zn}(\text{CN})_4^{2-}$	H_2O	+106.0	+0.069 $\pm$ 0.010	(a)
$\text{Cd}(\text{CN})_4^{2-}$	H_2O	+102.7	+0.081 $\pm$ 0.020	(a)
$\text{Hg}(\text{CN})_4^{2-}$	H_2O	+102.1	+0.067 $\pm$ 0.010	(a)
			$\sigma(^{18}\text{O}^{15}\text{N}) - \sigma(^{16}\text{O}^{15}\text{N})$ (per single ^{18}O introduced)	
$\text{NO}_2^- (\text{Na}^+)$	H_2O	-229.7	+0.138	(b)
			+0.13	(c)
$\text{NO}_3^- (\text{Na}^+)$	H_2O	+3.5	+0.056	(c)

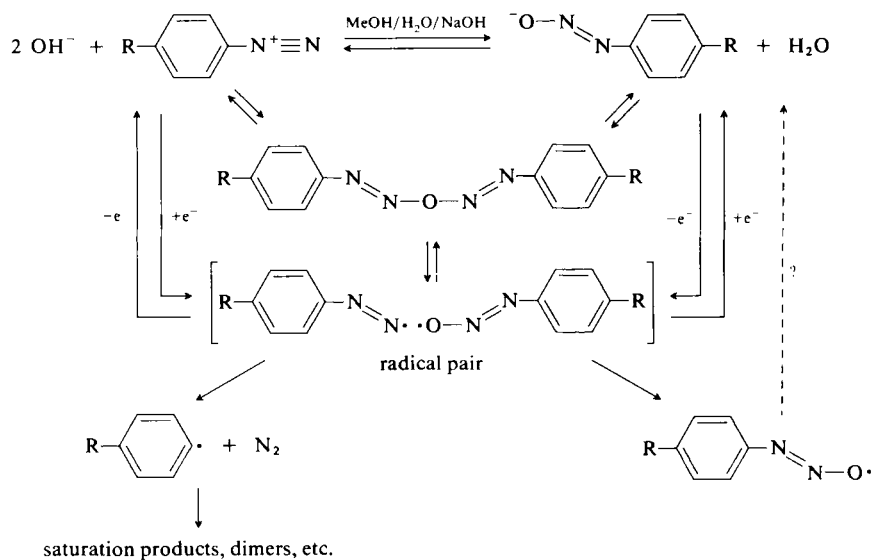
For additional data, see ref. 1, Table 8 therein.

(a) Data from ref. 1510; ^{15}N labelled CN; ^{15}N spectra, 40.55 MHz, field parallel to sample tube; referred originally to 0.4 M aqueous KCN, +106.1 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

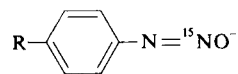
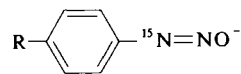
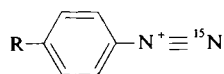
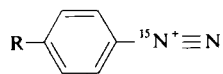
(b) Data from ref. 227; ^{15}N labelled ion; ^{15}N spectra, 47.6 MHz, field parallel to sample tube, shielding referred to nitromethane taken from footnote (c) in this Table.

(c) Data from ref. 226; ^{15}N labelled ions; ^{15}N spectra, 30.42 MHz, field parallel to sample tube, referred originally to aqueous NaNO_3 , +3.5 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

TABLE 8

Chemically induced dynamic nuclear polarization (CIDNP) in ^{15}N NMR spectra

CIDNP signals

 N_2 Predicted from
Kaptein's rules

enhanced absorption

emission

enhanced absorption

emission

—

Experimental shieldings
and intensities

R = Cl	+148.5 ppm enhanced absorption	+62.4 ppm emission	+1.6 ppm enhanced absorption	−144.4 ppm emission	+70.3 ppm
R = H	+143.6 ppm enhanced absorption	not observed, reaction too fast	+18.6 ppm enhanced absorption	−140.9 ppm emission	+69.4 ppm

Data from ref. 209; ^{15}N singly labelled ions, BF_4^- salts; ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, +60 °C; nitrogen shieldings in this table refer to neat nitromethane, originally referred to NO_3^- in aqueous NH_4NO_3 , +4.0 ppm from nitromethane (Table 6), conversion scheme II (Table 4).

For additional data, see ref. 1, Table 9 therein.

Table 9

Some examples of temperature dependence of nitrogen shielding in various molecules and ions

Compound	Solution or state	Nitrogen shielding referred to neat nitromethane (in ppm, at temperature specified)	Temperature gradient of nitrogen shielding in ppm/degree (average if relationship is non-linear)	Temperature range	Notes
Me_3N	in CD_3OH	+362.9 (30°C)	+0.0225 ± 0.0025	-60 to 0°C	(a)
$\text{Me}_3\text{NH}^+\text{Cl}^-$	in H_2O	+348.2 (30°C)	+0.005 ± 0.003	30 to 90°C	(a)
$\text{NH}_3\text{OH}^+\text{Cl}^-$	in H_2O	+296.2 (30°C)	0.0	30 to 100°C	(a)
$\text{Me}_3\text{N}\rightarrow\text{O}$	in H_2O	+274.6 (30°C)	+0.005 ± 0.003	30 to 90°C	(a)
$\text{Me}_3\text{N}^+-\text{OH}, \text{Cl}^-$	in H_2O	+267.3 (30°C)	+0.005 ± 0.003	30 to 90°C	(a)
$\text{H}_2\text{N}-\text{OMe}$	in H_2O	+240.9 (30°C)	-0.005 ± 0.002	25 to 95°C	(a)

Me ₂ C=NOH	in H ₂ O	+53.3 (30°C)	-0.048 ±0.003	13 to 66°C	(a)
			-0.059 ±0.0015	66 to 99°C	(a)
	in MeOH	+44.7 (30°C)	-0.053 ±0.002	-80 to 20°C	(a)
	in 1-octanol	+40.1 (30°C)	-0.0425 ±0.003	30 to 150°C	(a)
	melt	+44.0 (30°C, extrapolated)	-0.041 ±0.003	70 to 140°C	(a)
MeCH=NOH (Z-isomer)	in H ₂ O	+38.1 (30°C)	-0.039 ±0.001	0 to 95°C	(a)
MeCH=NOH (E-isomer)	in H ₂ O	+34.1 (30°C)	-0.031 ±0.007	0 to 95°C	(a)
PhCH=NOH (E-isomer)	neat liquid	+26.6 (30°C)	-0.043 ±0.002	30 to 150°C	(a)
	in MeOH	+17.2 (30°C)	-0.001 ±0.0005	-80 to 20°C	(a)

Table 9 (continued)

	in 1-octanol	+12.8 (30°C)	-0.003 ±0.001	30 to 150°C	(a)
PhCH=NOMe (E-isomer)	in MeOH	-2.9 (30°C)	-0.003 ±0.002	0 to 60°C	(a)
	in 1-octanol	-5.9 (30°C)	-0.003 ±0.001	30 to 115°C	(a)
Me ₃ N ⁺ CH ₂ CH=NOH (E-isomer)	in H ₂ O	-3.1 (30°C)	-0.021 ±0.0006	2 to 62°C	(a)
			-0.0125 ±0.001	62 to 102°C	(a)
K ⁺ NO ₃ ⁻	0.3 M in H ₂ O	+3.5 (30°C)	0.000	2 to 90°C	(a)
HNO ₃	2 M in 70% D ₂ O/H ₂ O	+6.1 (30°C)	+0.04 (averaged)	15 to 90°C	(a)
	2 M in H ₂ O	+5.4 (30°C)	+0.023 (averaged)	20 to 99°C	(a)
	neat liquid	+380.4 (300 K)	+0.068	300 to 360 K	(b)
NH ₃	in H ₂ O	+376.1 (30°C)	+0.017 (averaged)	0 to 99°C	(a)
	gaseous	+400.9 (300 K)	+0.00655 ±0.00082	300 to 350 K	(b)

N_2	gaseous	+74.7(300 K)	-0.0011 ± 0.0001	220 to 360 K	(b)
$PhNO_2$	2 M in Me_2SO_4	+9.3(30°C)	0.000	-20 to 180	(a)
Silatranes (see Table 27)					
R = Me	in PhCl	+359.7(300 K)	-0.027 ± 0.001	243 to 403 K	(c)
	melt	+357.3(300 K, extrapolated)	-0.021 ± 0.001	423 to 523 K	(c)
R = CH_2Cl	in PhCl	+355.2(300 K)	-0.014 ± 0.01	243 to 403 K	(c)

(a) Data from ref. 247; ^{15}N enriched compounds, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to 2 M $PhNO_2$ in Me_2SO_4 , +9.3 ppm from neat nitromethane, as can be reckoned from KNO_3 shielding reported there and compared with data in Table 6; uncorrected for bulk susceptibility effects, conversion scheme II (Table 4).

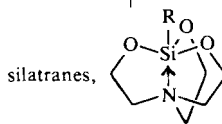
(b) Data from ref. 56, and references therein; see Table 11, note (a).

(c) Data from ref. 270; ^{15}N enriched compounds, ^{15}N spectra, details in Table 20, note (a).

TABLE 10

Characteristic nitrogen shielding ranges for various classes of molecules and ions (referred to external neat nitromethane)

-600 ppm	-500	-400	-300	-200	-100	0	+100	+200	+300	+400 ppm
									ammonia, NH_3	xxx
									ammonia adsorbed on zeolites	xx
									NH_3 as amino ligand in complexes	xxxxxx
									alkylamines, NR_3 (R = alkyl group or part of saturated ring system)	xxxxxxxxxx
									silylamines, $\text{R}_3\text{Si}-\text{NR}_2$	xxxxxxxxxx
									silatranes,	xxx
									silatrane analogues of Ge, B, VO, MoO_2	xxxxxx
									ammonium ion, NH_4^+	xxxxxx
									alkylammonium ions, NR_4^+ (at least one R = alkyl)	xxxxxxxxxx
									arylamines, NR_3 (at least one R = aryl)	xxxxxxxxxx
									arylammonium ions, NR_4^+ (at least one R = aryl)	xxx



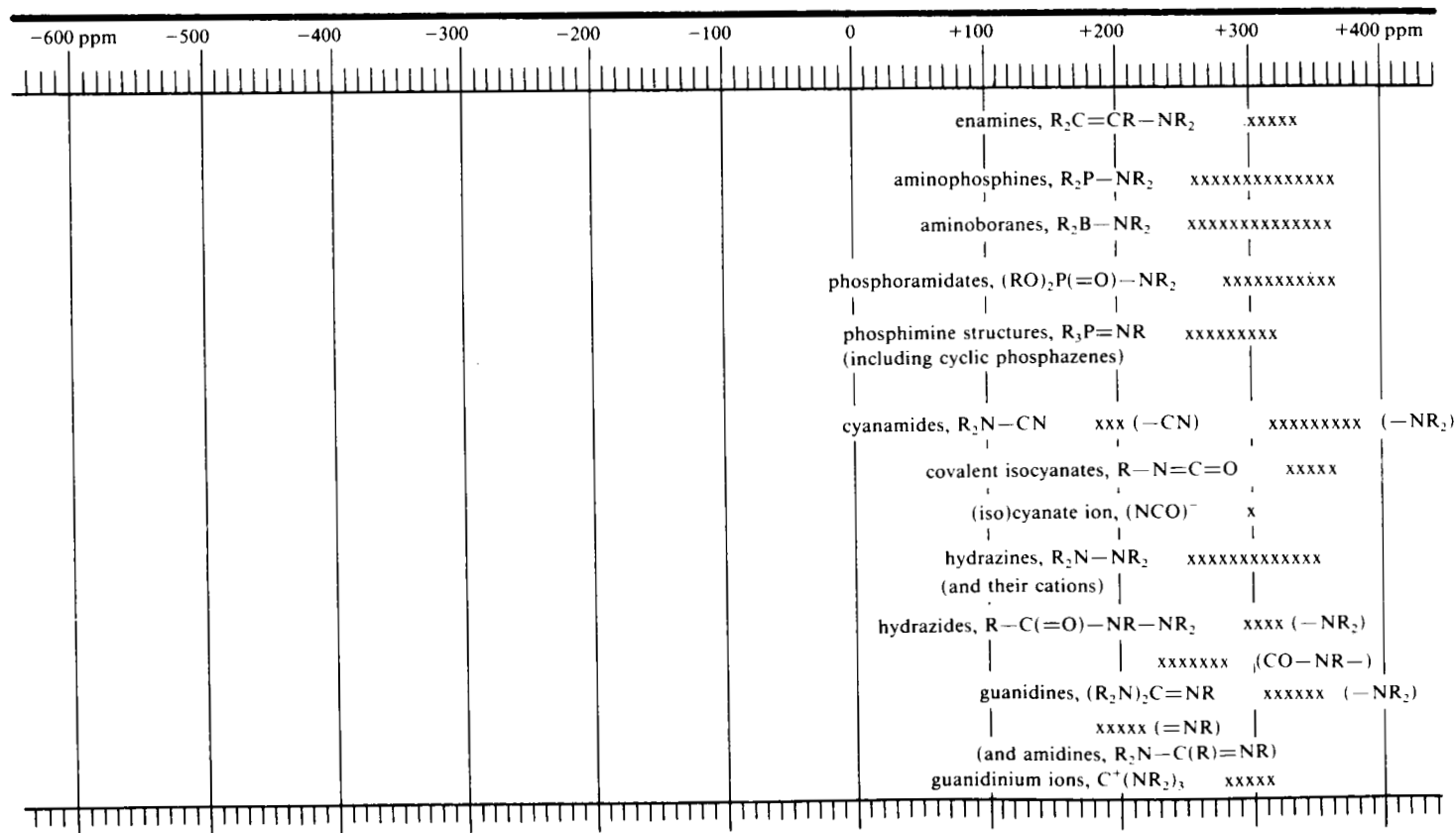


TABLE 10—cont.

-600 ppm	-500	-400	-300	-200	-100	0	+100	+200	+300	+400 ppm
						enaminones, $\text{RC}(=\text{O})-\text{CR}=\text{CR}-\text{NR}_2$ (and their vinylogues)		xxxxxxxxxxxxx		
							ureas, $(\text{R}_2\text{N})_2\text{C}=\text{O}$	xxxxxxx		
							carbamates, $\text{RO}-\text{C}(=\text{O})-\text{NR}_2$	xxxxxxx		
						covalent azides, $\text{R}-\text{N}=\text{N}^+=\text{N}^-$	xxxxx ($=\text{N}^+=$) xxxxxxxxx ($=\text{N}^-$)		xxxxxxxxx ($\text{R}-\text{N}=\text{N}^-$)	
						azide ion, N_3^-	x (central N)		x (terminal N)	
							sulphone imines, $\text{R}_2\text{S}(=\text{X})=\text{NR}$		xx	
							sulphilimines, $\text{R}_2\text{S}=\text{NH}$		xxx	
						$\text{X}_2\text{S}=\text{N}-\text{R}$ (X = halogen)	xxxxxxxxxxxxxxxxxxxxx			
						amino/ammonium moieties of α -amino acids			xxxx	

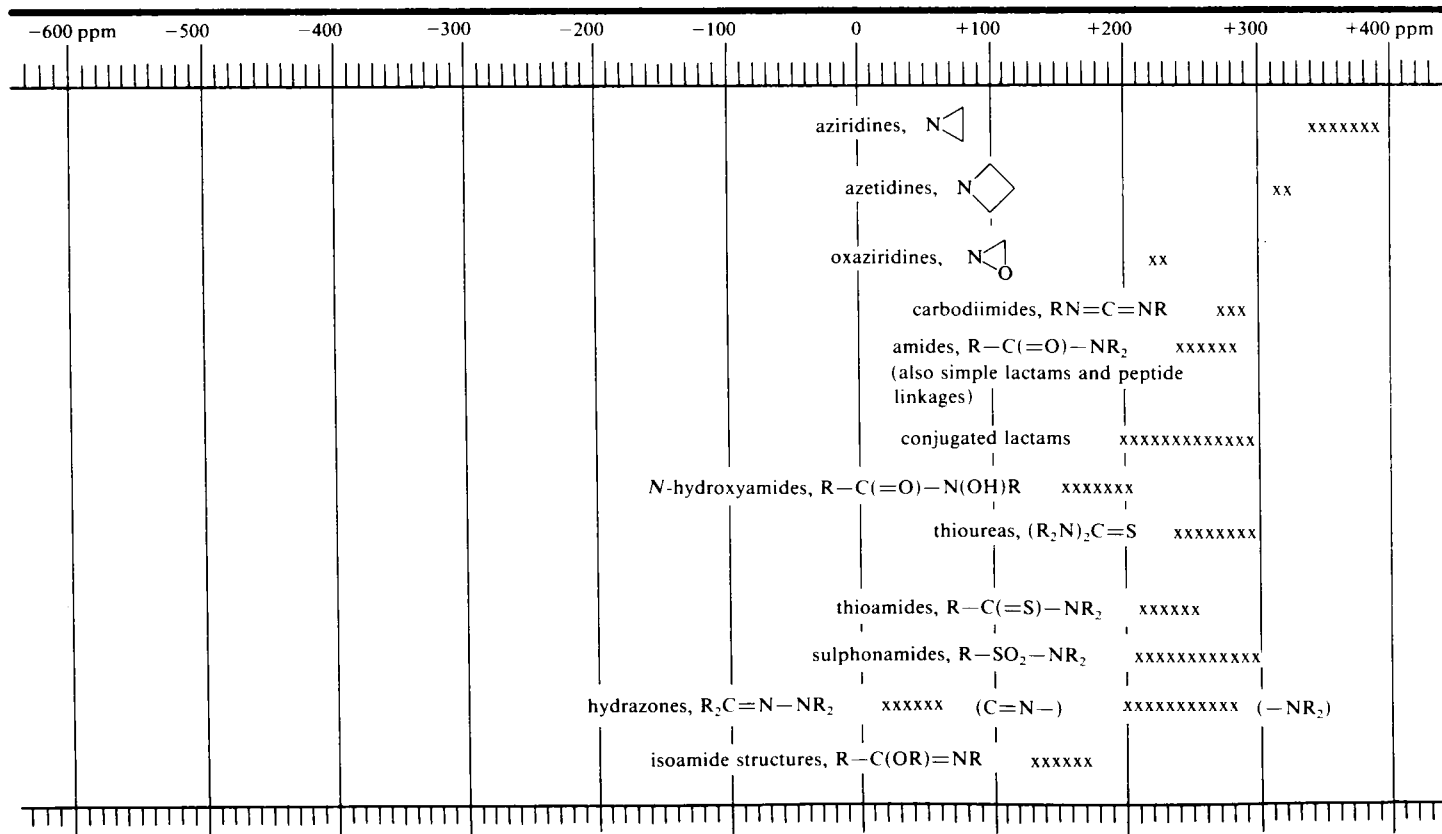


TABLE 10—cont.

-600 ppm	-500	-400	-300	-200	-100	0	+100	+200	+300	+400 ppm
							amine <i>N</i> -oxides, $R_3N \rightarrow O$	xxx		
							hydroxylamines, R_2N-OR	xxxxxxxxxxxxx		
							hydroxylammonium ions, R_3N^+-OR	xxxxx		
							halogeno-amines, R_2N-X , RNX_2 ($X = Cl, Br$)	xxxxxxxxxxxxxxxxx		
							imides, $R-C(=O)-NR-C(=O)-R$	xxxxxxx		
							ketenimines, $R_2C=C=N-R$	xxxxx		
			azolium ions, 					xxxxxxx		
			azinium ions, 					xxxxxxxxxxxxxxx		

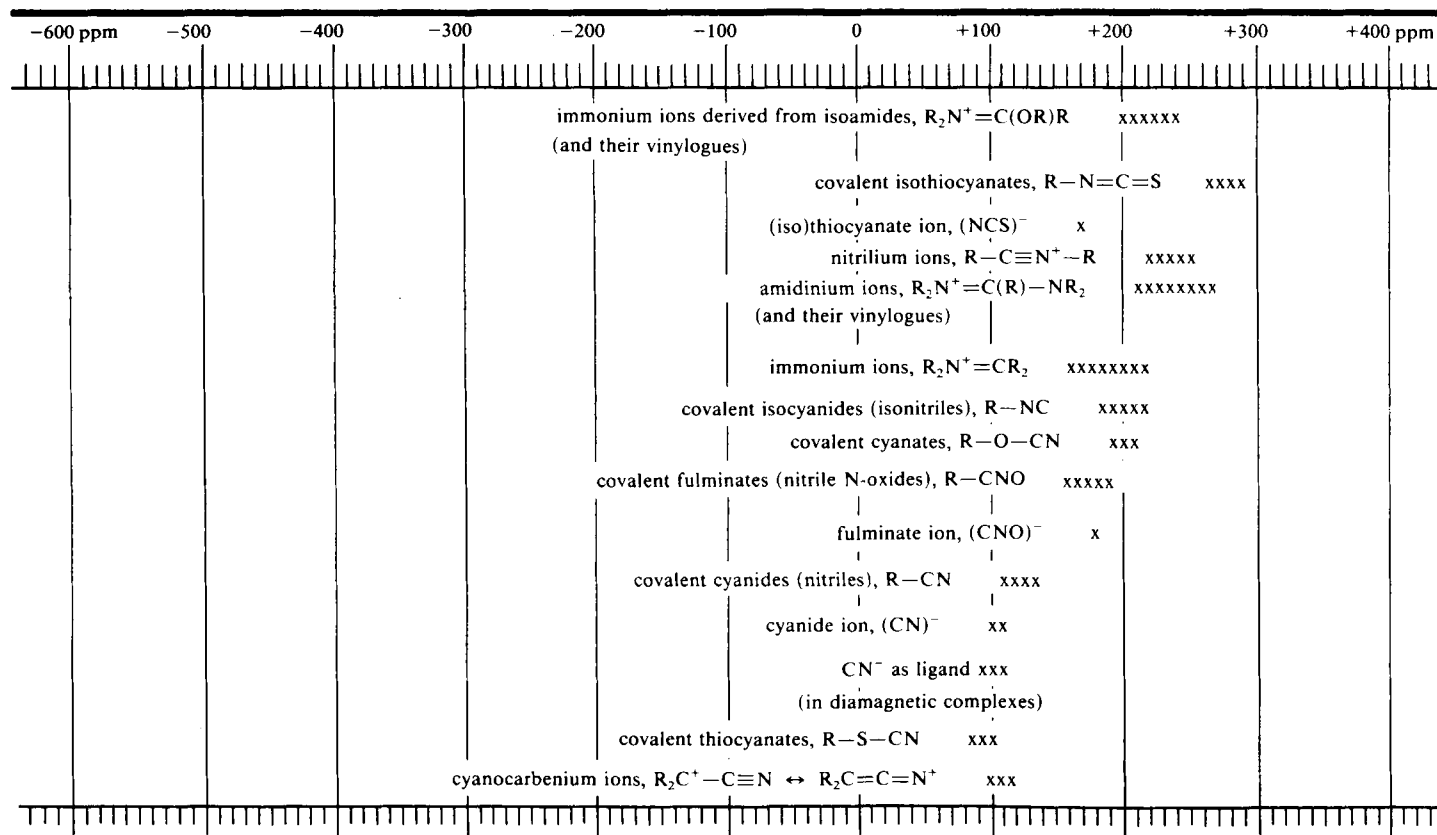
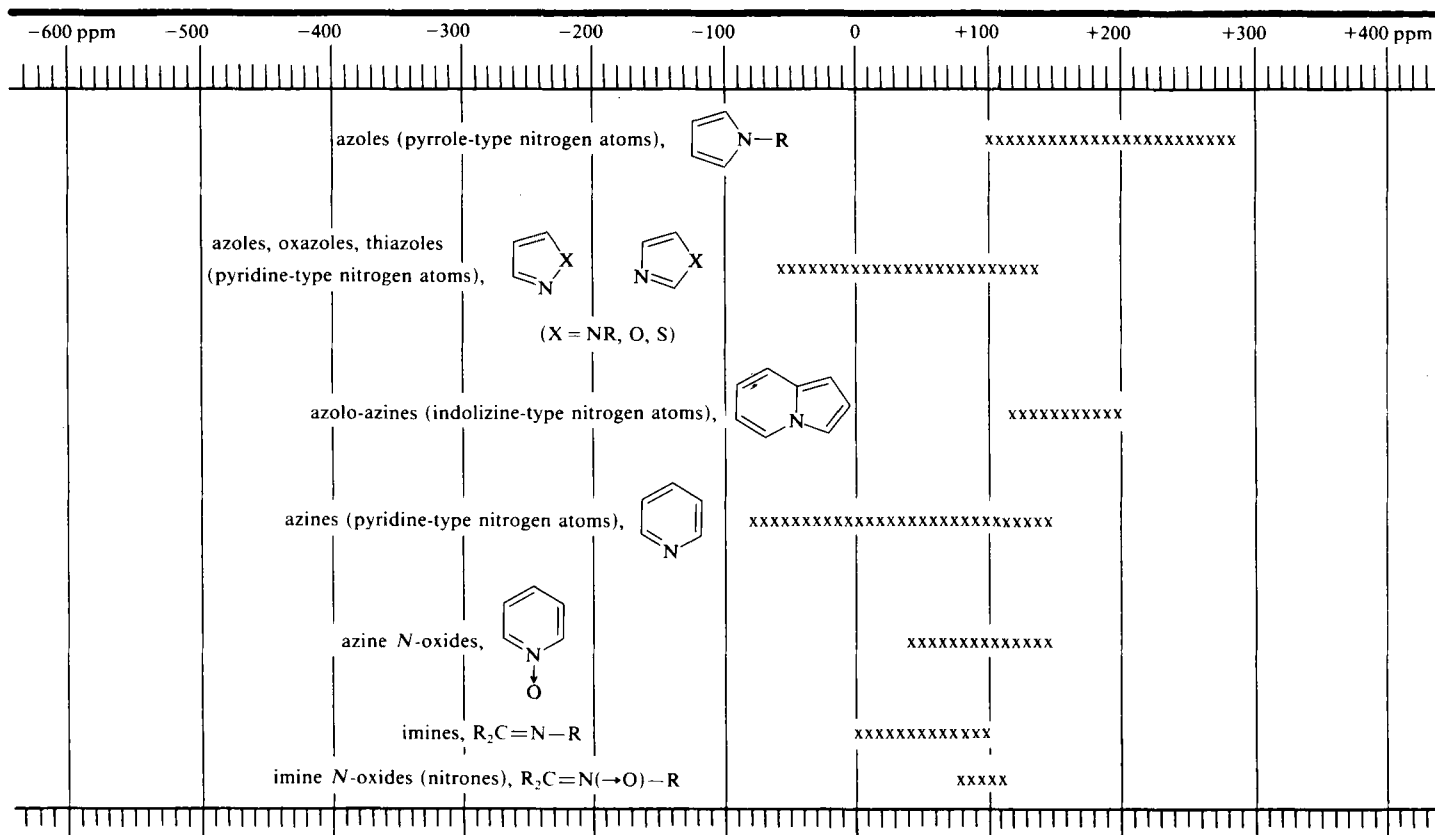
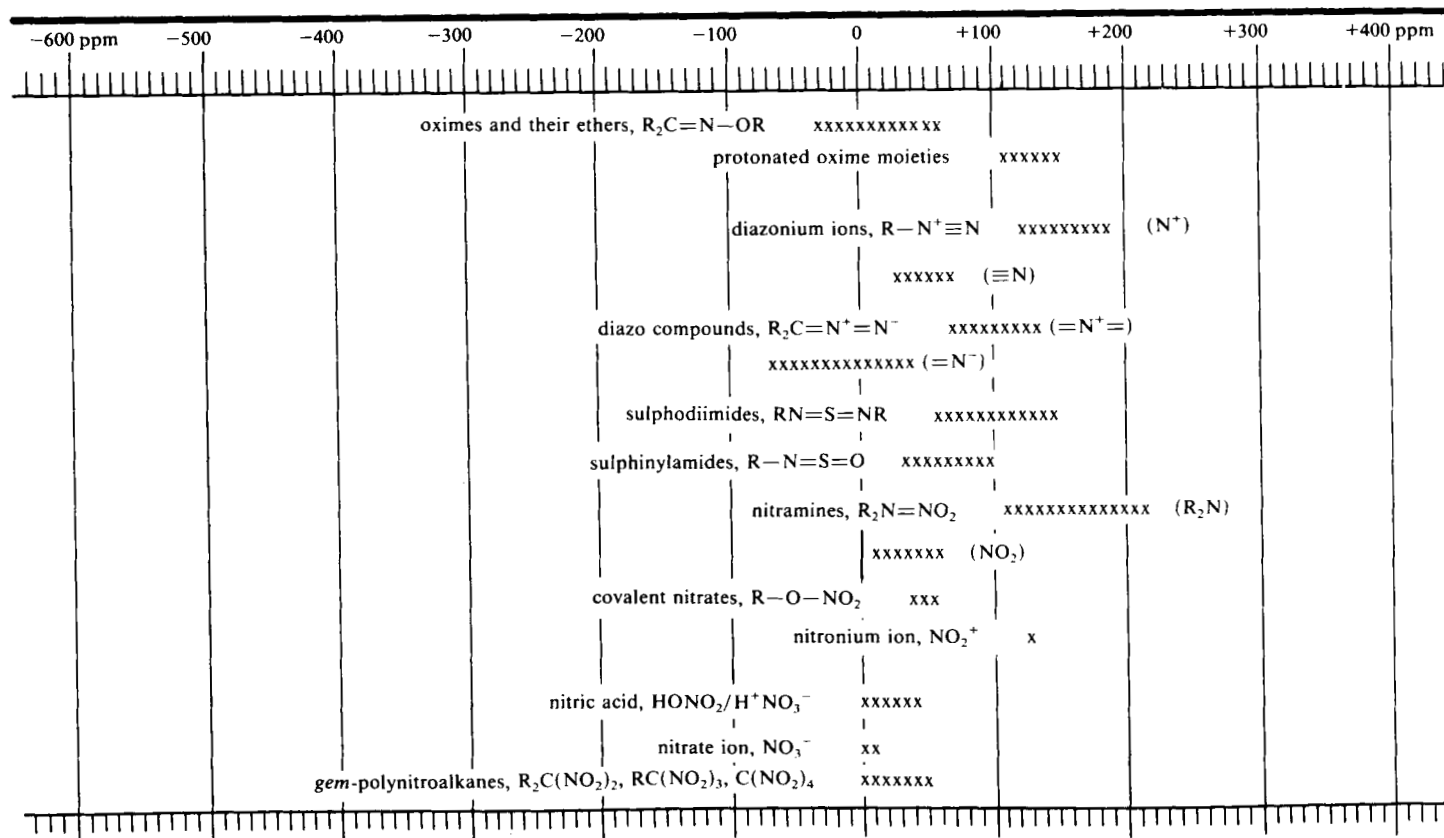
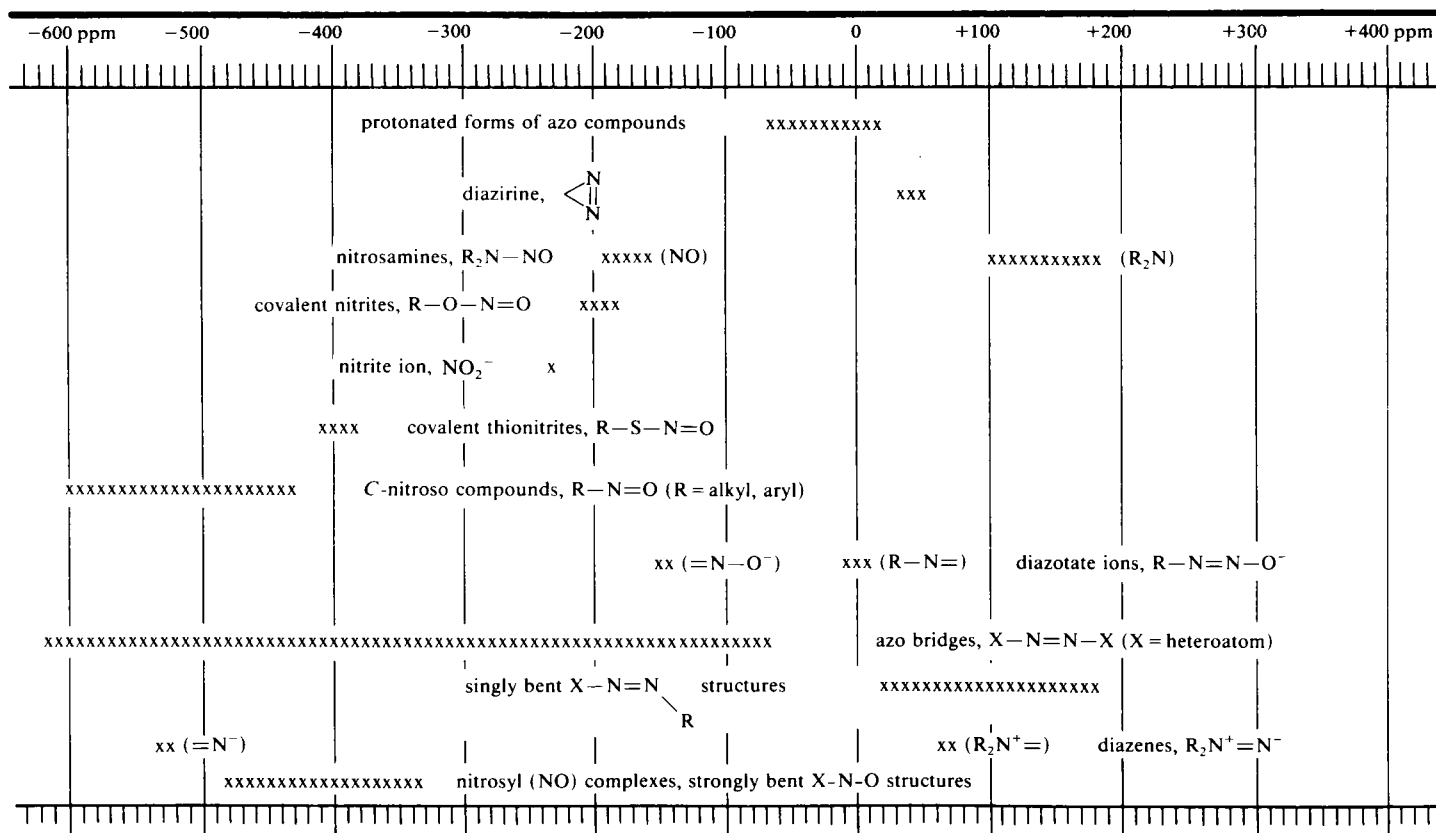


TABLE 10—cont.







Data from the present work as well as from refs. 1-4 and references therein; values quoted in this table represent maximum ranges observed for diamagnetic molecules and ions.

Table 11

Nitrogen shieldings in ammonia

Molecule	Solvent or state	Nitrogen shielding referred to neat liquid nitromethane	Notes
NH ₃	gaseous, 300.3 K, extrapolated to zero pressure	+400.86	(a)
	gaseous, 300 K, 0.4 MPa	+399.9	(b)
	neat liquid	+380.4	(a)
		+381.9	(c)
		+380.2	(d)
		+382	(g)
	inf.dil. in Me ₂ O	+390.1	(e)
	inf.dil. in Me ₃ CH	+387.8	(e)
	inf.dil. in Me ₂ NH	+387.7	(e)
	inf.dil. in Et ₂ O	+387.1	(e)
	inf.dil. in Me ₄ C	+386.7	(e)
	inf.dil. in MeNH ₂	+385.5	(e)
	inf.dil. in Et ₃ N	+385.4	(e)
	inf.dil. in Et ₂ NH	+385.1	(e)
	inf.dil. in MeOH	+384.4	(e)
	inf.dil. in EtNH ₂	+384.2	(e)
	inf.dil. in CCl ₄	+381.9	(e)
	inf.dil. in EtOH	+381.2	(e)
	inf.dil. in H ₂ O	+378.4	(e)
NH ₃ adsorbed in 88 HY-type zeolite	av. number of NH ₃ molecules per large cavity:		
	20.5 (300 K)	+369	(f)
	17.1 (300 K)	+364	(f)
	14.6 (300 K)	+364	(f)
	9.0 (300 K)	+362	(f)

Table 11 (continued)

	4.4 (380 K)	+361	(f)
	2.3 (380 K)	+361	(f)
	1.9 (380 K)	+361	(f)
NH ₃ as ligand in amino-type complexes			
	see Tables 127, 128		
NH ₃ + TlNO ₃	10 M TlNO ₃ in NH ₃	+359	(g)

(a) Data from ref. 56, ¹⁵N enriched ammonia, ¹⁵N spectra, 9.12 MHz, field perpendicular to sample tube; referred originally to neat liquid nitromethane (300 K), uncorrected for bulk susceptibility effects.

(b) Data from ref. 261, ¹⁵N enriched ammonia, details as in (a), corrected for bulk susceptibility effects.

(c) See ref. 1, p.158, high-precision ¹⁴N data, 300 K, bulk susceptibility effects eliminated by use of concentric spherical sample containers.

(d) See ref. 109, ¹⁵N data containing bulk susceptibility effects due to field perpendicular to sample tube.

(e) See ref. 4, p.151, and references therein; ¹⁵N data corrected for bulk susceptibility.

(f) Data from ref. 262, ¹⁵N enriched ammonia; ¹⁵N spectra, 9.12 MHz, field perpendicular to sample tube; referred originally to neat liquid nitromethane, uncorrected for bulk susceptibility effects.

(g) Data from ref. 263, PFT ¹⁴N spectra, 6.49 MHz, field perpendicular to sample tube, originally referred to NO₃⁻ in aqueous NH₄NO₃, +4 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

TABLE 12

Nitrogen shieldings in some alkylamines

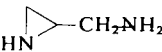
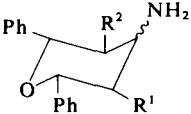
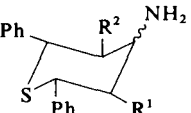
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
MeNH ₂	various	+385 to +376	(a, b)
EtNH ₂	2 M in H ₂ O	+351.0	(c)
	various	ca. +355	(b)
Pr ⁿ NH ₂	2 M in H ₂ O	+355.4	(c)
	2 M in MeOH	+359.3	(c)
	various	+361 to +355	(b)
Bu ⁿ NH ₂	various	+360 to +358	(a, b)
Bu ⁱ NH ₂	various	+364 to +363	(a, b)
	50% in CDCl ₃	+363.9 (NH ₂)	(d)
HOCH ₂ CH ₂ NH ₂	2 M in H ₂ O	+362.1	(c)
	2 M in MeOH	+365.9	(c)
	neat liquid	+363.5	(e)
H ₂ NCH ₂ CH ₂ NH ₂	2 M in H ₂ O	+360.3	(c)
	2 M in MeOH	+364.5	(c)
Me ₃ SiOCH ₂ CH ₂ NH ₂	neat liquid	+365.1	(e)
Et ₃ SiOCH ₂ CH ₂ NH ₂	20% in CDCl ₃	+364.9	(e)
Pr ⁱ NH ₂	various	ca. +338	(a, b)
Bu ^s NH ₂	various	+342 to +340	(b)
cyclohexylamine	various	ca. +340	(a, b)
	0.4 M in CDCl ₃		
R ¹ = R ² = H		+346.1 (ax), +339.0 (eq.)	(f)
R ¹ = Me, R ² = H		+355.9 (ax.), +344.1 (eq.)	(f)
R ¹ = Et, R ² = H		+357.3 (ax.), +344.5 (eq.)	(f)
R ¹ = R ² = Me		+365.2 (ax.), +349.2 (eq.)	(f)
	0.4 M in CDCl ₃		
R ¹ = R ² = H		+347.0 (ax), +338.0 (eq.) ^g	(f)
R ¹ = Me, R ² = H		+356.5 (ax.), +341.7 (eq.)	(f)
R ¹ = Et, R ² = H		+357.7 (ax.), +342.6 (eq.)	(f)

TABLE 12—*cont.*

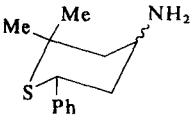
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
	0.4 M in CDCl_3	+340.8 (ax.), +337.9 (eq.) ⁸	(f)
Bu^iNH_2	various	+324 to +322	(a, b)
$(\text{Et})\text{Me}_2\text{CNH}_2$	various	ca. +328	(b)
Me_2NH	various	+374 to +371	(a, b)
Et_2NH	2 M in H_2O	+330.8	(c)
	2 M in MeOH	+333.3	(c)
	various	+334 to +332	(a, b)
Pr^n_2NH	2 M in MeOH	+339.8	(c)
	various	+342 to +340	(b)
$(\text{HOCH}_2\text{CH}_2)_2\text{NH}$	2 M in H_2O	+350.9	(c)
	2 M in MeOH	+352.7	(c)
	neat liquid	+351.4	(e)
$\text{EtNHCH}_2\text{CH}_2\text{NH}_2$	2 M in H_2O	{ +339.1 (NHEt) +354.5 (NH_2)	(c) (c)
$(\text{H}_2\text{NCH}_2\text{CH}_2)_2\text{NH}$	2 M in H_2O	{ +347.2 (NH) +359.6 (NH_2)	(c) (c)
	2 M in MeOH	{ +350.8 (NH_2) +359.8 (NH_2)	(c) (c)
$(\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2)_2$	2 M in H_2O	{ +346.8 (NH) +359.6 (NH_2)	(c) (c)
		+346.6 (central NH)	(c)
$(\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2)_2\text{NH}$	2 M in H_2O	+346.9 (NH)	(c)
		+359.7 (NH_2)	(c)
$(\text{Bu}^i)(\text{Pr}^i)\text{NH}$	neat liquid	+298.4	(h)
Pr^i_2NH	various	+307 to +304	(a, b)
Bu^i_2NH	neat liquid	+292.8	(h)
$(\text{Me}_3\text{SiOCH}_2\text{CH}_2)_2\text{NH}$	neat liquid	+353.6	(e)
Me_3N	0.2 M in CD_3OH		
	+0.1 M CD_3ONa	+362.9	(i)
	various	+373 to +362	(a, b)
Et_3N	2 M in MeOH	+331.7	(c)
	various	+334 to +332	(b)
$\text{Et}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	2 M in H_2O	{ +334.1 (NEt_2) +359.1 (NH_2)	(c) (c)
$\text{Et}_2\text{NCH}_2\text{CH}_2\text{NHEt}$	2 M in H_2O	{ +335.0 (NEt_2) +338.4 (NHEt)	(c) (c)
		+343.1	(c)
$\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{NH})_n\text{CH}_2\text{CH}_2\text{NH}_2$	in H_2O	+343.8 (NR_3)	(c)
+branched structures		+344.9	(c)
"Polyethyleneimine")	(pH = 11.0)	+346.4	(c)
		+346.8	(c)
		+359.5 (NH_2)	(c)

TABLE 12—*cont.*

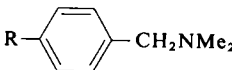
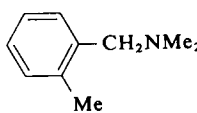
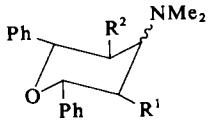
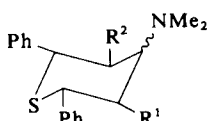
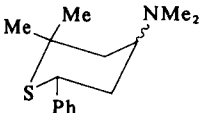
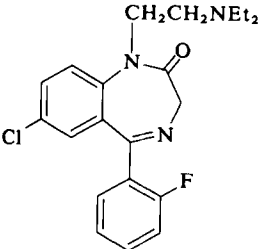
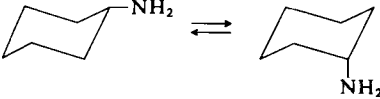
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
$\text{HOCH}_2\text{CH}_2\text{NMe}_2$	neat liquid	+358.0	(e)
$\text{Me}_3\text{SiOCH}_2\text{CH}_2\text{NMe}_2$	neat liquid	+359.9	(e)
$\text{Me}_2\text{Si}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2$	neat liquid	+359.9	(e)
$\text{MeSi}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_3$	neat liquid	+359.7	(e)
$\text{Me}_2\text{Si}(\text{Ph})\text{OCH}_2\text{CH}_2\text{NMe}_2$	in CDCl_3	+358.3	(e)
$\text{Me}_2\text{Si}(\text{Ph})\text{O}(\text{CH}_2)_3\text{NMe}_2$	in CDCl_3	+355.8	(e)
$\text{MeSi}(\text{Ph})(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2$	neat liquid	+359.9	(e)
$\text{Ph}_2\text{Si}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2$	neat liquid	+359.9	(e)
$(\text{HOCH}_2\text{CH}_2)_2\text{NMe}$	neat liquid	+353.2	(e)
$(\text{HOCH}_2\text{CH}_2)_2\text{NEt}$	neat liquid	+345.9	(e)
$(\text{HOCH}_2\text{CH}_2)\text{NPr}^n$	neat liquid	+348.2	(e)
$(\text{HOCH}_2\text{CH}_2)_2\text{NBu}^i$	neat liquid	+334.0	(e)
$(\text{HOCH}_2\text{CH}_2)_2\text{NPh}$	in CDCl_3	+322.5	(e)
$(\text{Me}_3\text{SiOCH}_2\text{CH}_2)_2\text{NMe}$	neat liquid	+354.6	(e)
$(\text{HOCH}_2\text{CH}_2)_3\text{N}$	neat liquid	+354.0	(e)
$(\text{Me}_3\text{SiOCH}_2\text{CH}_2)_3\text{N}$	neat liquid	+350.7	(e)
	2 M in MeCN-d_3		
R = NMe_2		+355.5 (CH_2NMe_2)	(j)
OMe		+355.1	(j)
Me		+356.4	(j)
H		+355.9	(j)
Br		+356.8	(j)
NO_2		+357.3 (NMe_2)	(j)
	neat liquid	+354.4	(k)
	0.4 M in CDCl_3		
$\text{R}^1 = \text{R}^2 = \text{H}$		+353.6 (ax.), +348.9 (eq.)	(f)
$\text{R}^1 = \text{Me}, \text{R}^2 = \text{H}$		+354.9 (ax.), +360.5 (eq.)	(f)
$\text{R}^1 = \text{Et}, \text{R}^2 = \text{H}$		+356.1 (ax.), +361.6 (eq.)	(f)
$\text{R}^1 = \text{R}^2 = \text{Me}$		+367.1 (eq.)	(f)
	0.4 M in CDCl_3		

TABLE 12—*cont.*

Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
$R^1 = R^2 = H$		+353.2 (ax.), +350.4 (eq.)	(f)
$R^1 = Me, R^2 = H$		+353.2 (ax.), +359.4 (eq.)	(f)
$R^1 = Et, R^2 = H$		+354.6 (ax.), +360.6 (eq.)	(f)
	0.4 M in $CDCl_3$	+351.3 (ax.), +351.3 (eq.)	(f)
 ("Flurazepam")	in $DMSO-d_6$	+363.0 (NEt_2)	(l)
	in $toluene-d_8$ 20 °C -100 °C in CD_2Cl_2 -100 °C	+337.5 +336.8 (eq.) +347.3 (ax.) +332.8 (eq.) +344.3 (ax.)	(m) (m) (m) (m) (m)

For additional data, see Tables 13–17 and ref. 1 (Table 17 therein); ref. 4 (pp. 151–153).

(a) See ref. 4, pp. 151–153, and references therein.

(b) See ref. 1, Table 17, and references therein.

(c) Data from ref. 606; ^{15}N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NO_3^- in aqueous NH_4NO_3 , +4.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

(d) Data from ref. 607; ^{15}N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(e) Data from ref. 269; ^{15}N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to neat nitromethane via calibrated HNO_3 sample, uncorrected for bulk-susceptibility effects; also ref. 608, and the same details.

(f) Data from ref. 265; ^{15}N natural abundance spectra, 27.4 MHz, field parallel to sample tube, originally referred to NH_4^+ in 5 M NH_4NO_3 in 2 M HNO_3 , +359.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); originally reported relative to "anhydrous liquid NH_3 " standard, taken at +21.6 ppm from the standard employed (this is erroneous since the conversion constant applies to field perpendicular to sample tube).

TABLE 12—*cont.*

(g) Solution in benzene- d_6 .

(h) Data from ref. 609; ^{15}N natural abundance spectra, 25.3 MHz, field parallel to sample tube, 0.08 M $\text{Cr}(\text{acac})_3$ added as relaxation reagent, originally referred to neat nitromethane via calibrated NO_3^- standard, uncorrected for bulk-susceptibility effects.

(i) Data from ref. 247; ^{15}N -enriched samples, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to 2 M PhNO_2 in Me_2SO_4 , +9.3 ppm from neat nitromethane, as can be reckoned from aqueous KNO_3 shielding reported there (−5.8 ppm from the standard employed), conversion scheme II, assuming KNO_3 shielding +3.5 ppm from nitromethane (Tables 4 and 6).

(j) Data from ref. 610; ^{15}N natural abundance spectra, 10.13 MHz, field perpendicular to sample tube, $\text{Cr}(\text{acac})_3$ added as relaxation reagent; originally referred to internal CD_3CN taken at +137.2 ppm from neat nitromethane; originally reported relative to nitromethane, but since the conversion constant should be +135.8 ppm (Table 6), 1.4 ppm were subtracted from original data to yield values that should not contain bulk-susceptibility effects.

(k) Data from ref. 611; ^{15}N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NO_3^- in an acidified solution, +1.5 ppm from neat nitromethane according to measurements there, conversion scheme IV (Table 4); $\text{Cr}(\text{acac})_3$ added as relaxation reagent, and this is probably responsible for the NO_3^- shielding reported (compare with data in Table 6).

(l) Data from ref. 363; ^{15}N natural abundance spectra, 20.28 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(m) Data from ref. 266; ^{15}N -labelled compound, ^{15}N spectra, 20.28 MHz, field parallel to sample tube, originally referred to satd. aqueous NH_4Cl , +352.9 ppm from neat nitromethane (Table 6), conversion scheme II, Table 4; originally reported relative to liquid NH_3 standard taken at +27.3 ppm from NH_4Cl ; this is erroneous, since the conversion constant applies to field perpendicular to sample tube (Table 6).

Table 13

Nitrogen shieldings and protonation effects in thermospermine and related polyamines

Compound and solution	Nitrogen shielding referred to neat nitromethane		
	in free amino group pH > 12.5	in ammonium moiety of fully protonated molecule pH < 2.5	protonation shift of nitrogen shielding
$\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_4\text{NH}_2$	+354.9 (1-N)	+347.3	-7.6
(1) (4) (8) (12)	+338.2 (4-N)	+334.8	-3.4
Thermospermine, 1.11 M in H_2O	+337.5 (8-N)	+334.4	-3.1
	+354.3 (12-N)	+347.1	-7.2
$\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_4\text{NH}_2$	+355.0 (1-N)	+347.3	-7.7
(1) (4) (8)	+337.9 (4-N)	+334.5	-3.4
Spermidine, 1.57 M in H_2O	+354.6 (8-N)	+347.1	-7.5
$\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_3\text{NH}_2$	+355.0 (1-N,	+347.3	-7.7
(1) (4) (8) (11)	11-N)		
Thermine, 0.98 M in H_2O	+338.3 (4-N,	+334.8	-3.5
	8-N)		

Table 13 (continued)

$\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_4\text{NH}(\text{CH}_2)_3\text{NH}_2$	+354.9 (1-N,	+347.3	-7.6
(1) (4) (9) (12)	12-N)		
Spermine, 0.79 M in H_2O	+337.7 (4-N,	+334.4	-3.3
	9-N)		

pK_a values derived from ^{15}N NMR titration curves

	pK_1	pK_2	pK_3	pK_4
Thermospermine	11.62 ± 0.04	10.57 ± 0.06	9.35 ± 0.17	8.31 ± 0.33
Spermidine	11.56 ± 0.13	10.80 ± 0.07	9.52 ± 0.03	-
Thermine	11.74 ± 0.46	10.86 ± 0.09	9.64 ± 0.10	8.64 ± 0.07
Spermine	11.50 ± 0.21	10.95 ± 0.16	0.79 ± 0.14	8.90 ± 0.46

Data from ref. 612 ^{15}N natural abundance spectra, 10.09 MHz, field perpendicular to sample tube, originally referred to NH_4^+ in NH_4NO_3 satd. in DMSO, +358.1 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

TABLE 14

Nitrogen shieldings in some cyclic amines

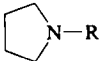
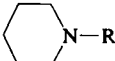
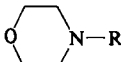
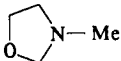
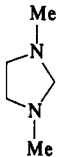
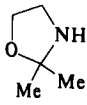
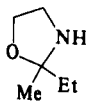
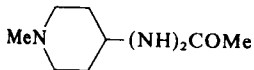
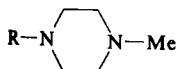
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
			
R = H	various	ca. +342	(a, b)
R = Me	various	ca. +340	(b)
			
R = H	various	ca. +343	(a, b)
R = Me	various	+344 to +341	(b)
			
R = H	various	ca. +350	(a, b)
R = Me	various	ca. +348	(b)
	in DMSO	+322.7	(c)
	in DMSO	+342.8	(c)
	in DMSO	+327.0	(c)
	in CDCl ₃	+324.5	(c)
	neat liquid	+305.4	(c)
	in DMSO	+315.8	(c)
	in CDCl ₃	+313.7	(c)
	neat liquid	+319.4	(c)
	in DMSO	+319.5	(c)
	in CDCl ₃	+318.4	(c)
	in DMSO	+342.1 (NMe)	(d)
	neat liquids		

TABLE 14—*cont.*

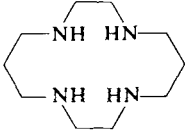
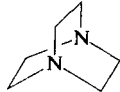
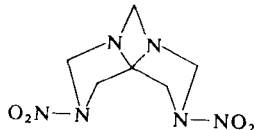
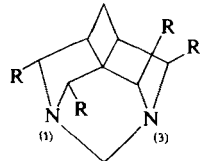
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane		Notes
R				
Et		+331.9 (NR)	+344.5 (NMe)	(e)
Pr ⁿ		+335.6	+344.6	(e)
Bu ⁿ		+335.3	+344.5	(e)
CH ₂ CMe ₃		+341.1	+345.1	(e)
CH ₂ CH ₂ CMe ₃		+334.8	+344.5	(e)
CH ₂ SiMe ₃		+342.5	+345.4	(e)
CH ₂ CH ₂ SiMe ₃		+331.1	+344.3	(e)
CH ₂ CH ₂ CH ₂ SiMe ₃		+334.6	+344.3	(e)
CH ₂ SiEt ₃		+343.3	+344.9	(e)
CH ₂ CH ₂ SiEt ₃		+330.3	+344.4	(e)
CH ₂ CH ₂ CH ₂ SiEt ₃		+334.7	+344.4	(e)
 ("cyclam")	1.0 M in DMSO	+344.9		(f)
 (hexamethylenetetramine, urotropine)	in CDCl ₃	+333.1		(g)
 (diazabicyclo[2.2.2]octane, DABCO)	in H ₂ O, pH = 12	+369		(h)
 O ₂ N—N—N—NO ₂	in acetone	+328.7 (amino-N)		(g)
 R = <i>p</i> -MeC ₆ H ₄	in CD ₂ Cl ₂	+300.0 (1-N) +286.5 (3-N)		(i) (i)

TABLE 14—*cont.*

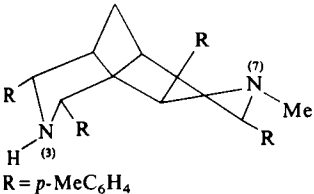
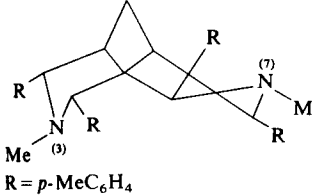
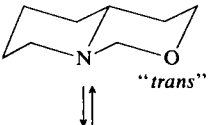
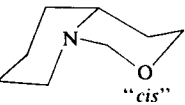
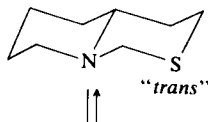
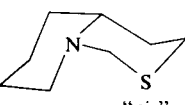
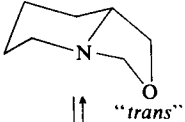
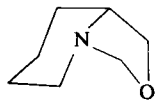
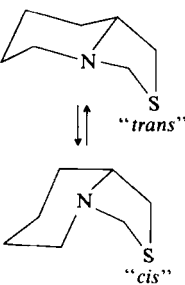
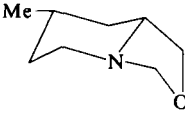
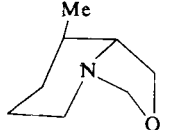
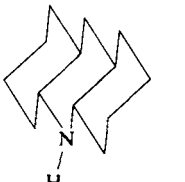
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
 R = <i>p</i>-MeC₆H₄	in CD ₂ Cl ₂	+300.1 (3-N) +305.4 (7-N)	(i) (i)
 R = <i>p</i>-MeC₆H₄	in CD ₂ Cl ₂	+307.2 (3-N) +305.4 (7-N)	(i) (i)
 "trans"	50% in CS ₂ /THF (1:1)	+314.8 (equilibrium, 27 °C)	(j)
 "cis"		+313.5 (<i>trans</i> , -95 °C)	(j)
 "trans"	50% in CS ₂ /THF (1:1)	+322.0 (equilibrium, 27 °C)	(j)
 "cis"		+313.4 (<i>trans</i> , -95 °C) +336.4 (<i>cis</i> , -95 °C)	(j) (j)
 "trans"	50% in CS ₂ /THF (1:1)	+313.5 (equilibrium, 27 °C)	(j)
 "cis"		+312.6 (<i>trans</i> , -111 °C) +313.2 (<i>cis</i> , -111 °C)	(j) (j)

TABLE 14—*cont.*

Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
	50% in CS ₂ /THF (1:1)	+311.1 (equilibrium, 27 °C) +309.5 (<i>trans</i> , -82 °C) +312.0 (<i>cis</i> , -82 °C)	(j) (j) (j)
	50% in CS ₂ /THF (1:1)	+314.8	(j)
	50% in CS ₂ /THF (1:1)	+315.5	(j)
	in benzene-d ₆	+311.1	(k)

For additional data, see ref. 1, Tables 19–22 therein.

(a) See ref. 4, pp. 152–157, and references therein.

(b) See ref. 1, Tables 19–22, and references therein.

(c) Data from ref. 120; ¹⁵N natural abundance spectra, 10.1 MHz, field perpendicular to sample tube Cr(acac)₃ added as relaxation reagent; originally referred to neat nitromethane, uncorrected for bulk susceptibility effects.

(d) Data from ref. 378; ¹⁵N natural abundance spectra, 18.25 MHz, field parallel to sample tube originally referred to 1 M HNO₃, +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(e) Data from ref. 614; ¹⁵N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube originally referred to neat nitromethane; uncorrected for bulk-susceptibility effects.

(f) Data from ref. 273; ¹⁵N natural abundance spectra, 18.25 MHz, field parallel to sample tube originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(g) Data from ref. 462; ¹⁵N-labelled compounds, ¹⁵N spectra, 20.27 MHz, field parallel to sample tube, originally referred to nitrobenzene, and originally recalibrated to neat nitromethane, uncorrected for bulk-susceptibility effects; 0.01–0.001 M solutions.

TABLE 14—*cont.*

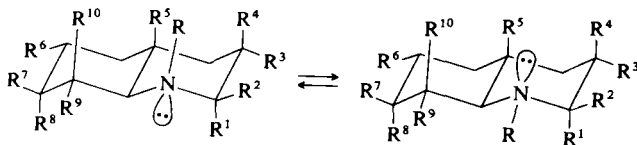
(h) Data from ref. 45; ^{15}N natural abundance spectra, 36.5 MHz, field parallel to sample tube, originally referred to neat formamide, +268 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(i) Data from ref. 471; ^{15}N -labelled compounds, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to 1 M NH_4Cl in 10 M HCl , +349.9 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); originally reported relative to liquid NH_3 , taken at +30.3 ppm from the standard employed; assignments based on NH coupling and nuclear Overhauser effects.

(j) Data from ref. 615; ^{15}N natural abundance spectra, 9.04 MHz, field perpendicular to sample tube, originally referred to satd. aqueous NH_4NO_3 (NH_4^+ , +359.6 ppm from neat nitromethane, Table 6), conversion scheme II (Table 4); originally reported relative to liquid NH_3 .

(k) Data from ref. 389; ^{15}N natural abundance spectra, 20.28 MHz, field parallel to sample tube, originally reported relative to liquid NH_3 , taken at +112.4 ppm from formamide used as actual reference, +268.6 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

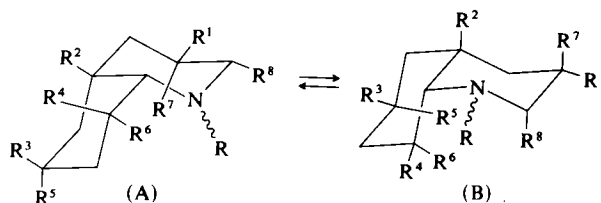
TABLE 15

Nitrogen shieldings in decahydroquinolines^a*trans*-decahydroquinoline systems

Nitrogen shielding referred
to neat nitromethane for N—R
moieties specified

Substituents R ⁿ (other than H)	R = H	R = Me
none	+325.9	+331.7
R ¹ = Me	+317.1	+336.8
R ² = Me	+308.0	+319.6
R ³ = Me	+325.1	+331.7
R ⁴ = Me	+336.1	+339.4
R ⁵ = Me	+332.7	+336.7
R ⁶ = Me	+326.6	+331.6
R ⁹ = Me	+330.6	+354.2
R ¹⁰ = Me	+328.8	+334.4
R ⁹ = Bu ^t	+325.9	+352.0
R ¹⁰ = Bu ^t	+324.5	+333.3
R ¹ = R ⁹ = Me	+321.3	+346.0
R ² = R ⁹ = Me	+313.4	+344.4
R ¹ = R ¹⁰ = Me	+320.0	+339.9
R ² = R ¹⁰ = Me	+310.2	+321.9
R ³ = R ⁵ = Me	+333.0	+337.6
R ⁵ = R ⁹ = Me	+338.9	+353.7
R ⁷ —R ⁹ = —(CH ₂) ₄ —	+331.9	—
R ⁸ —R ⁹ = —(CH ₂) ₄ —	+332.1	—
R ⁷ —R ¹⁰ = —(CH ₂) ₄ —	+329.9	—

TABLE 15—cont.

*cis*-decahydroquinoline systems

Nitrogen shielding referred
to neat nitromethane for N—R
moieties specified
(A/B isomer ratio in parentheses)

Substituents R ⁿ (other than H)		
	R = H	R = Me
none	+336.5 (90:10)	+342.8 (70:30)
R ¹ = Me	+337.0 (100:0)	+343.7 (>95:<5)
R ² = Me	+335.0 (95:5)	+345.0 (77:23)
R ³ = Me	+334.7 (11:89)	+340.5 (<5:>95)
R ⁴ = Me	+336.6 (41:59)	—
R ⁵ = Me	+337.5 (100:0)	+344.0 (100:0)
R ⁶ = Me	+346.8 (100:0)	+341.1 (100:0)
R ⁷ = Me	+331.6 (0:100)	+343.2 (0:100)
R ⁸ = Me (b)	+320.1	—
R ² = R ⁶ = Me	+345.2 (100:0)	+340.1 (100:0)
R ¹ = R ² = Me	+333.8 (100:0)	+341.7 (100:0)
R ² = R ⁷ = Me	+340.8 (0:100)	+351.4 (0:100)
R ⁶ = Bu ^t (b)	+347.0	—

(a) Unless otherwise indicated, data are from ref. 232 (*trans* systems) and ref. 616 (*cis* systems); ¹⁵N natural abundance spectra, 10.09 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; originally reported relative to NH₃ liquid taken at +380.2 ppm from nitromethane; 2–4 M solutions in benzene.

(b) Data from ref. 389; ¹⁵N natural abundance spectra, 20.28 MHz, field parallel to sample tube, originally referred to neat formamide, +268.6 ppm from nitromethane (Table 6), conversion scheme IV (Table 4); originally reported relative to NH₃ standard taken at +112.4 ppm from the standard employed; 3–5 M solutions in benzene.

TABLE 16

Nitrogen shieldings in some aziridines, azetidines and oxaziridines

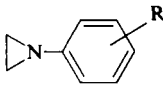
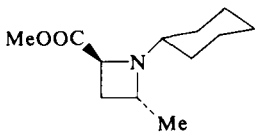
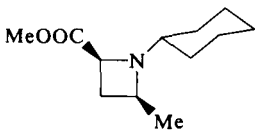
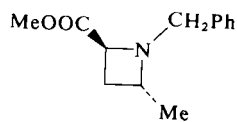
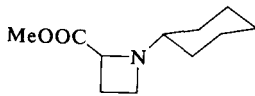
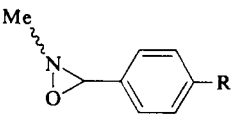
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	50% in CDCl ₃		
R ¹ R ²		+305.7	
H H		+390.4	(a)
H Me		+370.7	(a)
H Et		+372.8	(a)
H CONH ₂		+366.4 (NH)	(a)
H CONHNH ₂		+367.2 (NH, ring)	(a)
H CH ₂ NH ₂		+375.3 (NH)	(a)
H CN		+367.0 (NH)	(a)
H COOMe		+364.3	(a)
Me Me		+351.9	(a)
	4 M in CDCl ₃		
R			
H		+340.4	(b)
4-NMe ₂		+345.2 (ring)	(b)
4-OMe		+344.1	(b)
4-Me		+342.2	(b)
4-F		+342.8	(b)
4-Cl		+340.6	(b)
4-CN		+334.5 (ring)	(b)
4-NO ₂		+332.9 (ring)	(b)
2-Me		+342.3	(b)
2,6-Me ₂		+342.4	(b)
	in MeNO ₂	+306	(c)
	in MeNO ₂	+316	(c)

TABLE 16—*cont.*

Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	in MeNO ₂	+309	(c)
	in MeNO ₂	+320	(c)
	2 M in MeCN		
R			
OME		+227.9 (<i>cis</i>)	(d)
		+232.9 (<i>trans</i>)	(d)
Me		+229.2 (<i>cis</i>)	(d)
		+233.3 (<i>trans</i>)	(d)
H		+228.7 (<i>cis</i>)	(d)
		+232.2 (<i>trans</i>)	(d)
Br		+226.8 (<i>cis</i>)	(d)
		+230.3 (<i>trans</i>)	(d)
NO ₂		+226.4 (<i>cis</i>) (N, ring)	(d)
		+229.6 (<i>trans</i>) (N, ring)	(d)

For additional data see ref. 1, Table 23 therein.

(a) Data from ref. 607; ¹⁵N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(b) Data from ref. 44; ¹⁵N natural abundance spectra, 10.09 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; originally reported relative to liquid NH₃ standard, taken at +380.2 ppm from nitromethane.

(c) Data from ref. 617; ¹⁵N natural abundance spectra, 10.1 MHz, referred originally to internal nitromethane standard and solvent; no bulk-susceptibility effects apart from those resulting from solvent-solute interaction.

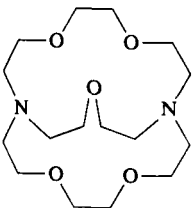
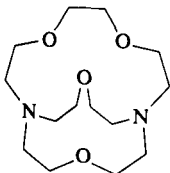
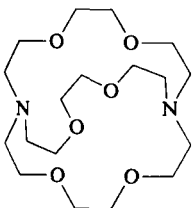
(d) Data from ref. 610; ¹⁵N natural abundance spectra, 10.13 MHz, originally referred to internal MeCN solvent/standard taken at +137.2 ppm from neat nitromethane; since the conversion constant should be +135.8 ppm (Table 6), 1.4 ppm were subtracted from original data.

TABLE 17

Nitrogen shieldings in amino moieties in some coronands and cryptands,
their hydrochlorides and metal-salt complexes

Ligand	Salt or acid added	Nitrogen shielding (referred to neat nitromethane) of amino moieties in ligand	
		In CHCl_3 (0.2–0.8 M)	in MeOH (0.2–0.9 M)
	none LiSCN	+359.0 +359.7	
	none 2 HCl LiSCN NaSCN	+351.1 +349.1 (0.2 M) +349.6 (0.5 M) +352.6 +355.3	+342.7
	none 2 HCl NaSCN $\text{Ca}(\text{NO}_3)_2$	+351.6 +358.1 +350.0	+350.5 +340.5
	none NaSCN KSCN $\text{Sr}(\text{NO}_3)_2$ $\text{Ba}(\text{SCN})_2$ AgNO_3 TlNO_3 $\text{Bu}^+\text{NH}_3^+\text{Cl}^-$	+350.6 +351.9 +354.1 	+347.4 +345.2 +337.3 +355.9 +331.9 +358.1
	none 2 HCl NaSCN KSCN $\text{Sr}(\text{NO}_3)_2$ $\text{Ba}(\text{SCN})_2$ AgNO_3 TlNO_3	+350.8 +356.1 +354.0 +353.8	+349.6 +337.8 +350.5 +345.3 +339.4

TABLE 17—*cont.*

Ligand	Salt or acid added	Nitrogen shielding (referred to neat nitromethane) of amino moieties in ligand	
		in CHCl_3 (0.2–0.8 M)	in MeOH (0.2–0.9 M)
	none	+351.2 (0.2 M)	+350.3
		+351.4 (0.7 M)	
	2 HCl	+349.5	+341.8
	NaSCN	+355.6	
	KSCN	+349.7	+350.6
	CaCl_2	+346.9	
	$\text{Sr}(\text{NO}_3)_2$	+345.6	
	$\text{Ba}(\text{SCN})_2$	+340.5	
	none	+352.3 (0.4 M)	+350.8
		+352.7 (1.5 M)	
	2 HCl		+343.0
	LiCl	+358.1	
	NaSCN	+357.6	
	$\text{Mg}(\text{SCN})_2$	+357.0	
	$\text{Ca}(\text{NO}_3)_2$	+346.6	+347.0
	none	+349.7	+349.8
	2 HCl		+341.0
	NaSCN	+356.6	
	KSCN	+349.4	
	NH_4Cl	+344.8	
	$\text{Sr}(\text{NO}_3)_2$	+346.9	
	$\text{Ba}(\text{SCN})_2$	+340.1	+340.5
	AgNO_3	+344.7	
	TiNO_3	+333.4	

Data from ref. 267; ^{15}N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO_3 , corrected for bulk-susceptibility effects; conversion constant +4.4 ppm relative to neat nitromethane was therefore employed (Table 6) in order to obtain shieldings referred to nitromethane that do not contain bulk-susceptibility effects.

TABLE 18

Nitrogen shieldings in some enamines, enaminones and related structures

Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes		
HC(=O)CH=CH-CH=CH-NMe ₂	0.5 M in H ₂ O	+279.3	(a)		
	0.5 M in MeOH	+295.4	(a)		
	0.5 M in DMSO	+299.5	(a)		
	0.5 M in CHCl ₃	+305.7	(a)		
	satd. in CCl ₄	+314.2	(a)		
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{C} \\ \diagup \quad \diagdown \\ \text{CH}=\text{CH} \end{array} \begin{array}{c} \text{R}^2 \\ \diagup \\ \text{N}-\text{R}^3 \end{array} \leftrightarrow \begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{C} \\ \diagup \quad \diagdown \\ \text{CH}=\text{CH} \end{array} \begin{array}{c} \text{NR}^2\text{R}^3 \end{array}$ (A) <i>cis-s-cis</i> (Z, s-Z) $\leftrightarrow \begin{array}{c} \text{R}^1 \\ \diagup \\ \text{O}=\text{C} \\ \diagdown \quad \diagup \\ \text{CH}=\text{CH} \end{array} \begin{array}{c} \text{NR}^2\text{R}^3 \end{array}$ (C) <i>trans-s-trans</i> (E, s-E) (if R¹ ≠ H, <i>trans-s-skew</i>)					
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{C} \\ \diagup \quad \diagdown \\ \text{CH}=\text{CH} \end{array} \begin{array}{c} \text{R}^2 \\ \diagup \\ \text{N}-\text{R}^3 \end{array} \leftrightarrow \begin{array}{c} \text{O} \\ \parallel \\ \text{R}^1-\text{C} \\ \diagup \quad \diagdown \\ \text{CH}=\text{CH} \end{array} \begin{array}{c} \text{NR}^2\text{R}^3 \end{array}$ (B) <i>trans-s-cis</i> (E, s-Z)					
R ¹	R ²	R ³			
H	Me	Me	0.5 M in H ₂ O	+276.4	(a)
			0.5 M in MeOH	+288.9	(a)
			5-10 M in benzene-d ₆	+295.6 (B ⇌ C)	(b)
			0.5 M in DMSO	+296.9	(a)
			0.5 M in CHCl ₃	+299.4	(a)
			2 M in CDCl ₃	+289.0	(c)
			0.5 M in HCONMe ₂	+299.6	(a)
			0.5 M in CH ₂ Cl ₂	+300.5	(a)
			0.5 M in acetone	+302.6	(a)
			0.5 M in dioxane	+304.8	(a)
			satd. in CCl ₄	+305.0	(a)
			0.5 M in benzene	+306.2	(a)
Me	H	Me	5-10 M in benzene-d ₆	+285.9 (A)	(b)
			(24 °C)	+294.9 (B ⇌ C)	(b)
			5-10 M in CDCl ₃	+284.2 (A)	(b)
			(24 °C)	+293.8 (B ⇌ C)	(b)
			5-10 M in acetone-d ₆	+284.7 (A)	(b)
			(0 °C)	+295.9 (B ⇌ C)	(b)
				+280.1 (A)	(b)
			(-80 °C)	+289.9 (B)	(b)
				+292.8 (C)	(b)

TABLE 18—*cont.*

Compound			Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
Et	H	Me	5-10 M in CD ₂ Cl ₂		
			(23 °C)	+284.9 (A)	(b)
				+294.8 (B $\rightleftharpoons$ C)	(b)
			(-60 °C)	+281.7 (A)	(b)
				+288.4 (B)	(b)
				+291.0 (C)	(b)
			5-10 M in CDCl ₃		
			(23 °C)	+285.1 (A)	(b)
				+294.3 (B $\rightleftharpoons$ C)	(b)
			(-60 °C)	+281.6 (A)	(b)
Pr ⁱ	H	Me		+290.0 (B)	(b)
				+292.8 (C)	(b)
			5-10 M in acetone-d ₆		
			(-80 °C)	+281.2 (A)	(b)
				+291.8 (B)	(b)
				+294.4 (C)	(b)
			5-10 M in tetrahydropyran-d ₈		
			(0 °C)	+286.1 (A)	(b)
				+296.1 (B $\rightleftharpoons$ C)	(b)
			(-65 °C)	+282.6 (A)	(b)
Bu ^t	H	Me		+292.9 (B)	(b)
				+295.5 (C)	(b)
			5-10 M in benzene-d ₆		
			(10 °C)	+286.5 (A)	(b)
				+294.9 (B $\rightleftharpoons$ C)	(b)
			5-10 M in acetone-d ₆		
			+Cr(acac) ₃ (24 °C)	+302.5 (B $\rightleftharpoons$ C)	(b)
			in TFA-d (24 °C)		
			(protonated form)	+230.9 (B—H ⁺)	(d)
				+233.7 (C—H ⁺)	(d)
Bu ^t	Me	Me		+303.7 (B—C)	(b)
			5-10 M in benzene-d ₆		
			(24 °C)		
			in TFA-d (24 °C)		
			(protonated form)	+227.7 (B—H ⁺)	(d)
			5-10 M in acetone-d ₆		
			(25 °C)	+294.9 (B)	(d)
			in TFA-d (24 °C)		
			(protonated form)	+228.3 (B—H ⁺)	(d)
Ph	Me	Me	5-10 M in acetone-d ₆		
			(25 °C)	+294.9 (B)	(d)
			in TFA-d (24 °C)		
			(protonated form)	+228.3 (B—H ⁺)	(d)
Me	Et	Et	5-10 M in CDCl ₃		
			(24 °C)	+271.4 (B—C)	(d)
			in TFA-d (24 °C)		
			protonated forms	+203.0 (B—H ⁺)	(d)
				+205.2 (C—H ⁺)	(d)

TABLE 18—*cont.*

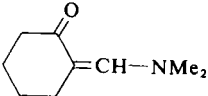
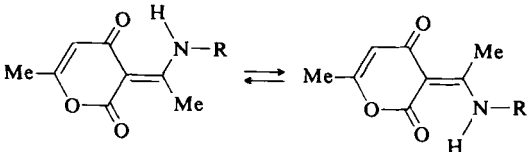
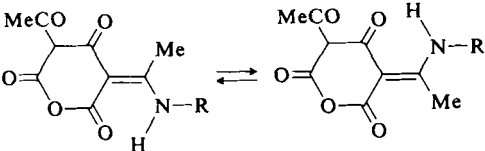
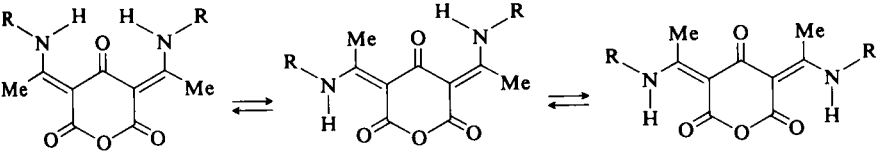
Compound			Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
Et	Et	Et	5–10 M in acetone-d ₆ (24 °C)	+275.3 (B C)	(b)
Pr ⁱ	Et	Et	5–10 M in acetone-d ₆ (28 °C)	+274.4 (B C)	(b)
			in TFA-d (24 °C)	+202.1 (B–H ⁺)	(d)
			(protonated forms)	+206.6 (C–H ⁺)	(d)
MeOOC–C(NO ₂)=CH–NH ₂			in CH ₂ Cl ₂ /DMSO	+253 ± 8 (NH ₂)	(e)
MeOOC–C(NO ₂)=CH–NHMe			in CH ₂ Cl ₂	+269 ± 5 (NHMe)	(e)
Et–C(=O)–C(Me)=CH–NMe ₂			5–10 M in benzene-d ₆	+312.1	(d)
			in TFA-d	+176.1	(d)
			(C-protonation)		
Me–C(=O)–C(Me)=CH–NMe ₂			5–10 M in benzene-d ₆	+312.7	(d)
			in TFA-d	+175.5	(d)
			(C-protonation)		
			5–10 M in acetone-d ₆	+303.8	(d)
			in TFA-d		
			(O-protonation)	+227.0	(d)
			(C-protonation)	+173.0	(d)
					
R = Me			in CDCl ₃	+240.6	(f)
R = Ph			in CDCl ₃	+218.1	(f)
			in acidified DMSO (pH = 2)	+220.2	(f)
					
R = Me			in CDCl ₃	+241.0	(f)
			in acidified DMSO (pH = 2)	+240.7	(f)
R = Ph			in CDCl ₃	+219.5	(f)

TABLE 18—*cont.*

Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
			
R = Me	in CDCl ₃	+250.3; +248.4	(f)
	in acidified DMSO (pH = 2)	+244.9; +241.8	(f)
R = Ph	in CDCl ₃	+226.0; +223.5	(f)
	in acidified DMSO (pH = 2)	+226.1; +222.9	(f)

For additional data see ref. 1, Tables 26 and 27 therein

(a) Data from ref. 32; ¹⁵N-labelled compounds, ¹⁵N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to aqueous KNO₂, -228.9 ppm from neat nitromethane, conversion scheme II; originally reported relative to "aqueous NH₄Cl" at +590.7 ppm from the standard employed, probably NH₄NO₃ or (NH₄)₂SO₄ (Tables 6, 4).

(b) Data from ref. 618; ¹⁵N natural abundance INEPT spectra, 20.28 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(c) Data from ref. 619; ¹⁵N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NO₃⁻ standard, calibrated (+1.5 ppm) against neat nitromethane, conversion scheme IV (Table 4); Cr(acac)₃ used as relaxation reagent; the latter is probably responsible for the value of 1.5 ppm, which is different from those for NO₃⁻ shown in Table 6.

(d) Data from ref. 123; details as in footnote (b).

(e) Data from ref. 620; low-precision ¹⁴N NMR measurements, 6.4 MHz, originally referred to neat nitromethane.

(f) Data from ref. 437; ¹⁵N-labelled compounds, ¹⁵N spectra, 27.4 MHz, field parallel to sample tube, originally referred to NO₃⁻ in 5 M NH₄NO₃ in 2 M HNO₃, +4.6 ppm from neat nitromethane (Table 6), conversion scheme II; originally reported relative to liquid NH₃ standard, taken at +380.2 ppm from nitromethane; this is incorrect since the latter value refers to field perpendicular to sample tube.

Table 19

Some additional data on nitrogen shieldings in enamines

Compound	Solvent	Isomer (designation see Table 18)	Nitrogen shielding referred to neat nitromethane
EtCO-CH=CH-NH_2	benzene-d ₆	A	+289.6
		$\text{B} \rightleftharpoons \text{C}$	+300.0
$\text{Pr}^i\text{CO-CH=CH-NH}_2$	benzene-d ₆	A	+290.5
	THF-d ₈	A	+287.5
		$\text{B} \rightleftharpoons \text{C}$	+297.8
$\text{Bu}^t\text{CO-CH=CH-NH}_2$	benzene-d ₆	A	+289.8
		$\text{B} \rightleftharpoons \text{C}$	+300.0
PhCO-CH=CH-NH_2	THF-d ₈	A	+287.8
		$\text{B} \rightleftharpoons \text{C}$	+300.1
MeCO-CMe=CMe-NH_2	benzene-d ₆	A	+274.4
$(\text{MeCO})_2\text{C=CH-NH}_2$	CDCl_3	A, B, C	+273.0
MeCO-CH=CH-NHMe	CD_2Cl_2	A	+281.7
		B	+288.4
		C	+291.0
EtCO-CH=CH-NHMe	benzene-d ₆	A	+286.4
		$\text{B} \rightleftharpoons \text{C}$	+296.0
$\text{Pr}^i\text{CO-CH=CH-NHMe}$	THF-d ₈	A	+286.1
		$\text{B} \rightleftharpoons \text{C}$	+296.1
$\text{Bu}^t\text{CO-CH=CH-NHMe}$	benzene-d ₆	A	+286.5
		B	+294.9

Table 19 (continued)

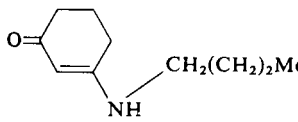
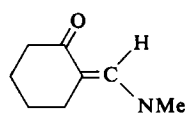
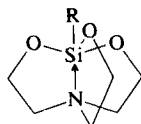
$\text{Pr}^i\text{CO}-\text{CH}=\text{CH}-\text{NH}-\text{Bu}^t$	CDCl_3	A	+247.3
	benzene- d_6	A	+250.5
	CDCl_3	C	+274.2
$\text{MeCO}-\text{CH}=\text{CMe}-\text{NHCHMe}_2$	CDCl_3	A	+249.2
	benzene- d_6	A	+253.0
$\text{EtCO}-\text{CMe}=\text{CH}-\text{NHMe}$	CD_2Cl_2	A	+291.5
		$\text{B} \rightleftharpoons \text{C}$	+303.1
$\text{EtCO}-\text{CMe}=\text{CH}-\text{NHEt}$	CD_2Cl_2	A	+273.5
		$\text{B} \rightleftharpoons \text{C}$	+286.0
$(\text{MeCO})_2-\text{C}=\text{CH}-\text{NHMe}$	CDCl_3	A, B, C	+268.0
$(\text{MeCO})_2-\text{C}=\text{CH}-\text{NHPh}$	CDCl_3	A, B, C	+249.2
$\text{HCO}-\text{CH}=\text{CH}-\text{NMe}_2$	benzene- d_6	C	+294.1
	acetone- d_6	C	+293.3
	$\text{MeOH}-\text{d}_4$	C	+283.5
$\text{PrCO}-\text{CH}=\text{CH}-\text{NMe}_2$	benzene- d_6	$\text{B} \rightleftharpoons \text{C}$	+303.6
	acetone- d_6	$\text{B} \rightleftharpoons \text{C}$	+302.2
	$\text{MeOH}-\text{d}_4$	$\text{B} \rightleftharpoons \text{C}$	+282.4
$\text{PhCO}-\text{CH}=\text{CH}-\text{NMe}_2$	$\text{MeOH}-\text{d}_4$	$\text{B} \rightleftharpoons \text{C}$	+284.9
$\text{Bu}^t\text{CO}-\text{CH}=\text{CH}-\text{NMe}_2$	benzene- d_6	B	+303.7
$\text{Bu}^t\text{CO}-\text{CD}=\text{CH}-\text{NMe}_2$	TFA- d	B	+227.7

Table 19 (continued)

	benzene-d ₆	B	+304.0
	acetone-d ₆	B	+303.8
	MeOH-d ₄	B	+290.7
MeCO-CMe=CH-NMe ₂	benzene-d ₆	B $\rightleftharpoons$ C	+312.6
EtCO-CMe=CH-NMe ₂	benzene-d ₆	B $\rightleftharpoons$ C	+311.3
EtOCO-CH=CH-NHMe	CDCl ₃	A	+296.9
		B $\rightleftharpoons$ C	+305.0
EtOCO-CMe=CH-NHMe	CD ₂ Cl ₂	A	+302.3
		B $\rightleftharpoons$ C	+310.1
EtOCO-CH=CMe-NHCH ₂ Ph	CDCl ₃	A	+278.1
	benzene-d ₆	A	+283.7
Me ₂ NCO-CH=CH-NMe ₂	benzene-d ₆	A	+312.8
Me ₂ NCO-CD=CH-NMe ₂	MeOH-d ₄	B	+305.2
Bu ^t NHCO-CH=CH-NMe ₂	CDCl ₃	B	+314.2
Et ₂ NCO-CH=CH-NHMe	benzene-d ₆	A	+302.1
		B	+306.4
Pr ₂ ⁱ NCO-CH=CH-NHMe	benzene-d ₆	A	+302.9
		B	+307.0

Data from ref. 129 ¹⁵N natural abundance INEPT spectra, 20.28 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk susceptibility effects.

TABLE 20

Nitrogen shieldings in some silatranes^a

Nitrogen shielding referred to neat nitromethane

R	gas ^b	solid ^b	in CCl ₄	in benzene	in chloro- benzene	in THF	in CHCl ₃	in Bu ^t OH	in CH ₂ Cl ₂	in CD ₃ CN	in CD ₃ OD	in DMSO	in D ₂ O
Me	+370.7	+355.6	+363.4	+362.2	+360.9	+360.5	+359.4 +357.3 ^c	+359.2	+358.8	+357.5	+356.8	+356.4	+353.5
H ₂ C=CH—	—	—	+361.6	+359.7	+358.3	+358.4	+356.8	+357.2	+356.4	+355.3	+355.3	+354.4	+352.4
CH ₂ Cl	—	+351.9	+357.0	+355.9	+355.1	+354.6	+354.1	+353.9	+353.9	+353.5	+353.2	+352.6	+351.2
CHCl ₂	—	+349.2	—	—	+352.7	—	+351.8	—	—	—	—	+350.6	+350.0
CH ₂ I	—	—	—	—	+356.0	—	+354.8	—	—	—	—	+352.6	—
Ph	—	+353.6	—	—	+358.0	—	+356.3	—	—	—	—	+354.4	—
H	—	+351.6	—	—	+355.9	—	+354.4	—	—	—	—	+353.6	+351.7
Cl	—	—	—	—	—	—	+348.8	—	—	—	—	+347.8	+347.3
F	—	—	—	—	—	—	+349.3	—	—	—	—	+348.4	—
OMe	—	+350.1	—	—	—	—	+352.7	—	—	—	—	+351.3	—

(a) Unless otherwise indicated, data from ref. 137; ¹⁵N enriched samples, ¹H-¹⁵N INDOR spectra, 80/8.106 MHz, originally referred to neat nitromethane via internal SiMe₄ standard frequency; thus data do not contain bulk-susceptibility effects, but do contain solvent effects on proton shift of SiMe₄; 0.1–1 M solutions.

(b) Data from ref. 270; ¹⁵N-enriched compounds; ¹⁵N gas-phase spectra as in footnote (a); for solid samples, ¹⁵N CP-MASS spectra, 20.28 MHz, originally referred to solid (NH₄)₂SO₄, +355.7 ppm from neat liquid nitromethane (Table 6), conversion scheme IV (Table 4); temperature dependence of nitrogen shielding in some silatranes was also determined (Table 9).

(c) Data from ref. 268; ¹⁵N-enriched samples, ¹⁵N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; ca. 5% solutions.

TABLE 21

Nitrogen shieldings in some germatranes, boratranes and analogous structures

Compound	Nitrogen shielding referred to neat nitromethane			Notes
	in CCl ₄	in CHCl ₃	in DMSO	

X	R				
Ge	Me		+367.1	+365.7	(a)
		+369.1	+367.1	+365.8	(b)
Ge	Bu ^t	+369.2	+367.6	+365.9	(b)
Ge	Et		+367.1		(d)
Ge	CH=CH ₂	+368.2	+366.2	+365.5	(b)
Ge	Ph	+368.2	+366.3	+365.0	(b)
Ge	OPh	+365.2	+362.9	+362.4	(b)
Ge	OEt		+362.6		(d)
			+360.3	+359.5	(a, d)
Ge	Cl		+360.3	+359.8	(b)
Ge	Br		+360.0	+358.6	(b)
Ge	α -naphthyl		+366.4		(c)
Ge	β -naphthyl		+365.9		(c)
B	—		+319.9	+319.9	(a)
			+319.9		(c)
V=O	—			+324.8	(b)
Mo	—			+318.6	(b)

(a) Data from ref. 137; for details see Table 20, note (a).

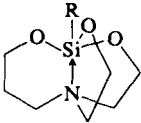
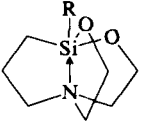
(b) Data from ref. 138; 0.05 mol % solutions, details as in Table 20, note (a).

(c) Data from ref. 268 and Table 20, note (c).

(d) Data from ref. 139; details as in Table 20, note (a).

TABLE 22

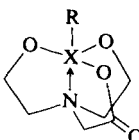
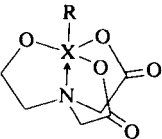
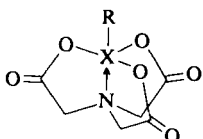
Nitrogen shieldings in some analogues of silatrane
structures (0.5 M solutions in CDCl_3)

Compound	Nitrogen shielding referred to neat nitromethane
	
R = Me	+356.2
CH_2Cl	+347.5
$\text{CH}=\text{CH}_2$	+352.7
Ph	+352.5
	
R = Me	+356.9
Ph	+353.8

Data from ref. 268; ^{15}N -enriched samples, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

TABLE 23

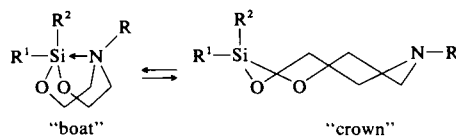
Nitrogen shieldings in some silatranones and germatranones

General formula		Nitrogen shielding referred to neat nitromethane for solutions in DMSO and substituent specified (R)				
		Me	Et	Ph	CH ₂ Cl	Cl
	X = Si	+344.3	+342.2	+343.0	+340.1	—
	X = Ge	+346.9	+346.4	—	—	+344.9
	X = Si	+335.0	+334.2	+333.8	+333.2	—
	X = Ge	+324.4	—	—	—	—
	X = Si	+319.9	—	—	+320.6	—
	X = Ge	+309.8	+310.1	—	—	+311.9
		Nitrogen shielding referred to neat nitromethane for CDCl ₃ solutions of related open-chain structures				
N(CH ₂ CH ₂ OSiMe ₃) ₃		+350.7				
Me ₃ SiOOCCH ₂ N(CH ₂ CH ₂ OSiMe ₃) ₂		+352.0				
(Me ₃ SiOOCCH ₂) ₂ NCH ₂ CH ₂ OSiMe ₃		+354.0				
(Me ₃ SiOOCCH ₂) ₃ N		+358.5				

Data from ref. 621; ¹⁵N natural abundance spectra, 9.12 and 36.48 MHz, field respectively perpendicular and parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; since resonance frequencies were not specified for individual compounds, uncertainty in the shieldings can reach 1.4 ppm; saturated solutions.

TABLE 24

Nitrogen shieldings in some 1,3-dioxo-6-aza-2-silacyclooctanes



Substituents

Nitrogen shielding in amino moiety of ring system referred to neat nitromethane

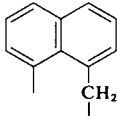
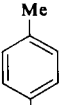
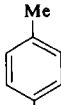
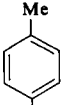
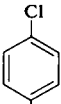
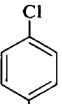
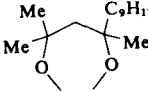
R ¹	R ²	R	in CCl ₄	in benzene	in toluene	in chloro- benzene	in CHCl ₃	in CH ₂ Cl ₂	in pyridine -d ₅	in acetone	in nitro- benzene	in CD ₃ OD	in CD ₃ CN	in DMSO	Notes
Ph	Ph	H	+357.9	+356.5	+357.5	+355.7	+355.7 +354.5	+354.7	+352.9	+354.7	+353.3	+354.2	+352.3	+351.0	(a) (b)
		Me	+359.6	+358.1	+358.6	+357.3	+355.8	+354.8	+354.8	+355.3	+354.6	—	+353.2	+352.2	(a)
Ph	Ph	Me	+363.9	+363.6	+363.7	+363.3	+362.3 +362.2	+362.2	+362.4	+362.8	+362.4	+362.9	+362.3	+361.5	(a) (b)
Ph	H	Me	+361.5	+360.6	+360.9	+359.0	+357.8	+357.1	+356.9	+357.5	+357.0	—	+356.2	+354.4	(a)
CH=CH ₂	Me	Me	—	—	—	—	+364.5	—	—	—	—	—	—	—	(b)
Ph	Me	Me	—	—	—	—	+364.3	—	—	—	—	—	—	—	(b)
Ph	Pr ⁿ	Me	—	—	—	—	+364.4	—	—	—	—	—	—	—	(b)
Ph	CMe	Me	—	—	—	—	+358.3	—	—	—	—	—	—	—	(b)

TABLE 24—*cont.*

R ¹	R ²	R	in CCl ₄	in benzene	in toluene	in chloro- benzene	in CHCl ₃	in CH ₂ Cl ₂	in pyridine -d ₅	in acetone	in nitro- benzene	in CD ₃ OD	in CD ₃ CN	in DMSO	Notes
	OMe	Me	—	—	—	—	+358.8	—	—	—	—	—	—	—	(b)
	Me	Me	—	—	—	—	+363.0	—	—	—	—	—	—	—	(b)
Ph	Ph	Et	—	—	—	—	+354.0	—	—	—	—	—	—	—	(b)
Ph	Ph	Pr ⁿ	—	—	—	—	+353.5	—	—	—	—	—	—	—	(b)
Ph	Ph	Bu ^t	—	—	—	—	+336.1	—	—	—	—	—	—	—	(b)
 		Me	—	—	—	—	+362.7	—	—	—	—	—	—	—	(b)
 		Me	—	—	—	—	+361.2	—	—	—	—	—	—	—	(b)
		Me	—	—	—	—	+352.2	—	—	—	—	—	—	—	(b)
Me	Me	Me	—	—	—	—	+364.9	—	—	—	—	—	—	—	(b)
Me	Me	Ph	+322.7	—	—	—	—	—	—	—	—	—	—	—	(b)

(a) Data from ref. 140; ¹⁵N-enriched (up to 20%) compounds; ¹H-¹⁵N INDOR spectra, 80/8.106 MHz, originally referred to nitromethane via frequency of ¹H resonance of internal SiMe₄ standard; values of shieldings quoted do not contain bulk-susceptibility effects, but they do include solvent effects on proton shielding in SiMe₄.

(b) Data from ref. 269; ¹⁵N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to neat nitromethane via calibrated HNO₃ sample, uncorrected for bulk-susceptibility effects; also ref. 608, with the same details.

TABLE 25

Nitrogen shieldings in amino groups bound to phosphorus atoms

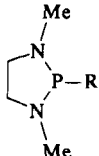
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
	neat liquids		
R			
NMe ₂		+341.3 (NMe)	(a)
NEt ₂		+331.1 (NMe ₂)	(a)
		+342.8 (NMe)	(a)
		+299.7 (NEt ₂)	(a)
NPr ₂ ⁱ		+349.6 (NMe)	(a)
		+281.4 (NPr ₂)	(a)
		+341.4 (NMe)	(a)
		+303.1 (N)	(a)
Cl		+319.7	(a)
M ₂ N—PMe ₂	neat + 10% CHCl ₃	+374.5	(b)
Me ₂ N—PPh ₂	neat + 10% CHCl ₃	+372.2	(b)
Me ₂ N—PF ₂	neat + 10% CHCl ₃	+317.5	(b)
Me ₂ N—P(Cl)Me	neat + 10% CHCl ₃	+331.5	(b)
Me ₂ N—P(Cl)Ph	neat + 10% CHCl ₃	+334.2	(b)
Me ₂ N—PCl ₂	neat + 10% CHCl ₃	+321.5	(b)
(Me ₂ N) ₂ PMe	neat + 10% CHCl ₃	+343.5	(b)
(Me ₂ N) ₂ PPh	neat + 10% CHCl ₃	+348.2	(b)
(Me ₂ N) ₂ PCl	neat + 10% CHCl ₃	+331.6	(b)
(Me ₂ N) ₂ P	neat + 10% CHCl ₃	+350.9	(b)
(Me ₂ N) ₂ P—NEt ₂	neat + 10% CHCl ₃	+353.4 (NMe ₂)	(b)
		+319.5 (NEt ₂)	(b)
(Me ₂ N) ₂ P—NPr ₂ ⁱ	neat + 10% CHCl ₃	+359.0 (NMe ₂)	(b)
		+299.2 (NPr ₂)	(b)
(Me ₂ N) ₂ P—OMe	neat + 10% CHCl ₃	+343.0	(b)
(Me ₂ N)(Et ₂ N)PCl	neat + 10% CHCl ₃	+327.5 (NMe ₂)	(b)
		+307.0 (NEt ₂)	(b)
(Me ₂ N)(Et ₂ N)P—NPr ₂ ⁱ	neat + 10% CHCl ₃	+359.3 (NMe ₂)	(b)
		+332.3 (NEt ₂)	(b)
		+300.5 (NPr ₂)	(b)
(Me ₂ N)(Pr ₂ ⁱ N)PCl	neat + 10% CHCl ₃	+327.5 (NMe ₂)	(b)
		+288.8 (NPr ₂)	(b)
Me ₂ N—P(OEt) ₂	neat + 10% CHCl ₃	+355.0	(b)
Et ₂ N—P(Cl)Ph	neat + 10% CHCl ₃	+306.8	(b)

TABLE 25—*cont.*

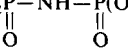
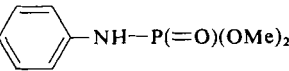
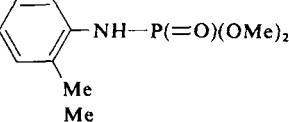
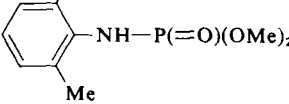
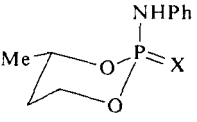
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
$\text{Et}_2\text{N}-\text{PCl}_2$	neat + 10% CHCl_3	+293.4	(b)
$(\text{Et}_2\text{N})_2\text{PCl}$	neat + 10% CHCl_3	+304.5	(b)
$(\text{Et}_2\text{N})_3\text{P}$	neat + 10% CHCl_3	+323.8	(b)
$(\text{Et}_2\text{N})_2\text{P}-\text{NPr}_2$	neat + 10% CHCl_3	+332.4 (NEt_2)	(b)
		+302.1 (NPr_2)	(b)
$(\text{Et}_2\text{N})(\text{Pr}^i\text{N})\text{PCl}$	neat + 10% CHCl_3	+305.2 (NEt_2)	(b)
		+286.6 (NPr_2)	(b)
$\text{Pr}^n_2\text{N}-\text{P}(\text{Cl})\text{Ph}$	neat + 10% CHCl_3	+310.2	(b)
$\text{Pr}^i_2\text{N}-\text{P}(\text{Cl})\text{Ph}$	neat + 10% CHCl_3	+287.5	(b)
$\text{Pr}^i_2\text{N}-\text{PCl}_2$	neat + 10% CHCl_3	+293.4	(b)
$(\text{Pr}^i\text{N})_2\text{PCl}$	neat + 10% CHCl_3	+285.2	(b)
$\text{Bu}^n_2\text{N}-\text{P}(\text{Cl})\text{Ph}$	neat + 10% CHCl_3	+310.9	(b)
$\text{Bu}^s_2\text{N}-\text{P}(\text{Cl})\text{Ph}$	neat + 10% CHCl_3	+287.0	(b)
$\text{Bu}^s_2\text{N}-\text{PCl}_2$	neat + 10% CHCl_3	+275.8	(b)
$\text{PhCH}_2\text{N}(\text{Me})-\text{P}(\text{Cl})\text{Ph}$	neat + 10% CHCl_3	+321.1	(b)
$(\text{PhCH}_2)_2\text{N}-\text{P}(\text{Cl})\text{Ph}$	neat + 10% CHCl_3	+305.2	(b)
$\text{PhCH}_2\text{N}(\text{Me})-\text{PCl}_2$	neat + 10% CHCl_3	+308.2	(b)
$(\text{Bu}^i)(\text{Pr}^i)\text{N}-\text{PCl}_2$	neat liquid	+266.6	(c)
$\text{Bu}^i_2\text{N}-\text{PCl}_2$	neat liquid	+259.2	(c)
$(\text{EtO})_2\text{P}-\text{NH}-\text{P}(\text{OEt})_2$	in CDCl_3	+301.6	(k)
	1.5 M in CDCl_3	+310.4	(d)
	1.5 M in CDCl_3	+318.6	(d)
	1.5 M in CDCl_3	+317.8	(d)
	1.5 M in CDCl_3	+326.4	(d)
$\text{PhN}(\text{Me})-\text{P}(\text{=O})(\text{OMe})_2$	1.5 M in aniline/ CHCl_3 (1:1)	+325.2	(d)
	in pyridine + 10% C_6D_6		
X = O		+308.7	(e)
X = S		+293.9	(e)
X = Se		+289.6	(e)

TABLE 25—*cont.*

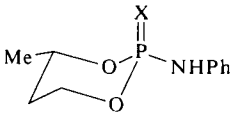
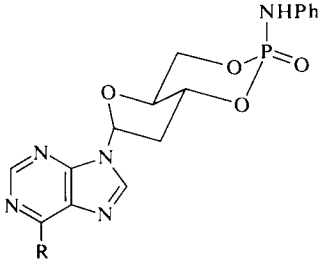
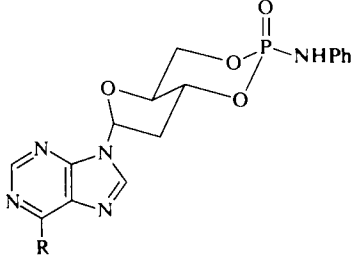
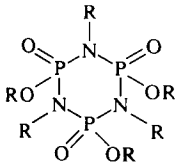
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
	in pyridine + 10% C ₆ D ₆		
X = O		+304.6	(e)
X = S		+289.9	(e)
X = Se		+286.2	(e)
	in pyridine + 10% C ₆ D ₆		
R = NH ₂		+307.5 (NHPh)	(e)
R = N(COPh) ₂		+307.2 (NHPh)	(e)
	in pyridine + 10% C ₆ D ₆		
R = NH ₂		+304.8 (NHPh)	(e)
R = N(COPh) ₂		+308.7 (NHPh)	(e)
	in CDCl ₃		
R = Me		+300.5	(f)
R = Et		+301.2	(g)

TABLE 25—*cont.*

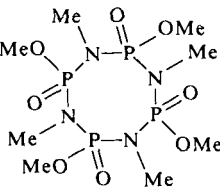
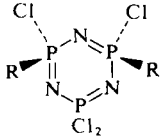
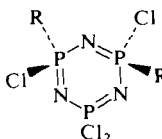
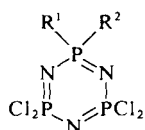
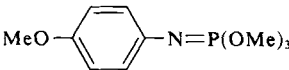
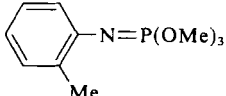
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
	in CDCl ₃	+318.5	(g)
 R = NHMe	in CDCl ₃	+327.0 (NHMe)	(h)
 R = NHMe R = NMe ₂	in CDCl ₃ in CDCl ₃	+325.1 (NHMe) +329.6 (NMe ₂)	(h) (h)
 R ¹ = R ² = NH ₂ R ¹ = Cl, R ² = NH ₂ R ¹ = R ² = NHMe R ¹ = Cl, R ² = NHMe R ¹ = Cl, R ² = NMe ₂ R ¹ = R ² = NHPh R ¹ = Cl, R ² = NHPh	in CDCl ₃	+332.0 (NH ₂) +318.8 (NH ₂) +342.5 (NHMe) +326.6 (NHMe) +331.2 (NMe ₂) +298.1 (NHPh) +286.6 (NHPh)	(h) (h) (h) (h) (h) (h) (h)
PhN=P(OMe) ₃	1.5 M in aniline/CHCl ₃	+311.1	(d)
	1.5 M in aniline/CHCl ₃	+315.8	(d)
	1.5 M in aniline/CHCl ₃	+315.5	(d)

TABLE 25—*cont.*

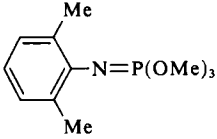
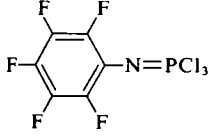
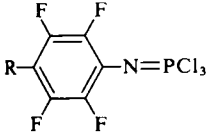
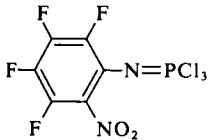
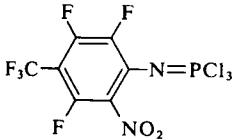
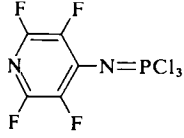
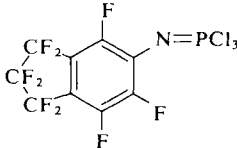
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
	1.5 M in aniline/CHCl ₃	+325.1	(d)
	in benzene	+252.0	(i)
	satd. in CH ₂ Cl ₂	+253.0	(j)
	in benzene		
R = OMe		+251.4	(i)
R = Me		+245.5	(i)
R = Cl		+244.9	(i)
R = F		+252.0	(i)
R = CF ₃		+245.5	(i)
R = CN		+244.4 (N=P)	(i)
R = NO ₂		+245.5 (N=P)	(i)
	in benzene	+244.3 (N=P)	(i)
	in benzene	+248.6 (N=P)	(i)
	in benzene	+242.2 (N=P)	(i)

TABLE 25—*cont.*

Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
	in benzene	+243.6	(i)

For additional data, see ref. 1, Table 30 therein

(a) Data from ref. 479; ^{15}N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube originally referred to NO_3^- standard calibrated against neat nitromethane (+3.1 ppm), conversion scheme IV (Table 4); $\text{Cr}(\text{acac})_3$ used as relaxation reagent.

(b) Data from ref. 36; details as in footnote (a), except for the calibrated value of +1.5 ppm for NO_3^- standard against neat nitromethane.

(c) Data from ref. 609; ^{15}N natural abundance spectra, 25.3 MHz, field parallel to sample tube originally referred to NO_3^- standard calibrated (+5.1 ppm) against neat nitromethane, conversion scheme IV (Table 4).

(d) Unpublished results by B. Kirschleger, J. Villieres and F. Lefèvre, quoted in ref. 609; see footnote (c) above.

(e) Data from ref. 476; ^{15}N -labelled aniline moiety, ^{15}N spectra, 25.35 MHz, field parallel to sample tube, referred to aqueous NO_3^- , +3.5 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(f) Data from ref. 473; ^{15}N -labelled compound, ^{15}N spectrum, 20.282 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(g) As in footnote (f) above, but 9.12 MHz, field perpendicular to sample tube.

(h) Data from ref. 622; ^{15}N -labelled amino groups, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

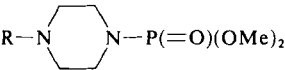
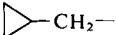
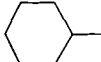
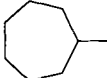
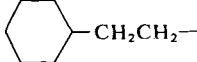
(i) Data from ref. 623; ^{15}N -labelled $\text{N}=\text{P}$ moiety, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(j) Data from ref. 624; ^{15}N -labelled compound, ^{15}N spectrum, 9.12 MHz, field perpendicular to sample tube, originally referred to liquid NH_3 , +380.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(k) Data from ref. 625; ^{15}N -labelled compound, ^{15}N spectra, 10.14 MHz, field perpendicular to sample tube, originally referred to aqueous $(\text{NH}_4)_2\text{SO}_4$, +357.7 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

TABLE 26

Nitrogen shieldings in some dimethylphosphono derivatives of piperazine

Structure	Nitrogen shielding referred to neat nitromethane, for satd. solution in CDCl ₃	
	RN moiety	NP(=O)(OMe) ₂ moiety
		
R = Pr ⁱ	+324.1	+335.0
Bu ⁱ	+327.8	+334.5
	+326.8	+334.8
	+325.2	+335.0
	+324.6	+334.9
	+323.1	+334.8
	+326.4	+335.0
CH ₂ =CH-CH ₂ -	+330.1	+334.9
Ph	+312.6	+334.7
Ph-CH ₂ -	+327.9	+334.8

Data from ref. 626; ¹⁵N natural abundance spectra, 20.3 MHz, field parallel to sample tube, originally referred to satd. aqueous NH₄Cl, +352.9 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); originally reported relative to liquid NH₃ standard taken at +27.3 ppm from the standard employed.

TABLE 27

Nitrogen shieldings in some amino groups bound to elements other than carbon or phosphorus

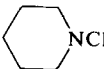
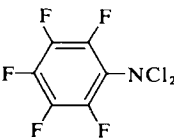
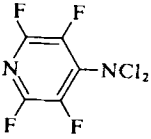
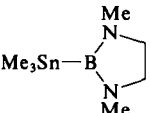
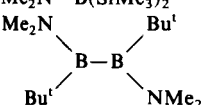
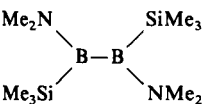
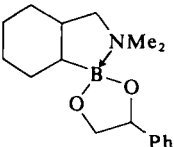
Compound	Solution or state	Nitrogen shieldings referred to neat nitromethane	Notes
Me_2NCl	neat liquid	+292.7	(a)
Et_2NCl	neat liquid	+258.8	(a)
Pr^i_2NCl	neat liquid	+239.2	(a)
Bu^i_2NCl	neat liquid	+227.6	(a)
$\text{Bu}^i(\text{Me}_3\text{Si})\text{NCl}$	neat liquid	+278.6	(a)
	neat liquid	+276.0	(a)
Et_2NBr	neat liquid	+259.1	(a)
Pr^i_2NBr	neat liquid	+233.5	(a)
	satd. in CH_2Cl_2	+276.0	(b)
	satd. in CH_2Cl_2	+285.1	(b)
	satd. in CH_2Cl_2	+280.0 (NCl_2)	(b)
$(\text{Me}_3\text{Si})_2\text{NH}$	neat liquid	+353.2	(a)
$\text{Bu}^i(\text{Me}_3\text{Si})\text{NH}$	neat liquid	+323.0	(a)
$(\text{Me}_2\text{N})_2\text{S}$	neat liquid	+327.0	(c)
$\text{Me}_2\text{N}-\text{SO}_2\text{Me}$	neat liquid	+302.0	(c)
$\text{Me}_2\text{N}-\text{SO}_2\text{Ph}$	neat liquid	+299.2	(c)
other sulphonamide structures	see Table 69		
$\text{Me}_2\text{N}-\text{SOCl}$	neat liquid	+261.0	(c)
$\text{Me}_3\text{Sn}-\text{NHPh}$	in benzene	+327.6	(d)
$(\text{Me}_3\text{Sn})_2\text{NPh}$	in benzene	+333.6	(d)
$\text{Me}_3\text{Sn}-\text{N}(\text{Me})\text{Ph}$	in benzene	+330.8	(d)
$\text{Me}_2\text{Sn}[\text{N}(\text{Me})\text{Ph}]_2$	in benzene	+323.6	(d)
$\text{MeSn}[\text{N}(\text{Me})\text{Ph}]_3$	in benzene	+321.3	(d)
$\text{Sn}[\text{N}(\text{Me})\text{Ph}]_4$	in benzene	+319.6	(d)
$\text{Me}_3\text{Sn}-\text{N}(\text{PMe}_2)\text{Ph}$	in benzene	+332.5	(d)

TABLE 27—*cont.*

Compound	Solution or state	Nitrogen shieldings referred to neat nitromethane	Notes
$\text{Me}_3\text{Sn}-\text{N}[\text{P}(\text{S})\text{Me}_2]\text{Ph}$	in benzene	+307.5	(d)
$\text{Me}_3\text{Pb}-\text{N}(\text{Me})\text{Ph}$	in benzene	+321.5	(d)
$\text{B}(\text{NHMe})_3$	0.1 M in CDCl_3	+341.1	(e)
$\text{Me}_2\text{N}-\text{B}(\text{Me})\text{Cl}$	in CH_2Cl_2	+302	(f)
$\text{Me}_2\text{N}-\text{B}(\text{Me})\text{Br}$	in CH_2Cl_2	+284	(f)
$\text{Me}_2-\text{B}(\text{Me})\text{SMe}$	in CH_2Cl_2	+296	(f)
$(\text{Me}_2\text{N})_2\text{BMe}$	in CH_2Cl_2	+341	(f)
$\text{Me}_2\text{N}-\text{BMe}_2$	in CH_2Cl_2	+300	(f, g)
$\text{Me}_3\text{Sn}-\text{B}(\text{NMe}_2)_2$	in benzene/ CDCl_3	+314	(g)
$(\text{Me}_3\text{Sn})_2\text{B}-\text{NMe}_2$	in benzene/ CDCl_3	+224	(g)
	in benzene/ CDCl_3	+293	(g)
$\text{Me}_2\text{N}-\text{B}(\text{SnMe}_3)-\text{B}(\text{SnMe}_3)\text{NMe}_2$	in benzene/ CDCl_3	+254	(g)
$\text{Me}_2\text{B}-\text{N}(\text{SnMe}_3)_2$	in benzene/ CDCl_3	+276	(g)
$\text{Me}_2\text{N}-\text{BBu}^t_2$	in benzene/ CDCl_3	+301	(g)
$\text{Me}_2\text{N}-\text{B}(\text{SiMe}_3)_2$	in benzene/ CDCl_3	+244	(g)
	in benzene/ CDCl_3	+285	(g)
	in benzene/ CDCl_3	+264	(g)
$\text{Me}_3\text{Si}-\text{B}(\text{NMe}_2)_2$	in benzene/ CDCl_3	+281	(g)
	in acetone- d_6	+328.7	(h)
$\text{Et}_2\text{N}-\text{B}(\text{C}_6\text{H}_4)\text{SnMe}_2$	in benzene/ CDCl_3	+259	(i)
Me_2NLi	in cyclohexane/THF	ca. +600	(j)

(a) Data from ref. 609; ^{15}N natural abundance spectra, 25.3 MHz, field parallel to sample tube, originally referred to NO_3^- standard calibrated (+5.1 ppm) against neat nitromethane, conversion scheme IV (Table 4); $\text{Cr}(\text{acac})_3$ added as relaxation reagent.

TABLE 27—*cont.*

(b) Data from ref. 624; ^{15}N -labelled compounds, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to liquid NH_3 , +380.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(c) Unpublished results by J. Doree and G. Martin, quoted in ref. 609; see footnote (a).

(d) Data from ref. 627; ^{15}N -labelled compounds, ^1H - ^{15}N double resonance spectra, 60/6 MHz, field perpendicular to sample tube, originally referred to Me_4NI in DMSO, +337.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

(e) Data from ref. 129; ^{15}N -labelled compound, ^{15}N spectrum, 10.14 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(f) Data from ref. 628; ^{14}N continuous-wave spectra, 7.2 MHz, field perpendicular to sample tube, originally referred to aqueous NaNO_3 , +3.7 ppm from neat nitromethane (Table 6), precision uncertain since no details are given about measurements of nitrogen shieldings from broad ^{14}N resonance signals.

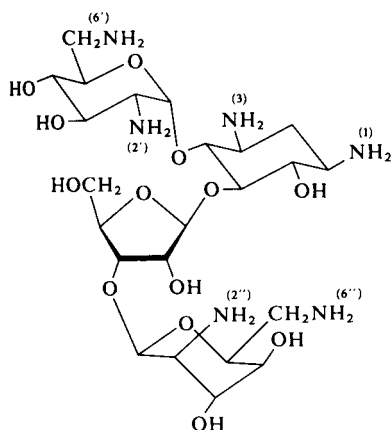
(g) Data from ref. 629; ^{14}N PFT spectra, 14.4 MHz, field parallel to sample tube, details as in footnote (f).

(h) Data from ref. 611; ^{15}N natural abundance spectrum, 9.12 MHz, field perpendicular to sample tube, originally referred to NO_3^- standard, calibrated (+1.5 ppm) against neat nitromethane, conversion scheme IV (Table 4); $\text{Cr}(\text{acac})_3$ added as relaxation reagent; the latter probably affected the conversion constant which is significantly different from NO_3^- shieldings given in Table 6.

(i) Data from ref. 630; details as in footnote (g).

(j) Unpublished work by B. Kirschleger, J. Villieres and F. Lefèvre, quoted in ref. 609; see footnote (a).

TABLE 28

Nitrogen shieldings in some aminosugars and their derivatives in H₂O/D₂O solutions

("Neomycin B")

free base

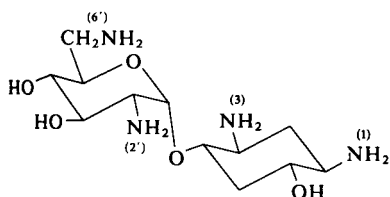
sulphate, pH = 6.7

hexahydrochloride

hexa-*N*-acetyl derivative

Nitrogen shielding referred to neat nitromethane, of amino/ammonium/amido moieties

1-N	3-N	2'-N	6'-N	2''-N	6''-N
+349.8	+347.5	+357.9	+365.8	+364.7	+363.8
+342.6	+344.4	+347.4	+354.0	+351.8	+353.6
+341.9	+340.3	+346.1	+353.3	+350.5	+352.9
+250.3	+250.5	+257.4	+263.8	+261.3	+261.7



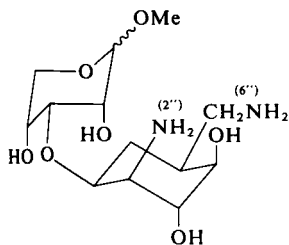
("Neamine")

free base

tetrahydrochloride

tetra-*N*-acetyl derivative

+349.2	+347.7	+357.8	+365.1	—	—
+342.0	+340.9	+346.2	+353.0	—	—
+250.1	+248.3	+257.1	+264.2	—	—



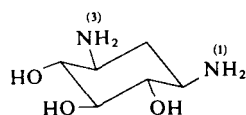
("Methyl Neobiosaminide B")

free base

dihydrochloride

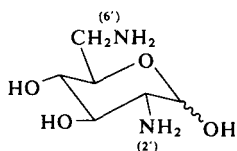
di-*N*-acetyl derivative

—	—	—	—	+363.8	+363.6
—	—	—	—	+350.4	+353.3
—	—	—	—	+260.7	+261.6

TABLE 28—*cont.*

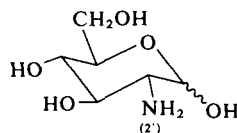
("2-Deoxystreptamine")

free base	+348.9	+348.9	—	—	—	—
dihydrochloride	+341.7	+341.7	—	—	—	—
dihydrobromide	+341.6	+341.6	—	—	—	—
di- <i>N</i> -acetyl derivative	+249.7	+249.7	—	—	—	—



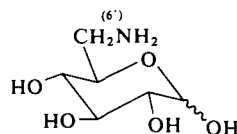
(2,6-diamino-2,6-dideoxyglucose)

free base	α	—	—	+356.6	+365.2	—	—
($\alpha/\beta = 75/25$)	β	—	—	+357.3	+365.5	—	—
dihydrochloride							
($\alpha/\beta = 71/29$)	α	—	—	+346.2	+353.3	—	—
	β	—	—	+347.9	+353.1	—	—



(2-amino-2-deoxyglucose)

hydrochloride	α	—	—	+345.7	—	—	—
	β	—	—	+347.2	—	—	—
<i>N</i> -acetyl derivative	α	—	—	+257.6	—	—	—
	β	—	—	+258.4	—	—	—



(6-amino-6-deoxyglucose)

hydrochloride		—	—	—	+353.6	—	—
($\alpha \rightleftharpoons \beta$)							
<i>N</i> -acetyl derivative		—	—	—	+262.6	—	—
($\alpha \rightleftharpoons \beta$)							

For additional data see ref. 1, Tables 32 and 33 therein

Data from ref. 274; ^{15}N natural abundance spectra, 40.53 MHz, field parallel to sample tube, originally referred to NO_3^- in aqueous NH_4NO_3 , +4.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); paramagnetic impurities were removed from the samples.

Table 29

Calculated nitrogen shieldings, pK_a values and protonation shifts for ammonium moieties in Neomycin B from ^{15}N NMR titration curves

Nitrogen atom in Neomycin B (see Table 28)	Nitrogen shielding (in ppm, referred to neat nitro- methane) for the corresponding ammonium moiety	Protonation shift of nitrogen shielding referred to free NH_2 groups	pK_a
1-N	$+342.1 \pm 0.1$	-7.5 ± 0.1	8.04 ± 0.03
3-N	$+340.2 \pm 0.1$	-6.4 ± 0.1	5.74 ± 0.04
2'-N	$+346.4 \pm 0.2$	-11.3 ± 0.3	7.55 ± 0.04
6'-N	$+353.7 \pm 0.1$	-12.0 ± 0.1	8.60 ± 0.02
2''-N	$+350.7 \pm 0.1$	-13.8 ± 0.2	7.60 ± 0.02
6''-N	$+353.1 \pm 0.1$	-10.8 ± 0.1	8.80 ± 0.01

Data from ref. 274; see Table 28.

Table 30

Nitrogen shieldings in ammonium and alkylammonium ions

Ion and gegenion	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
NH_4^+	various solutions and gegenions	see Table 6	
NH_4I	solid	+324.5	(a)
NH_4Br	solid	+338.5	(a)
NH_4Cl	solid	+341.0	(a)
NH_4SCN	solid	+346.1 (NH_4^+)	(a)
$(\text{NH}_4)_2\text{HPO}_4$	solid	+355.3	(a)
		+358.0	(a)
$(\text{NH}_4)_2\text{SO}_4$	solid	+355.7	(a,b)
NH_4HCO_3	solid	+356.6	(a)
$\text{NH}_4(\text{H}_2\text{PO}_4)$	solid	+356.8	(a)
NH_4NO_3	solid	+358.4 (NH_4^+)	(a)
$(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$ (tartrate)	solid	+360.3	(a)
$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	solid	+365.1	(a)

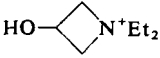
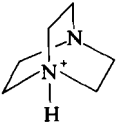
NH_4^+	(SO_4^{2-})	satd. in H_2O , pH = 4.76	+357.7	(c)
NH_4^+	$(\text{NH}_2\text{SO}_3^-)$	satd. in H_2O , pH = 4.33	+357.8	(c)
NH_4^+	$\text{NH}(\text{SO}_3)_2^{2-}$	in $\text{NH}_3/\text{H}_2\text{O}$, pH = 8.3	+358.8	(c)
NH_4^+	$\text{N}(\text{SO}_3)_3^{3-}$	in $\text{NH}_3/\text{H}_2\text{O}$, pH = 9.0	+358.5	(c)
NH_4^+	(AsF_6^-)	in HF	+369.6	(d)
NH_3F^+	$(\text{CF}_3\text{SO}_3^-)$	in $\text{CF}_3\text{SO}_3\text{H}$, 20°C	+252.1	(d)
		in HF, 10°C	+259.6	(d)
		-40°C	+257.6	(d)
		in HF/ AsF_5 , 10°C	+260.0	(d)
NF_4^+	(BF_4^-)	in HF	+92.3	(d)
NF_4^+	(AsF_6^-)	in HF	+92.2	(d)

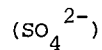
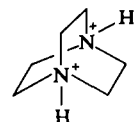
Table 30 (continued)

MeNH_3^+	(Cl^-)	various	+357 to +361	(e)
EtNH_3^+	(Cl^-)	2 M in $\text{H}_2\text{O}/\text{HCl}$	+343.9	(f)
$\text{Pr}^{\text{n}}\text{NH}_3^+$	(Cl^-)	2 M in $\text{H}_2\text{O}/\text{HCl}$	+346.2	(f)
$\text{Pr}^{\text{i}}\text{NH}_3^+$	(Cl^-)	in MeOH	ca. + 354	(e)
$\text{Bu}^{\text{t}}\text{NH}_3^+$	(Cl^-)	in MeOH	ca. + 324	(e)
Me_2NH_2^+	(Cl^-)	various	ca. + 356	(e)
Et_2NH_2^+	(Cl^-)	2 M in $\text{H}_2\text{O}/\text{HCl}$	+329.2	(f,g)
$\text{Pr}_2^{\text{n}}\text{NH}_2^+$	(Cl^-)	2 M in $\text{H}_2\text{O}/\text{HCl}$	+333.7	(f)
$\text{Pr}_2^{\text{i}}\text{NH}_2^+$	(Cl^-)	in MeOH	ca. +310	(e)
$\text{Bu}_2^{\text{t}}\text{NH}_2^+$	(Cl^-)	2 M in $\text{H}_2\text{O}/\text{HCl}$	+293.9	(h)
Me_3NH^+	(Cl^-)	0.3 M in H_2O , pH = 4.5	+348.2	(i)
Et_3NH^+	(Cl^-)	2 M in $\text{H}_2\text{O}/\text{HCl}$	+321.9	(f,g)
Me_4N^+	(Cl^-)	0.30 M in H_2O	+337.67 $\pm$ 0.11	(j)
		satd. in H_2O	+336.69 $\pm$ 0.09	(j)

Me_4N^+	(I^-)	0.30 M in H_2O	$+337.31 \pm 0.13$	(j)
		satd. in DMSO	+337.0	(j)
Et_4N^+	(Cl^-)	0.30 M in H_2O	$+316.29 \pm 0.13$	(j)
		satd. in H_2O	$+315.84 \pm 0.09$	(j)
		in $\text{H}_2\text{O}/\text{HCl}$, pH = 1	+316.7	(g)
Et_4N^+	(F^-)	in DMSO	+313.3	(k)
$\text{Bu}^t(\text{Me}_3\text{Si})\text{NH}_2^+$	(Cl^-)	2 M in $\text{H}_2\text{O}/\text{HCl}$	+322.2	(h)
$\text{HO}-\text{CH}_2\text{CH}_2\text{NH}_3^+$	(Cl^-)	2 M in $\text{H}_2\text{O}/\text{HCl}$	+351.1	(f)
$(\text{HO}-\text{CH}_2\text{CH}_2)_2\text{NH}_2^+$	(Cl^-)	2 M in $\text{H}_2\text{O}/\text{HCl}$	+343.3	(f)
$\text{H}_3\text{N}^+\text{CH}_2\text{CH}_2\text{NH}_3^+$	(Cl^-)	2 M in $\text{H}_2\text{O}/\text{HCl}$	+348.5	(f)
$\text{EtNH}_2^+\text{CH}_2\text{CH}_2\text{NH}_3^+$	(Cl^-)	2 M in $\text{H}_2\text{O}/\text{HCl}$	+322.0 (NH_2^+)	(f)
			+348.9 (NH_3^+)	(f)
$\text{Et}_2\text{NH}^+\text{CH}_2\text{CH}_2\text{NH}_3^+$	(Cl^-)	2 M in $\text{H}_2\text{O}/\text{HCl}$	+325.0 (NH^+)	(f)
			+348.7 (NH_3^+)	(f)
$\text{Et}_2\text{NH}^+\text{CH}_2\text{CH}_2\text{NH}_2^+\text{Et}$	(Cl^-)	2 M in $\text{H}_2\text{O}/\text{HCl}$	+325.0 (NH^+)	(f)
			+334.1 (NH_2^+)	(f)

Table 30 (continued)

$\text{H}_3\text{N}^+\text{CH}_2\text{CH}_2\text{NH}_2^+\text{CH}_2\text{CH}_2\text{NH}_3^+$ (Cl^-)	2 M in $\text{H}_2\text{O}/\text{HCl}$	+338.1 (NH_2^+)	(f)
		+347.9 (NH_3^+)	(f)
$\text{H}_3\text{N}^+\text{CH}_2\text{CH}_2\text{NH}_2^+\text{CH}_2\text{CH}_2\text{NH}_2^+\text{CH}_2\text{CH}_2\text{NH}_3^+$ (Cl^-)	2 M in $\text{H}_2\text{O}/\text{HCl}$	+337.8 (NH_2^+)	(f)
		+348.0 (NH_3^+)	(f)
$(\text{H}_3\text{N}^+\text{CH}_2\text{CH}_2\text{NH}_2^+\text{CH}_2\text{CH}_2)_2\text{NH}_2^+$ (Cl^-)	2 M in $\text{H}_2\text{O}/\text{HCl}$	+337.7 (NH_2^+)	(f)
		+346.1 (NH_3^+)	(f)
$\text{H}_3\text{N}^+-(\text{CH}_2\text{CH}_2\text{NH}_2^+)_n\text{CH}_2\text{CH}_2\text{NH}_3^+$ (Cl^-)	in $\text{H}_2\text{O}/\text{HCl}$	+337.6 ($\text{NH}^+, \text{NH}_2^+$)	(f)
+ branched structures		+348.5 (NH_3^+)	(f)
$(\text{MeCHOHCH}_2)\text{NH}^+\text{Et}_2$ (Cl^-)	in $\text{H}_2\text{O}/\text{HCl}$	+354.3 (NH_3^+)	(f)
$\text{HO}-\text{C}_4\text{H}_8\text{N}^+\text{Et}_2$ (Cl^-)	in $\text{H}_2\text{O}/\text{HCl}$	+326.5	(g)
 (Cl^-)	in $\text{H}_2\text{O}/\text{HCl}$	+324.6	(g)
 (SO_4^{2-})	in $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ pH = 6-8	+362 ($\text{NH}^+ \rightleftharpoons \text{N}$)	(1)

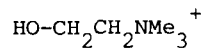


in $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$

+352

(1)

pH = 1



choline chloride

in CD_3OD

+330.8

(m)

in D_2O

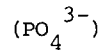
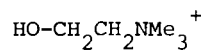
+332.6

(m)

in $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$

+330.7

(m)

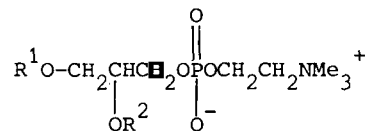


choline phosphate

in D_2O

+332.8

(m)



$\text{R}^1 = \text{R}^2 = \text{MeC}(=\text{O})-$

(phosphatidylcholine
from egg yolk)

in CDCl_3

+332.5

(m)

in CD_3OD

+330.9

(m)

in $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$

+331.2

(m)

Table 30 (continued)

$R^1 = \text{MeC(=O)-}$, $R^2 = \text{H}$ (lysophosphatidylcholine)	in CD_3OD	+331.5	(m)
	in D_2O	+333.1	(m)
	in $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$	+331.0	(m)
$R^1 = R^2 = \text{H}$ (<u>sn</u> -glycero-3-phosphocholine)	in D_2O	+332.7	(m)
	in $\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$	+331.1	(m)
$\begin{array}{c} \text{H}_{31}\text{C}_{15}\text{COOCH}_2\text{CHCH}_2\text{O} \begin{array}{c} \text{S} \\ \parallel \\ \text{P} \end{array} \begin{array}{c} \text{O} \\ \\ \text{O}^- \end{array} \text{CH}_2\text{CH}_2\text{NMe}_3^+ \\ \text{H}_{31}\text{C}_{15}\text{COO} \end{array}$	in MeOD	+328.5	(n)
	in CDCl_3	+329.5	(n)
(1,2-dipalmitoyl- <u>sn</u> -glycero-3-thiophosphocholine)			

For additional data, see footnote (e)

(a) Data from ref. 264, ^{15}N natural abundance spectra (only NH_4Cl and NH_4I enriched with ^{15}N), 18.25 MHz, CP-MASS technique, originally referred to solid NH_4Cl ; recalculated using $(\text{NH}_4)_2\text{SO}_4$ (solid) shielding, +355.7 ppm from neat nitromethane, Table 6 and ref. 270, uncorrected for bulk susceptibility effects.

- (b) Data from ref. 270, ^{15}N enriched compound, ^{15}N CP-MASS spectrum, 20.28 MHz, referred to neat nitromethane, uncorrected for bulk susceptibility effects.
- (c) Data from ref. 631, ^{15}N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NO_3^- standard calibrated (+1.5 ppm) against neat nitromethane, conversion scheme IV (Table 4).
- (d) Data from ref. 99, ^{15}N natural abundance spectra, 28.9 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk susceptibility effects.
- (e) See ref. 1, Table 34 therein, and ref. 4, p.163.
- (f) Data from ref. 606, ^{15}N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NO_3^- in aqueous NH_4NO_3 , +4.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); pH = 1.
- (g) Data from ref. 632, ^{15}N natural abundance spectra as in footnote (f).
- (h) Data from ref. 609, ^{15}N natural abundance spectra, 25.3 MHz, field parallel to sample tube, originally referred to NO_3^- standard calibrated (+5.1 ppm) against neat nitromethane, conversion scheme IV (Table 4).
- (i) Data from ref. 247, ^{15}N labelled compounds, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to 2 M PhNO_2 in Me_2SO_4 , + 9.3 ppm from neat nitromethane as can be reckoned from aqueous KNO_3 shielding (+3.5 ppm from nitromethane, Table 6) reported, -5.8 ppm, conversion scheme II (Table 4).
- (j) Table 6 and references therein.

Table 30 (continued)

- (k) Data from ref. 359, ^{15}N natural abundance spectrum, 9.12 MHz, field perpendicular to sample tube, originally referred to liquid NH_3 , + 380.2 ppm from nitromethane (Table 6), conversion scheme IV (Table 4).
- (l) Data from ref. 45, ^{15}N natural abundance spectra, 36.5 MHz, field parallel to sample tube, referred originally to neat formamide (+268 ppm from neat nitromethane, Table 6), conversion scheme IV (Table 4).
- (m) Data from ref. 500, high-resolution ^{14}N spectra, 5.742 MHz, field perpendicular to sample tube, originally referred to aqueous KNO_3 , +3.7 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).
- (n) Data from ref. 633, ^{14}N spectra, 21.6 MHz, field parallel to sample tube, originally referred to 5.4 M NH_4Cl in H_2O , +352.9 ppm from neat nitromethane, Table 6, conversion scheme II (Table 4).

Table 31

Nitrogen shieldings in some trimethylamine adducts with boron trihalides (solutions in CH_2Cl_2)

Structure	Nitrogen shielding referred to neat nitromethane
$\text{Me}_3\text{N} \rightarrow \text{BF}_3$	+342.0
$\text{Me}_3\text{N} \rightarrow \text{BF}_2\text{Cl}$	+338.0
$\text{Me}_3\text{N} \rightarrow \text{BF}_2\text{Br}$	+340.4
$\text{Me}_3\text{N} \rightarrow \text{BF}_2\text{I}$	+344.3
$\text{Me}_3\text{N} \rightarrow \text{BFCI}_2$	+335.9
$\text{Me}_3\text{N} \rightarrow \text{BFBr}_2$	+339.1
$\text{Me}_3\text{N} \rightarrow \text{BCl}_3$	+334.0
$\text{Me}_3\text{N} \rightarrow \text{BFI}_2$	+346.5
$\text{Me}_3\text{N} \rightarrow \text{BCl}_2\text{Br}$	+334.6
$\text{Me}_3\text{N} \rightarrow \text{BCl}_2\text{I}$	+336.0
$\text{Me}_3\text{N} \rightarrow \text{BClBr}_2$	+335.6
$\text{Me}_3\text{N} \rightarrow \text{BClBrI}$	+336.7
$\text{Me}_3\text{N} \rightarrow \text{BBr}_3$	+337.0
$\text{Me}_3\text{N} \rightarrow \text{BClI}_2$	+340.7
$\text{Me}_3\text{N} \rightarrow \text{BBr}_2\text{I}$	+339.8
$\text{Me}_3\text{N} \rightarrow \text{BBrI}_2$	+343.4
$\text{Me}_3\text{N} \rightarrow \text{BI}_3$	+347.8

Data from ref.124, ^{15}N labelled trimethylamine, ^{15}N spectra, INEPT technique, 40.51 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk susceptibility effects. For additional data, see ref.4, p.161.

TABLE 32

Nitrogen shieldings in some polyelectrolytes of polyaminamide type^a

Structure and comments	Solvent	pH	Nitrogen shieldings referred to neat nitromethane	
			amide	amine/ ammonium
$-[-\text{CO}-(\text{CH}_2)_4-\text{CO}-\underset{\text{(A)}}{\text{NH}}-\text{CH}_2\text{CH}_2-\underset{\text{(B)}}{\text{NH}}-\text{CH}_2\text{CH}_2-\underset{\text{(A)}}{\text{NH}}-]-$ poly(diethylenetriamine)adipamide, polyelectrolyte I	H ₂ O/NaOH	13.1	+258.9 (A)	+347.9 (B)
		10.3	+258.8 (A)	+347.9 (B)
	H ₂ O/HCl	0.4	+263.3 (A)	+338.2 (BH ⁺)
	H ₂ O/HBr	1.0	+263.3 (A)	+337.2 (BH ⁺)
	H ₂ O/HI	1.0	+263.1 (A)	+337.6 (BH ⁺)
	H ₂ O/HNO ₃	1.0	+264.0 (A)	+338.6 (BH ⁺)
	H ₂ O/MeSO ₃ H	1.0	+263.8 (A)	+338.6 (BH ⁺)
$-[-\text{CO}-(\text{CH}_2)_4-\text{CO}-\underset{\text{(A)}}{\text{NH}}-\text{CH}_2\text{CH}_2-\left\{ \begin{array}{c} \text{NH}_2^+ \\ \text{NHMe}^+ \\ \text{NMe}_2^+ \end{array} \right\} -\underset{\text{(A)}}{\text{CH}_2\text{CH}_2\text{NH}}-]-$ polyelectrolyte I methylated with MeSO₃Me				
	H ₂ O/HCl ^b	1-2	+263.9 (A/B ⁰) +264.2 (A/B ¹) +265.5 (A/B ²)	+326.9 (B ⁰) +336.1 (B ¹) +338.7 (B ²)
$\begin{array}{c} \text{COO}^- \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \cdots -\underset{\text{(A)}}{\text{NH}}-\text{CH}_2\text{CH}_2-\underset{\text{(B}^1\text{)}}{\text{NH}^+}-\underset{\text{(A)}}{\text{CH}_2\text{CH}_2}-\underset{\text{(A)}}{\text{NH}}-\text{CO}-(\text{CH}_2)_4-\text{CO}-\underset{\text{(A)}}{\text{NH}}-\text{CH}_2\text{CH}_2-\underset{\text{(B}^0\text{)}}{\text{NH}_2^+}-\underset{\text{(A)}}{\text{CH}_2\text{CH}_2}-\underset{\text{(A)}}{\text{NH}}-\cdots \end{array}$ polyelectrolyte I alkylated with β-propiolactone	H ₂ O/HCl	1	+263.4 (A)	+328.7 (B ¹) +338.2 (B ⁰)
$\begin{array}{c} \text{SO}_3^- \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \cdots -\underset{\text{(A)}}{\text{NH}}-\text{CH}_2\text{CH}_2-\underset{\text{(B}^1\text{)}}{\text{NH}^+}-\underset{\text{(A)}}{\text{CH}_2\text{CH}_2}-\underset{\text{(A)}}{\text{NH}}-\text{CO}-(\text{CH}_2)_4-\text{CO}-\underset{\text{(A)}}{\text{NH}}-\text{CH}_2\text{CH}_2-\underset{\text{(B}^0\text{)}}{\text{NH}_2^+}-\underset{\text{(A)}}{\text{CH}_2\text{CH}_2}-\underset{\text{(A)}}{\text{NH}}-\cdots \end{array}$ polyelectrolyte I alkylated with γ-propanesultone	H ₂ O/HCl	1	+263.8 (A)	+327.5 (B ¹) +338.7 (B ⁰)

TABLE 32—*cont.*

Structure and comments	Solvent	pH	Nitrogen shieldings referred to neat nitromethane	
			amide	amine/ ammonium
$ \begin{array}{c} \text{Me} \\ \\ \text{CHOH} \\ \\ \text{CH}_2 \\ \\ \cdots\text{NH}-\text{CH}_2\text{CH}_2-\text{N}-\text{CH}_2\text{CH}_2-\text{NH}-\text{CO}-(\text{CH}_2)_4-\text{CO}-\text{NH}-\text{CH}_2\text{CH}_2-\text{NH}_2^+-\text{CH}_2\text{CH}_2-\text{NH}-\cdots \\ \text{(A)} \qquad \qquad \text{(B)} \qquad \qquad \text{(A)} \qquad \qquad \text{(A)} \qquad \qquad \text{(B}^0\text{)} \qquad \qquad \text{(A)} \end{array} $				
polyelectrolyte I alkylated with propylene oxide	H ₂ O/HCl	1	+269.2 (A)	+329.7 (B) +338.2 (B ⁰)
$ \begin{array}{c} \text{CH}_2\text{Cl} \\ \\ \text{CHOH} \\ \\ \text{CH}_2 \\ \\ \cdots-\text{CO}-(\text{CH}_2)_4-\text{CO}-\text{NH}-\text{CH}_2\text{CH}_2-\text{N}^+-\text{CH}_2\text{CH}_2-\text{NH}-\cdots \\ \text{(A)} \qquad \qquad \qquad \text{(B)} \qquad \qquad \text{(A)} \end{array} $				
and				
$ \begin{array}{c} \text{OH} \\ \\ \text{Cyclopropyl} \\ \\ \cdots-\text{CO}-(\text{CH}_2)_4-\text{CO}-\text{NH}-\text{CH}_2\text{CH}_2-\text{N}^+-\text{CH}_2\text{CH}_2-\text{NH}-\cdots \\ \text{(A')} \qquad \qquad \qquad \text{(B')} \qquad \qquad \text{(A')} \end{array} $				
polyelectrolyte I alkylated with epichlorohydrine	H ₂ O/HCl	1	+262.8 (A) +266.0 (A')	+333.5 (B) +327.1 (B')
$ \begin{array}{c} \cdots\text{NH}-\text{CH}_2\text{CH}_2-\text{N}(\text{R})-\text{CH}_2\text{CH}_2-\text{NH}-\text{CO}-(\text{CH}_2)_4-\text{CO}-\text{NH}-\text{CH}_2\text{CH}_2-\text{NH}_2^+-\text{CH}_2\text{CH}_2-\text{NH}-\cdots \\ \text{(A}^2\text{)} \qquad \qquad \text{(A)} \qquad \qquad \text{(A}^1\text{)} \qquad \qquad \text{(A}^0\text{)} \qquad \qquad \text{(BH}^+\text{)} \qquad \qquad \text{(A}^0\text{)} \end{array} $				
polyelectrolyte I acylated with succinic anhydride, maleic anhydride, ethyl chloroformate or methanesulphonyl chloride respectively				
R = -CO-CH ₂ CH ₂ -COOH	H ₂ O/HCl	1	+259.0 (A) +260.3 +261.7 +263.6 (A ⁰)	+338.6 (BH ⁺)
R = -CO-CH=CH-COOH	H ₂ O/HCl	1	+256.1 (A) +260.8 +262.1 +263.6 (A ⁰)	+338.6 (BH ⁺)
R = -COOEt	H ₂ O/HCl	1	-260.1 (A ¹ , A ²) +263.1 (A ⁰) +293.7 (A)	+337.9 (BH ⁺)

TABLE 32—*cont.*

Structure and comments	Solvent	pH	Nitrogen shieldings referred to neat nitromethane	
			amide	amine/ ammonium
R = COO ⁻	H ₂ O/NaOH	>7	+258.7 } +259.3 } +293.9 (A)	+347.0 (B)
R = -SO ₃ Me	H ₂ O/HCl	1	+259.4 (A ¹ , A ²) +263.9 (A ⁰) +290.0 (A)	
$-[\text{CO}-(\text{CH}_2)_4-\text{CO}-\underset{(A)}{\text{NH}}-\text{CH}_2\text{CH}_2\text{CH}_2-\underset{(B)}{\text{N}}(\text{Me})-\text{CH}_2\text{CH}_2\text{CH}_2-\underset{(A)}{\text{NH}}-]-$				
polyelectrolyte II	H ₂ O	11.0	+255.4 (A)	+343.4 (B)
	H ₂ O/HCl	1.0	+257.7 (A)	+333.6 (BH ⁺)
	H ₂ O/HBr	1.0	+257.5 (A)	+333.5 (BH ⁺)
	H ₂ O/HI	1.0	+257.6 (A)	+333.5 (BH ⁺)
	H ₂ O/HNO ₃	1.0	+258.1 (A)	+333.9 (BH ⁺)
	MeSO ₃ H	1.0	+257.9 (A)	+333.8 (BH ⁺)
$\cdots \underset{(A')}{\text{NH}}-(\text{CH}_2)_3-\underset{(B')}{\text{N}^+}(\text{Me})(\text{R})-(\text{CH}_2)_3-\underset{(A')}{\text{NH}}-\text{CO}-(\text{CH}_2)_4-\text{CO}-\underset{(A)}{\text{NH}}-(\text{CH}_2)_3-\underset{(B)}{\text{NH}^+}(\text{Me})-(\text{CH}_2)_3-\cdots$				
polyelectrolyte II alkylated with β-propiolactone or MeSO₃Me respectively				
R = -CH ₂ CH ₂ COOH	H ₂ O/HCl	1	+258.0 (A) +258.6 (A')	+334.0 (B) +322.1 (B')
R = Me	H ₂ O/HCl	1	+258.2 (A) +258.7 (A')	+333.9 (B) +322.1 (B')

(a) Unless otherwise indicated, data from ref. 632; ^{15}N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NO_3^- in 30% aqueous NH_4NO_3 (+4.0 ppm from neat nitromethane, Table 6), conversion scheme IV (Table 4).

(b) As in footnote (a), but 20.28 MHz INEPT spectra, field parallel to sample tube.

Table 33

Nitrogen shieldings in some amine N-oxides

Compound	Solution	Nitrogen referred to neat nitromethane	Notes
$\text{Me}_3\text{N} \rightarrow \text{O}$	0.6 M in H_2O pH = 10.5 satd. in acetone	+274.6 +273	(a) (b)
$\text{Et}_3\text{N} \rightarrow \text{O}$	in acetone	+265	(b)
$\text{Me}_2(\text{Ph})\text{N} \rightarrow \text{O}$	in acetone	+266	(b)
$\text{Et}_2(\text{Ph})\text{N} \rightarrow \text{O}$	in acetone	+249	(b)
$\text{O} \leftarrow (\text{Ph})\text{N} \text{---} \text{N}(\text{Ph}) \rightarrow \text{O}$	in CD_3OD	+264.1	(b)
$(\text{PMeC}_6\text{H}_4\text{SO}_2)_2\text{N} \rightarrow \text{O}$	0.2 M in DMSO	+143.0	(c)
Conjugate acids of amine N-oxides, $\text{R}_3\text{N}^+-\text{OH}$		see Table 37	

(a) Data from ref. 247, ^{15}N labelled compound, ^{15}N spectrum, 9.12 MHz, field perpendicular to sample tube, originally referred to 2 M PhNO_2 in Me_2SO_4 , +9.3 ppm from nitromethane as reckoned from $\text{KNO}_3/\text{H}_2\text{O}$ shielding (+3.5 ppm from neat nitromethane, Table 6) reported, -5.8 ppm from the standard employed; conversion scheme II (Table 4).

(b) See ref. 1, p.46, and references therein.

(c) Data from ref. 634, ^{15}N natural abundance spectrum, 18.24 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk susceptibility effects.

TABLE 34

Nitrogen shieldings in aniline and its derivatives

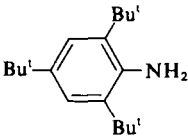
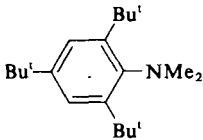
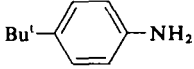
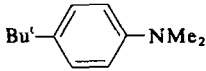
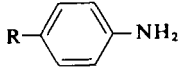
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
PhNH ₂	2 M in DMSO	+320.5	(a)
	in H ₂ O	+325.2	(e)
	various	+321 to +329	(b)
	2 M in DMSO	+319.8	(a)
	2 M in DMSO	+379.2	(a)
	2 M in DMSO	+328.3	(a)
	2 M in DMSO	+340.2	(a)
	2 M in DMSO		
R			
H		+320.5	(a)
NMe ₂		+326.8 (NH ₂)	(a)
OMe		+325.7	(a)
Me		+322.4	(a)
F		+324.6	(a)
Cl		+319.9	(a)
Br		+319.0	(a)
I		+317.8	(a)
CN		+307.0 (NH ₂)	(a)
NO ₂		+300.8 (NH ₂)	(a)
NH ₂		+324.2	(a)
COOH		+321.2	(a)

TABLE 34—*cont.*

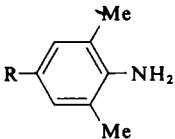
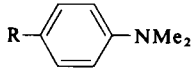
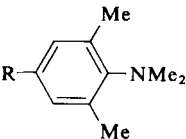
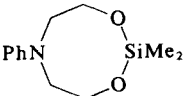
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
	2 M in DMSO		
R			
H		+324.5	(a)
NMe ₂		+326.9 (NH ₂)	(a)
OMe		+329.0	(a)
Me		+327.5	(a)
F		+327.1	(a)
Cl		+327.7	(a)
Br		+321.5	(a)
CN		+308.2 (NH ₂)	(a)
NO ₂		+299.2 (NH ₂)	(a)
NH ₂		+327.9	(a)
COOH		+312.4	(a)
	2 M in DMSO (if not otherwise indicated)		
R			
H		+335.2	(a)
NMe ₂		+337.6	(a)
OMe		+339.5	(a)
Me		+337.5	(a)
F		+337.5	(a)
Cl		+331.1	(a)
Br		+330.2	(a)
I		+332.0	(a)
CN		+320.6 (NMe ₂)	(a)
NO ₂		+311.6 (NMe ₂)	(c)
NH ₂		+341.8 (NMe ₂)	(a)
COOH		+321.2	(a)
CHO	(2 M in CDCl ₃)	+321.0	(d)
C(Cl)POCl ₂	(2 M in CDCl ₃)	+328.0	(d)
C(Cl)OPOCl ₂	(2 M in CDCl ₃)	+338.0	(d)

TABLE 34—*cont.*

Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
 R	2 M in DMSO		
H		+363.4	(a)
NMe ₂		+366.6	(a)
Me		+364.3	(a)
F		+366.3	(a)
Br		+362.6	(a)
CN		+362.0 (NMe ₂)	(c)
NO ₂		+352.5 (NMe ₂)	(c)
NH ₂		+366.5 (NMe ₂)	(a)
COOH		+358.7	(a)
 PhN	satd. in CCl ₄	+322.7	(d)

For additional data see footnote (b)

(a) Data from ref. 275; ¹⁵N natural abundance spectra, 10.09 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; originally reported relative to liquid NH₃ standard taken at +380.2 ppm from nitromethane; Cr(acac)₃ added as relaxation reagent.

(b) See ref. 1, Tables 24, 37 and 38 therein.

(c) Same as in footnote (a), but 27.4 MHz spectra, field parallel to sample tube.

(d) Data from ref. 619; ¹⁵N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NO₃⁻ standard calibrated (+1.5 ppm) against neat nitromethane, conversion scheme IV, Table 4.

(e) Data from ref. 276; ¹⁵N natural abundance spectrum, 18.25 MHz, field parallel to sample tube, originally referred to 1 M NHO₃, +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

TABLE 35

Nitrogen shieldings in arylamines other than simple aniline derivatives

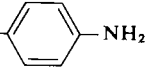
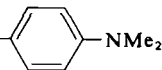
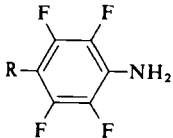
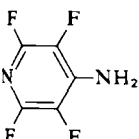
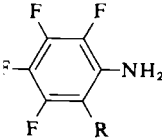
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
<i>trans</i> -PhN=N- 	1 M in DMSO in CDCl ₃ in CDCl ₃ +Cr(acac) ₃	+310.2 (NH ₂) +318.4 (NH ₂) +314.0 (NH ₂)	(a) (b) (b)
<i>trans</i> -PhN=N- 	in CDCl ₃ + Cr(acac) ₃	+325.5 (NMe ₂)	(b)
 R	satd. in CH ₂ Cl ₂		
Et ₂ N		+350.2 (NH ₂)	(c)
NH ₂		+364.2	(c)
OMe		+351.4	(c)
Me		+337.0	(c)
H		+350.3	(c)
F		+355.8	(c)
NO ₂		+329.2	(c)
	satd. in CH ₂ Cl ₂	+331.5 (NH ₂)	(c)
 R = NH ₂ NO ₂	satd. in CH ₂ Cl ₂	+348.6 +326.2 (NH ₂)	(c) (c)
	satd. in CH ₂ Cl ₂	+382.2 (NH ₂)	(c)

TABLE 35—*cont.*

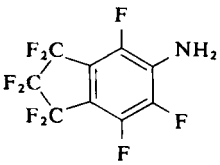
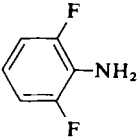
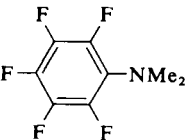
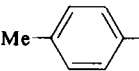
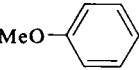
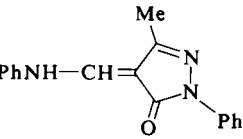
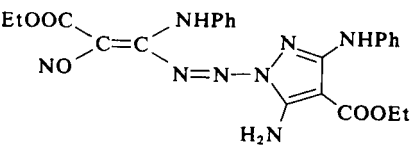
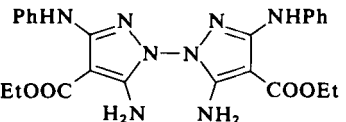
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
	satd. in CH_2Cl_2	+339.2	(c)
	satd. in CH_2Cl_2	+353.6	(c)
	satd. in CH_2Cl_2	+363.5	(c)
	in CH_2Cl_2	+276 ± 12 (NH)	(d)
	in CH_2Cl_2	+284 ± 13 (NH)	(d)
	in CDCl_3	+258.7 (PhNH)	(e)
its salt with Cu^{2+}	in CDCl_3	+185.1 (PhN-Cu)	(e)
its salt with Zn^{2+}	in CDCl_3	+69.0 (PhN-Zn)	(e)
	in DMSO	+264.3 (PhNHC=C) +284.9 (PhNH, ring)	(f) (f)
	in DMSO	+293.8 (NHPh)	(f)

TABLE 35—*cont.*

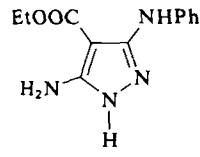
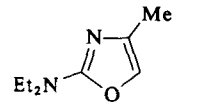
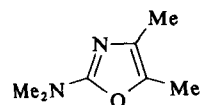
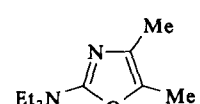
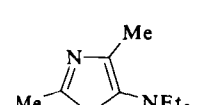
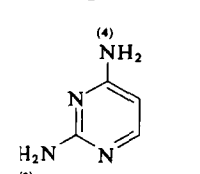
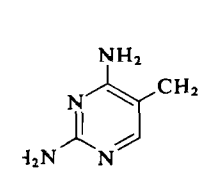
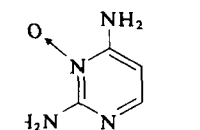
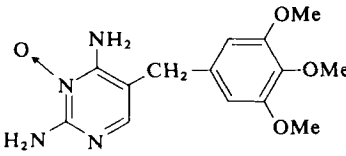
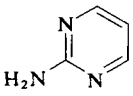
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
	in DMSO	+294.2 (NHPH)	(f)
	melt, 60 °C	+300 ± 15 (NEt ₂)	(g)
	melt, 95 °C	+312 ± 15 (NMe ₂)	(g)
	melt, 60 °C	+359 ± 15 (NEt ₂)	(g)
	melt, 95 °C	+348 ± 6 (NEt ₂)	(g)
	in H ₂ O, pH = 11	+299.2 (2-NH ₂) +297.9 (4-NH ₂)	(h)
	in H ₂ O, pH = 11	+303.0 (2-NH ₂)	(h)
	in H ₂ O, pH = 11	+305.2 (2,4-NH ₂) +303.9	(h)

TABLE 35—*cont.*

Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
	in H ₂ O, pH = 11	+308.4 +307.7 (2,4-NH ₂)	(h)
	in H ₂ O, pH = 11	+296.8 (NH ₂)	(h)
2',3'- <i>O</i> -isopropylidene-5'- <i>O</i> -Bu ^t -dimethylsilyl-cytidine	0.25 M in CHCl ₃ , 1:1 mixture with 2,3'- <i>O</i> -isopropylidene-5'- <i>O</i> -Bu ^t -dimethylsilyl-guanosine	+284.8 (NH ₂)	(i)
Amino groups in nucleosides		see Table 104	
For additional data see ref. 1, Table 39 therein			

(a) Data from ref. 378; ¹⁵N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO₃, +6.2 ppm from neat nitromethane, Table 6, conversion scheme IV (Table 4).

(b) Data from ref. 379; ¹⁵N natural abundance spectra, 10.095 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(c) Data from refs. 435, 624; ¹⁵N labelled amino groups, ¹⁵N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to liquid NH₃, +380.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(d) Data from ref. 620; low-precision ¹⁴N measurements, 6.4 MHz, originally referred to neat nitromethane.

(e) Data from ref. 452; ¹⁵N-labelled aniline moiety, ¹⁵N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to KNO₂/H₂O, -228.9 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

(f) Data from ref. 330; ¹⁵N-labelled amino groups, ¹⁵N spectra, 20.3 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

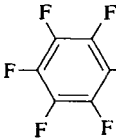
(g) Data from ref. 613; low-precision ¹⁴N measurements, 6.4 MHz, originally referred to neat nitromethane.

(h) Data from ref. 345; ¹⁵N natural abundance spectra, 9.04 MHz, field perpendicular to sample tube, originally referred to what was considered as aqueous NH₄Cl (+352.9 ppm from neat nitromethane, Table 6); however, using the latter value, one obtains shieldings referred to neat nitromethane that show systematic differences when compared with data for the same compounds and solvent in Table 121 in ref. 1; the differences suggest that NH₄NO₃ rather than NH₄Cl was actually employed as reference, +359.6 ppm (NH₄⁺) from neat nitromethane; the latter value was thus used for recalculation, scheme II (Table 4).

(i) Data from ref. 147; no experimental details given, ¹⁵N spectra, originally referred to liquid NH₃, (+380.2 ppm from neat nitromethane, Table 6).

TABLE 36

Nitrogen shieldings in some arylammonium ions

Ion	Solution	Nitrogen shielding referred to neat nitromethane	Notes
PhNH_3^+	various gegenions and solutions	+329 to +333	(a)
Phenyl-substituted anilinium ions	various gegenions and solutions	+319 to +341	(a)
PhNHMe_2^+	various gegenions and solutions	+329 to +331	(a)
Phenyl-substituted <i>N,N</i> -dimethylanilinium ions	various gegenions and solutions	+329 to +333	(a)
 $\text{C}_6\text{F}_5\text{NH}_3^+ (\text{SO}_3\text{F}^-)$	satd. in CH_2Cl_2	+354.7	(b)

(a) See ref. 1, Tables 38 and 40 and references therein.

(b) Data from refs. 435, 624; ^{15}N -labelled compound, ^{15}N spectrum, 9.12 MHz, field perpendicular to sample tube, originally referred to liquid NH_3 , +380.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

Table 37

Nitrogen shieldings in some hydroxylamines and related ions

Compound	Solutions and comments	Nitrogen shielding referred to neat nitromethane	Notes
$\text{NH}_2\text{OH} \rightleftharpoons \text{H}_3\text{N}^+\text{O}$	in H_2O	+265.5 (NH_2OH)	(a)
	(estimated values)	+278.0 (NH_3^+O)	(a)
NH_2OH	0.086 M, 25°C		
	in 0.086 M NaCl/0.114 M NaOH	+274.2	(a)
	in 0.086 M NaCl/0.214 M NaOH	+275.3	(a)
	in 0.086 M NaCl/0.414 M NaOH	+276.5	(a)
	in 0.086 M NaCl/0.914 M NaOH	+278.7	(a)
	(calcd. $\text{pK}_a = 14.02 \pm 0.03$)		
NH_2O^-	calcd. value from data above	+284.9 $\pm$ 0.6	(a)
NH_2OH	0.17 M, 25°C		
	in 1 M NaCl	+272.4	(a)
	in 0.5 M NaCl/0.44 M NaOH	+276.0	(a)

	in 0.17 M NaCl/0.83 M NaOH	+277.8	(a)
	in 0.086 M NaCl/0.914 M NaOH	+278.7	(a)
NH_2O^-	calcd. from data above for solution in 1 M NaCl and excess NaOH	+284.3	(a)
NH_2OH	0.17 M, 45°C		
	in 1 M NaCl	+271.0	(a)
	in 0.56 M NaCl/0.44 M NaOH	+273.4	(a)
	in 0.17 M NaCl/0.83 M NaOH	+275.3	(a)
NH_2O^-	calcd. from data above for solution in 1 M NaCl and excess NaOH	+283.8	(a)
NH_2O^-	0.17 M NH_2OH in 6 M NaOH, 28°C	+281.0	(a)
	0.17 M NH_2OH in 6 M NaOH, 7°C	+281.5	(a)
NH_3^+OH (Cl^-)	2 M in $\text{H}_2\text{O}/\text{HCl}$	+293.9	(b)
	0.4 M in 0.1 M HCl	+296.2	(c)
NMe_3^+OH (Cl^-)	0.4 M in 0.1 M HCl	+267.3	(c)

Table 37 (continued)

NH ₂ OMe	0.5 M in 0.5 M NaOH	+240.7	(a)
	0.3 M in 0.2 M KOH/0.3 M KCl	+240.9	(c)
NH ₃ ⁺ OMe (Cl ⁻)	2 M in H ₂ O/HCl	+272.1	(b)
Et ₂ N-OH	neat liquid + Cr(acac) ₃	+235.3	(b)
Et ₂ NH ⁺ OH (Cl ⁻)	2 M in H ₂ O/HCl	+265.9	(b)
Bu ₂ ^t N-OH	neat liquid + Cr(acac) ₃	+210.0	(b)
Bu ₂ ^t NH ⁺ OH (Cl ⁻)	2 M in H ₂ O/HCl	+259.1	(b)
Bu ₂ ^t N-OBu ^t	neat liquid + Cr(acac) ₃	+193.7	(b)
Bu ₂ ^t NH ⁺ OBu ^t (Cl ⁻)	2 M in H ₂ O/HCl	+243.0	(b)
Bu ^t NH ₂ ⁺ OH (Cl ⁻)	2 M in H ₂ O/HCl	+267.4	(b)
PMeC ₆ H ₄ SO ₂ NHOH	0.2 M in DMSO	+226.1	(d)
(PMeC ₆ H ₄ SO ₂) ₂ NHOH	0.2 M in DMSO	+170.9	(d)

- (a) Data from ref. 278, ^{15}N labelled compounds, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to 2 M HNO_3 , +5.4 ppm from neat nitromethane, as inferred from Table 6, conversion scheme II (Table 4).
- (b) Data from ref. 609, ^{15}N natural abundance spectra, 25.3 MHz, field parallel to sample tube, originally referred to NO_3^- standard calibrated (+5.1 ppm) against neat nitromethane, conversion scheme IV (Table 4).
- (c) Data from ref. 247, ^{15}N labelled compounds, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to 2 M PhNO_2 in Me_2SO_4 , +9.3 ppm from neat nitromethane, as can be reckoned from aqueous KNO_3 shielding (+3.5 ppm from neat nitromethane, Table 6) reported, -5.8 ppm from the standard employed.
- (d) Data from ref. 634, ^{15}N natural abundance spectra, 18.24 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk susceptibility effects.

TABLE 38

Nitrogen shieldings in some hydrazines, hydrazides and related structures

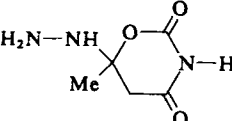
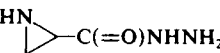
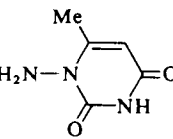
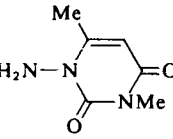
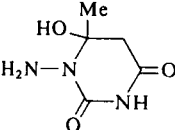
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
$\text{H}_2\text{N}-\text{NH}_2$	various	+331 to +335	(a)
various alkyl-substituted hydrazines	various	+285 to +328	(a)
PhNHNH_2	various	ca. +295 (NH)	(a)
		ca. +320 (NH_2)	(a)
various alicyclic hydrazines	various	+256 to +304	(a)
$\text{FB}(\text{Me})-\text{N}(\text{Me})-\text{N}(\text{Me})-\text{B}(\text{Me})\text{F}$	in CH_2Cl_2	+266	(b)
$\text{ClB}(\text{Me})-\text{N}(\text{Me})-\text{N}(\text{Me})-\text{B}(\text{Me})\text{Cl}$	in CH_2Cl_2	+240	(b)
$\text{BrB}(\text{Me})-\text{N}(\text{Me})-\text{N}(\text{Me})-\text{B}(\text{Me})\text{Br}$	in CH_2Cl_2	+241	(b)
	in DMSO	+313.3 (NH_2)	(c)
		+241.9 (NH, hydrazine)	(c)
		+233.8 (NH, ring)	(c)
$\text{MeC}(=\text{O})\text{NHNH}_2$	2 M in H_2O	+248.0 (NH)	(d)
		+327.2 (NH_2)	(d)
$\text{PhC}(=\text{O})\text{NHNH}_2$	1 M in DMSO	+252.3 (NH)	(d)
		+325.7 (NH_2)	(d)
	in CDCl_3	+248.8 (CONH)	(e)
		+324.5 (NH_2)	(e)
$\text{EtO}-\text{C}(=\text{O})\text{NHNH}_2$	2 M in H_2O	+282.9 (NH)	(d)
		+362.4 (NH_2)	(d)
$\text{MeC}(=\text{O})\text{NHNH}-\text{C}_6\text{H}_{10}\text{N}-\text{Me}$	1 M in DMSO	+237.3 (CONH)	(d)
		+298.8 (other NH)	(d)
		+342.1 (NMe)	(d)
$\text{Ph}-\text{NHNH}-\text{C}(=\text{O})-\text{NHNH}-\text{Ph}$	1 M in DMSO	+276.3 (CONH)	(d)
(carbazide structure)		+294.1 (NHPh)	(d)
$\text{Ph}-\text{NHNH}-\text{C}(=\text{O})-\text{N}=\text{N}-\text{Ph}$	1 M in DMSO	+276.9 (CONH)	(d)
		+294.4 (PhNH)	(d)
	in DMSO	+310.1 (NH_2)	(c)
		+224.2 (N)	(c)
		+220.7 (NH, ring)	(c)
	in DMSO	+307.3 (NH_2)	(c)
		+225.3 (N)	(c)
		+224.1 (NMe, ring)	(c)

TABLE 38—*cont.*

Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
	in DMSO	+317.0 (NH ₂) +242.6 (N) +228.0 (NH, ring)	(c) (c) (c)

For additional data, see footnote (a)

(a) See ref. 1, Tables 41–44 therein; also ref. 4, p. 170, and references therein.

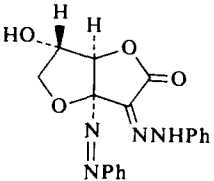
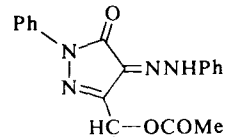
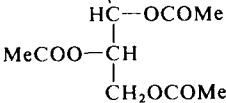
(b) Data from ref. 628; ¹⁴N spectra, 7.2 MHz, uncertain precision since no details are given, referred originally to aqueous NaNO₃, +3.7 ppm from neat nitromethane (Table 6).

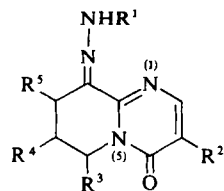
(c) Data from ref. 635; ¹⁵N natural abundance spectra, 10.09 MHz, field perpendicular to sample tube, originally referred to formamide in DMSO, +264.1 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4); ¹H-coupled and decoupled spectra.

(d) Data from ref. 378; ¹⁵N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO₃, +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

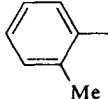
(e) Data from ref. 607; ¹⁵N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

TABLE 39
Nitrogen shieldings in some hydrazones

Compound	Solution or state	Nitrogen shielding referred to neat nitromethane			Notes
		C=N moiety	NR ₂ moiety	Other	
$R^1R^2C=N-NMe_2$ (R = alkyl)	neat liquids	+18 to +31	+277 to +291	—	(a)
$RCH=N-NHPh$ (R = substituted Ph)	in DMSO	+43 to +60	+230 to +239	—	(a)
$R^1CH=N-N=CHR^2$ (R = alkyl, aryl)	various	+14 to +21	—	—	(a)
	in CDCl ₃	+18.2	+212.5	-135.8 (N=N) -143.5	(b)
	in CDCl ₃	+15.3	+199.9	+69.2 (ring) +192.2 (NPh)	(b)
	in DMSO	+16.6	+197.5	+71.3 (ring) +188.7 (NPh)	(b)



0.5–1.0 M in CDCl₃

R ¹	R ²	R ³	R ⁴	R ⁵					
Ph	COOEt	Me	H	H	(Z-isomer)	+28.0	+212.8	+154.9 (1-N)	(c)
					(E-isomer)	?	+225.7	+194.7 (5-N)	
Ph	COOEt	H	Me	H	(Z-isomer)	+30.5	+214.6	+190.4 (5-N)	(c)
								+155.7 (1-N)	
Ph	COOEt	H	H	Me	(Z-isomer)	+29.6	+215.0	+206.8 (5-N)	(c)
								+155.3 (1-N)	
	COOEt	Me	H	H	(Z-isomer)	+33.3	+212.9	+206.0 (5-N)	(c)
					(E-isomer)	+41.2	+227.1	+149.0 (1-N)	
Ph	H	Me	H	H				+193.3 (5-N)	(c)
								+151.6 (1-N)	
Ph	H	Me	H	H	(Z-isomer)	+35.2	+218.3	+189.0 (5-N)	(c)
								+150.1 (1-N)	
Ph	H	Me	H	H				+196.0 (5-N)	(c)

(a) See ref. 1, Table 45 and references therein.

(b) Data from ref. 279; ¹⁵N natural abundance spectra, 40.5 MHz, field parallel to sample tube, originally referred to NO₃⁻ in aqueous NH₄NO₃, +4.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); ¹H-coupled and decoupled spectra, Cr(acac)₃ added as relaxation reagent.

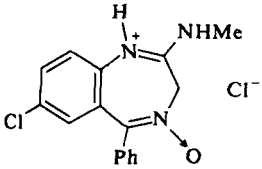
(c) Data from ref. 254; ¹⁵N natural abundance spectra, 10.04 MHz, field perpendicular to sample tube, originally referred to aqueous KNO₃ (+3.5 ppm from neat nitromethane), originally recalculated to neat nitromethane standard, conversion scheme II (Table 4).

TABLE 40

Nitrogen shieldings in some amidines and amidinium ions

Structure	Solution	Nitrogen shielding referred to neat nitromethane	Notes
Amidine structure, $\begin{array}{c} \text{R}_2\text{N} \\ \diagdown \\ \text{C}=\text{NR} \\ \diagup \\ \text{R} \end{array}$			
	in DMSO-d ₆ in acetone-d ₆	+263.4 (averaged)	(a)
		+265.3 (averaged)	(a)
	in CDCl ₃	+267.1 (averaged)	(a)
Amidinium structure, $\begin{array}{c} \text{R}_2\text{N} \\ \diagdown \\ \text{C}=\text{NR}_2^+ \\ \diagup \\ \text{R} \end{array}$			
$\text{Me}_2\text{N}-\text{CH}=\text{NMe}_2^+$ ↓ $\text{Me}_2\text{N}^+=\text{CH}-\text{NMe}_2$	ClO_4^- , in DMSO-d ₆ Cl^- , 2 M in MeCN	+282.5	(b)
$\text{Me}_2\text{N}-\text{C}(\text{Me})=\text{NMe}_2^+$ ↓ $\text{Me}_2\text{N}^+=\text{C}(\text{Me})-\text{NMe}_2$		+275.9	(c)
	MeSO_4^- , 2 M in CH_2Cl_2	+273.3	(c)

TABLE 40—*cont.*

Structure	Solution	Nitrogen shielding referred to neat nitromethane	Notes
 ("chlordiazepoxide")	in DMSO- d_6	+257.0 ($-\text{NH}^+=$) +363.0 ($-\text{NHMe}$)	(d) (d)

(a) Data from ref. 120; ^{15}N natural abundance spectra, 10.1 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; $\text{Cr}(\text{acac})_3$ added as relaxation reagent.

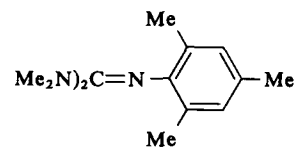
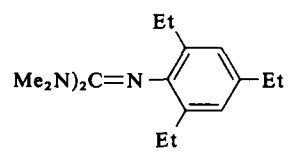
(b) Data from ref. 449; see Table 108, notes (k) and (l).

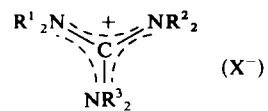
(c) Data from ref. 282; see Table 108, note (g).

(d) Data from ref. 363; ^{15}N natural abundance spectra, 20.28 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

Table 41

Nitrogen shieldings in guanidines and guanidinium ions

Compound or ion	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
Various alkyl- and aryl-substituted guanidines, $\text{RN}=\text{C}(\text{NR}_2)_2$	various	+175 to +211 ($\text{RN}=\text{C}$) +312 to +354 (NR_2)	(a) (a)
$(\text{Me}_2\text{N})_2\text{C}=\text{NPh}$	in CDCl_3	+178.3 ($\text{C}=\text{N}$) +325.8 +326.2 (NMe_2)	(b) (b) (b)
	in CDCl_3	+176.9 ($\text{C}=\text{N}$) +319.7 +329.7 (Nme_2)	(b) (b) (b)
	in CDCl_3	+177.1 ($\text{C}=\text{N}$) +314.7 +329.5 (NMe_2)	(b) (b) (b)
$(\text{Me}_2\text{N})_2\text{C}=\text{N}-\text{CH}_2\text{Ph}$	in CDCl_3	+186.3 ($\text{C}=\text{N}$) +323.7 +341.5 (NMe_2)	(b) (b) (b)

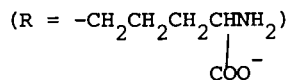


2 M in CH_2Cl_2

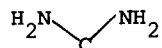
R^1	R^2	R^3	X^-		
Me	Me	Me	Cl^-	+305.4	(c)
Me	Me	Et	Cl^-	+300.5 (NMe_2)	(c)
				+283.7 (NEt_2)	(c)
Me	Me	H;Ph	Cl^-	+303.2 (NMe_2)	(c)
				+270.3 (NHPh)	(c)
Me	Me	H;Ph	CF_3COO^-	+302.8 (NMe_2)	(c)
				+268.9 (NHPh)	(c)
Me	Et	Et	Cl^-	+304.3 (NMe_2)	(c)
				+280.4 (NEt_2)	(c)
Et	Et	Et	Cl^-	+277.9	(c)

Table 41 (continued)

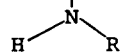
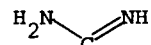
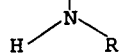
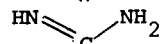
Guanidino moiety
in arginine



(1) (3)



(2)



in DMSO/H₂O (1:1),

pH = 14.1

-52°C

25°C

+265.2 (1-N or 3-N)

+300.0 (2-N)

+307.5 (1-N or 3-N)

+285.4 (averaged)

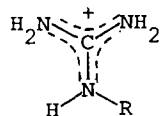
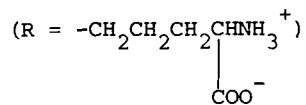
(d)

(d)

(d)

(d)

Guanidinium moiety
in arginine



in DMSO/H₂O (1:1),

pH = 7.0

-33°C

+305.0

(d)

+307.4

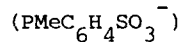
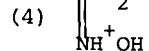
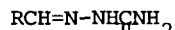
(d)

25°C

+306.2 (averaged)

(d)

(3) (1)



in DMSO

(2)

R = 2-pyridyl

+306.8 (1-N)

(e)

+241.7 (2-N)

(e)

+244.1 (3-N)

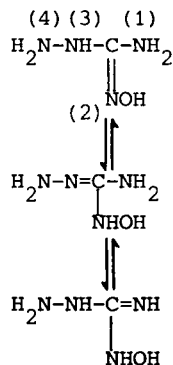
(e)

+64.2 (4-N)

(e)

Table 41 (continued)

R = 2-(3-Me-thiophenyl)		+308.2 (1-N)	(e)
		+242.1 (2-N)	(e)
		+245.4 (3-N)	(e)
		+63.6 (4-N)	(e)
R = 3-iodophenyl		+306.8 (1-N)	(e)
		+241.7 (2-N)	(e)
		+244.5 (3-N)	(e)
		? (4-N)	(e)
(4) (3) (1)			
$\begin{array}{c} \text{H}_2\text{N}-\text{NHCNH}_2 \\ \parallel \\ \text{NH}^+\text{OH} \\ (2) \end{array}$	(pMeC ₆ H ₄ SO ₃ ⁻)	in DMSO	+312.1 (1-N) (triplet) (e)
			+247.8 (2-N) (e)
			+286.7 (3-N) (doublet) (e)
			+327.1 (4-N) (broadened triplet) (e)
		in H ₂ O, pH = 4	+316 (1-N) (triplet) (e)
			+250 (2-N) (e)
			+288 (3-N) (doublet) (e)
			+330 (4-N) (e)



in H₂O, pH = 10

+328 (1-N)	(e)
+220 (2-N)	(e)
+300 (3-N)	(e)
+328 (4-N)	(e)

For additional data, see footnotes (a) and (f)

(a) See ref. 1, Tables 47 and 73 therein, also ref. 4, p.172; and references therein.

(b) Unpublished results by M. Franzen-Sieveking, D. Leibfritz, and R.L. Lichter, quoted in ref. 109, pp.68-69.

(c) Data from ref. 282, ¹⁵N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NO₃⁻ standard calibrated (+1.5 ppm) against neat nitromethane, conversion scheme IV (Table 4); Cr(acac)₃ added as relaxation reagent.

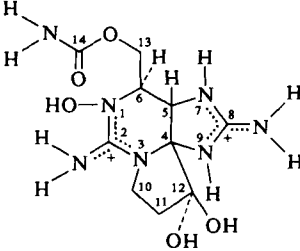
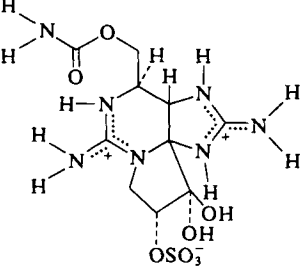
(d) Data from ref. 216, ¹⁵N labelled and unlabelled compounds, ¹⁵N spectra, 50.65 MHz, field parallel to sample tube, originally referred to 1 M HNO₃, +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(e) Data from ref. 283, details as in footnote (d), but 18.25 MHz spectra, ¹H-coupled and decoupled.

(f) For N-nitrosoguanidines, see Table 120; for N-nitro derivatives, see Table 113.

TABLE 42

Nitrogen shieldings in neosaxitoxin and gonyautoxin-II

Compound	Solvent	Nitrogen shielding referred to neat nitromethane
	D ₂ O-H ₂ O (5/95)	+310.5 (N-C8) +304.4 (N-C14) +292.5 (N-C2) +293.8 (N9) +280.2 (N7) +282.2 (N3) +241.1 (N1)
	D ₂ O-H ₂ O (5/95)	+310.8 (N-C8) +304.6 (N-C14) +294.2 (N-C2) +295.0 (N9) +280.2 (N7) +284.8 (N3) +300.8 (N1)

Data from ref. 285; ¹⁵N-labelled compounds, ¹⁵N spectra, 36.5 MHz, field parallel to sample tube, originally referred to NH₄⁺ in aqueous NH₄NO₃, +359.6 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

TABLE 43

Nitrogen shieldings in some ureas and related structures

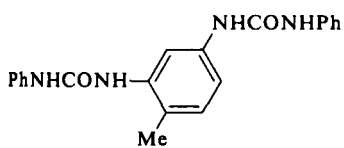
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
$\text{O}=\text{C}(\text{NH}_2)_2$	satd. in $\text{H}_2\text{O}/\text{EtOH}$	+305.0	(a)
	1 M in H_2O	+304.2	(b)
	in H_2O	+303.6	(c)
	in MeOH	+304	(d)
	in HCOOH	+303.7	(c)
	in TFA	+303.7	(c)
diprotanated species of urea	in "magic acid"	+246.4	(a)
$\text{H}_2\text{NC}(=\text{O})\text{NHMe}$	satd. in $\text{H}_2\text{O}/\text{EtOH}$	+307.4 (NH_2)	(a)
		+308.6 (NH)	(a)
$\text{H}_2\text{NC}(=\text{O})\text{NMe}_2$	satd. in $\text{H}_2\text{O}/\text{EtOH}$	+306.2 (NH_2)	(a)
		+308.0 (NMe_2)	(a)
$\text{H}_2\text{NC}(=\text{O})\text{NEt}_2$	satd. in $\text{H}_2\text{O}/\text{EtOH}$	+306.6 (NH_2)	(a)
		+283.9 (NEt_2)	(a)
$\text{MeNHC}(=\text{O})\text{NHMe}$	satd. in $\text{H}_2\text{O}/\text{EtOH}$	+308.6	(a)
$\text{MeNHC}(=\text{O})\text{NMe}_2$	satd. in $\text{H}_2\text{O}/\text{EtOH}$	+312.4 (NH)	(a)
		+318.3 (NMe_2)	(a)
$\text{Me}_2\text{NC}(=\text{O})\text{NMe}_2$	in CH_2Cl_2	+311.5	(g)
	neat liquid	+317.9	(a)
	neat liquid + SbCl_5	+307.4	(a)
	in "magic acid"		
	(diprotanated species)	+235.4	(a)
$\text{Me}_2\text{NC}(=\text{O})\text{NEt}_2$	satd. in CDCl_3	+317.5 (NMe_2)	(a)
		+292.5 (NEt_2)	(a)
	in $\text{CD}_2\text{Cl}_2 + \text{TiCl}_4$	+292.6 (NMe_2)	(a)
		+277.6 (NEt_2)	(a)
$\text{Me}_2\text{NC}(=\text{O})\text{NHPr}^i$	satd. in $\text{H}_2\text{O}/\text{EtOH}$	+312.6 (NMe_2)	(a)
		+277.4 (NH)	
$\text{Et}_2\text{NC}(=\text{O})\text{NEt}_2$	neat liquid	+291.0	(a)
$\text{Pr}^i\text{NHC}(=\text{O})\text{NHPr}^i$	satd. in $\text{H}_2\text{O}/\text{EtOH}$	+279.6	(a)
$\text{Bu}^n_2\text{C}(=\text{N})\text{NBu}^n_2$	in CH_2Cl_2	+295.8	(g)
$\text{H}_2\text{NC}(=\text{O})\text{NHPh}$	in MeOH	+305.9 (NH_2)	(c)
		+276.8 (NHPh)	(c)
	in TFA	+303.4 (NH_2)	(c)
		+277.5 (NHPh)	(c)
$\text{PhNHC}(=\text{O})\text{NHPh}$	in TFA	+277.1	(c)
$\text{HOCH}_2\text{NHC}(=\text{O})\text{NHCH}_2\text{OH}$	powdered solid	+282	(e)
	in TFA	+276.8	(c)
		+281.1	(c)

TABLE 43—*cont.*

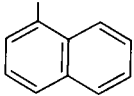
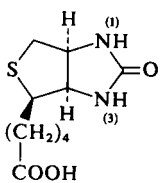
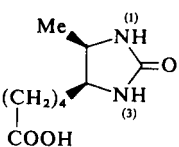
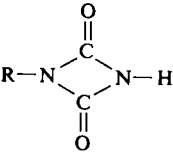
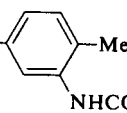
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
PhNHCONH 	in TFA	+276.8 (NHPh) +283.5 (NH, other)	(c) (c)
$\text{H}_2\text{NC(=O)NHC(=O)NH}_2$ (biuret)	in HCOOH	+261.3 (NH)	(c)
	in TFA	+295.4 (NH ₂) +263.7 (NH) +295.2 (NH ₂)	(c) (c) (c)
$\text{PhNHC(=O)NHC(=O)NHPh}$	in TFA	+262.6 (NH)	(c)
$\text{PhNHC(=O)N(Ph)C(=O)NHPh}$	in TFA	+270.7 (NHPh) +256.1 (NPh) +266.8 (NHPh)	(c) (c) (c)
 ("Biotin")	satd. in 0.1 M aqueous NaHCO ₃ 0.3 M in DMSO	+289.8 (1-N) +298.8 (3-N) +291.2 (1-N) +300.9 (3-N)	(f) (f) (f) (f)
 ("Desthiobiotin")	satd. in 0.1 M aqueous NaHCO ₃ 0.7 M in DMSO	+283.0 (1-N) +288.7 (3-N) +285.5 (1-N) +291.2 (3-N)	(f) (f) (f) (f)
	1 M in H ₂ O 1.8 M in H ₂ O 1 M in 0.1 M NaHCO ₃ 2 M in DMSO	+300.2 +300.7 +300.5 +302.9	(f) (f) (f) (f)
 $\text{R} = $ 	in TFA	+236.4 (N—R) +281.5 (NH)	(c) (c)
<i>N</i> -nitrosoureas		see Table 120	

TABLE 43—*cont.*

For additional data, see ref. 1, Tables 49–51 therein

(a) Data from ref. 239; ^{15}N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NO_3^- standard calibrated (-2.6 ppm) against neat nitromethane, conversion scheme IV (Table 4).

(b) Data from ref. 215; ^{15}N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO_3 , $+6.2$ ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4); ^1H -coupled spectra.

(c) Data from ref. 280; ^{15}N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NO_3^- in aqueous NH_4NO_3 , $+4.0$ ppm from nitromethane (Table 6), conversion scheme II (Table 4).

(d) Data from ref. 636; ^{14}N PFT spectra, 13.0 MHz, field parallel to sample tube, originally referred to aqueous NH_3 , $+376$ ppm from neat nitromethane (Table 1), conversion scheme IV (Table 4).

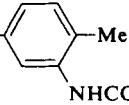
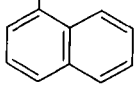
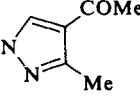
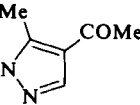
(e) Data from ref. 182; ^{15}N natural abundance CP-MASS spectra, 9.12 MHz, originally referred to solid $(\text{NH}_4)_2\text{SO}_4$ calibrated ($+360$ ppm) against neat nitromethane; uncorrected for bulk-susceptibility effects.

(f) Data from ref. 281; ^{15}N -labelled and unlabelled compounds, ^{15}N spectra, 18.25 MHz, details as in footnote (b).

(g) Data from ref. 637; details as in footnote (a), but referred directly to neat nitromethane.

TABLE 44

Nitrogen shieldings in some carbamates

Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
EtOC(=O)NH ₂ (ethyl carbamate)	in pyridine	+307.6	(a)
	in DMSO	+305.3	(a)
	in H ₂ O	+305.0	(a)
	in HCOOH	+305.9	(a)
	in TFA	+305.9	(a)
EtOC(=O)NHPh	in DMSO	+276.0	(a)
	in TFA	+276.2	(a)
EtOCONH- 	in pyridine	+276.6; +281.4	(a)
	in DMSO	+276.7; +281.3	(a)
	in HCOOH	+277.4; +281.5	(a)
	in TFA	+277.5; +281.5	(a)
EtOCONH- 	in TFA	+284.6	(a)
H ₂ NC(=O)NHCOOEt (ethyl allophanate)	in TFA	+262.8 (NH) +293.1 (NH ₂)	(a) (a)
PhNHC(=O)NHCOOEt	in TFA	+262.1 (NH) +267.1 (NHPh)	(a) (a)
PhNHC(=O)N(Ph)COOEt	in TFA	+264.5	(a)
EtO-CO-N 	in DMSO-d ₆	+166.7 (CO-N)	(b)
	in CDCl ₃	+167.9 (CO-N)	(b)
EtO-CO-N 	in DMSO-d ₆	+159.2 (CO-N)	(b)
	in CDCl ₃	+159.9 (CO-N)	(b)

For additional data, see ref. 1, Tables 52 and 53 therein

(a) Data from ref. 280; ¹⁵N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NO₃⁻ in aqueous NH₄NO₃, +4.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

(b) Data from ref. 120; ¹⁵N natural abundance spectra, 10.1 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; Cr(acac)₃ added as relaxation reagent.

TABLE 45

Nitrogen shieldings in some polyurethanes^a (solutions in CF₃COOH)

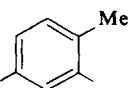
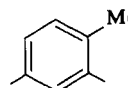
Structure	Nitrogen shielding referred to neat nitromethane
$-\text{[NH(CH}_2\text{)}_n\text{NH-CO-O-CH}_2\text{CH}_2\text{-O-CO-]--}$	
$n = 2$	+297.5
3	+297.7
4	+291.9
6	+290.7
8	+289.0
12	+289.8
$-\text{[NH(CH}_2\text{)}_n\text{NH-CO-O-(CH}_2\text{)}_n\text{-O-CO-]--}$	
$n = 2$	+290.7
3	+290.0
4	+289.6
6	+289.1
8	+289.0
12	+288.9
$-\text{[NH(CH}_2\text{)}_6\text{NH-CO-O-(CH}_2\text{CH}_2\text{O)}_3\text{-CO-]--}$	+290.6
$-\text{[N} \begin{array}{c} \diagup \quad \diagdown \\ \text{---} \quad \text{---} \\ \diagdown \quad \diagup \end{array} \text{N-CO-O-CH}_2\text{CH}_2\text{-O-CO-]--}$	+292.2
$-\text{[NH-} \begin{array}{c} \text{---} \quad \text{---} \\ \quad \\ \text{---} \quad \text{---} \end{array} \text{CH}_2\text{-} \begin{array}{c} \text{---} \quad \text{---} \\ \quad \\ \text{---} \quad \text{---} \end{array} \text{NH-CO-O-(CH}_2\text{CH}_2\text{O)}_n\text{-CO-]--}$	
$n = 1$	+277.8
2	+277.9
3	+277.8
4	+277.7
$-\text{NH} \begin{array}{c} \text{---} \quad \text{---} \\ \quad \\ \text{---} \quad \text{---} \end{array} \text{NH-CO-O-(CH}_2\text{)}_n\text{-O-CO-]--}$ 	
$n = 2$	+278.3; +281.8
3	+277.9; +281.8
4	+277.5; +277.7
6	+277.8; +281.6
12	+277.8; +281.7
$-\text{NH} \begin{array}{c} \text{---} \quad \text{---} \\ \quad \\ \text{---} \quad \text{---} \end{array} \text{NH-CO-O-(CH}_2\text{CH}_2\text{O)}_3\text{-CO-]--}$ 	
(A)	+277.9 (A)
(B)	+281.8 (B)

TABLE 45—*cont.*

Structure	Nitrogen shielding referred to neat nitromethane
$\text{--}[\text{--NH} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{Me} \end{array} \text{NH--CO--O--(CH}_2\text{)}_6\text{--O--CO--}]\text{--}$	+281.8
$\text{--}[\text{--NH} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{Me} \end{array} \text{NH--CO--O--(CH}_2\text{CH}_2\text{O)}_3\text{--CO--}]\text{--}$	+282.1
$\text{--}[\text{--NH} \begin{array}{c} \text{C}_8\text{H}_6 \\ \text{Me} \end{array} \text{NH--CO--O--(CH}_2\text{)}_6\text{--O--CO--}]\text{--}$	+284.5
$\text{--}[\text{--CO--(CH}_2\text{)}_4\text{--CO--O--(CH}_2\text{)}_4\text{--O--CO--NH} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{Me} \end{array} \text{NH--CO--NHNH--CO--NHNH--}]\text{--}$ (A) (B) (C) (D) (D) (C)	+277.1 (A) +280.6 (B) +278.4 (C) +279.9 (D)
Copolymer^b	
$\left\{ \begin{array}{l} \text{---O--(CH}_2\text{)}_6\text{--O--CO--NH} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{Me} \end{array} \text{NH--CO--O--(CH}_2\text{)}_6\text{--O---} \\ \text{---NH--(CH}_2\text{)}_6\text{--NH--CO--NH} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{Me} \end{array} \text{NH--CO--NH--(CH}_2\text{)}_6\text{--NH---} \end{array} \right\}$ (A) (B) (C) (D) (E) (F)	+277.1 (A) +280.4 (C) +282.0 (B) +282.2 (D) +285.7 (E) +285.9 (F)
Copolymer	
$\left\{ \begin{array}{l} \text{---O--(CH}_2\text{)}_4\text{--O--CO--NH} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{Me} \end{array} \text{NH--CO--O--(CH}_2\text{)}_4\text{--O---} \\ \text{---CO--NH} \begin{array}{c} \text{C}_8\text{H}_6 \\ \text{Me} \end{array} \text{NH--CO---} \end{array} \right\}$ (A) (B) (C)	+278.0 (A) +281.6 (B) +284.5 (C)

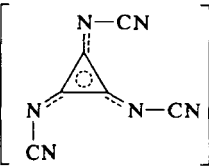
TABLE 45—cont.

(a) Data from ref. 280 unless otherwise indicated; ^{15}N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NO_3^- in aqueous NH_4NO_3 , +4.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

(b) 20.28 MHz spectra, field parallel to sample tube, other details as in footnote (a).

TABLE 46

Nitrogen shieldings in some cyanamide and carbodiimide structures

Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
Cyanamides			
$\text{R}_2\text{N}-\text{C}\equiv\text{N}$			
$\text{Me}_2\text{N}-\text{CN}$	neat liquid	+371.8 (NMe_2)	(a)
		+184.8 (CN)	(a)
$\text{H}_2\text{N}-\text{CN}$	in DMSO	+366 (NH_2)	(b)
		+196 (CN)	(b)
$\text{Ph}_2\text{N}-\text{CN}$	in acetone	ca. +335 (NPh_2)	(b)
		ca. +193 (CN)	(b)
	in D_2O	+312.5 (N)	(c)
		+215.2 (CN)	(c)
Carbodiimides			
$\text{R}-\text{N}=\text{C}=\text{N}-\text{R}'$			
$\text{R}=\text{R}'=\text{Pr}^i$	various solvents	+274 to +278	(d)
$\text{R}=\text{R}'=\text{cyclohexyl}$	various solvents	ca. +281	(d)
unsymmetrically substituted carbodiimides,			
$\text{R}, \text{R}' = \text{alkyl or Ph}$	various solvents	+270 to +297	(d)

(a) See ref. 1, p. 54 and reference therein.

(b) See ref. 3, p. 194 and references therein.

(c) Data from ref. 638; ^{15}N spectra, details not reported, originally referred to liquid NH_3 , +380.2 ppm from neat nitromethane (Table 6).

(d) See ref. 1, Table 55 and reference therein.

TABLE 47

Nitrogen shieldings in some amides

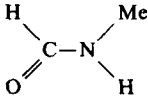
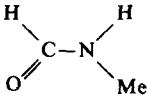
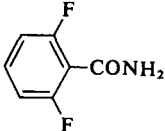
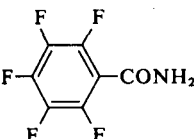
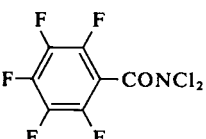
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
NC(=O)NH ₂ (formamide)	neat liquid	+268	(a)
	neat liquid	+268.1	(b)
	+10% DMSO-d ₆		
	various	+264 to +272	(c)
 (<i>E</i> -isomer)	neat liquid	+271 (<i>E</i> , <i>Z</i>)	(a)
 (<i>Z</i> -isomer)	neat liquid	+272.2 (<i>E</i>)	(b)
	+15% DMSO-d ₆	+270.6 (<i>Z</i>)	(b)
HC(=O)NMe ₂ (dimethylformamide, DMF)	neat liquid	+277.01 ± 0.11	(d)
	0.5 M in H ₂ O	+271.0	(f)
	0.5 M in MeOH	+276.5	(f)
	0.5 M in DMSO	+278.0	(f)
	0.5 M in CHCl ₃	+278.7	(f)
	50% in benzene	+283.2	(f)
	2 M in CDCl ₃	+274.9	(e)
HC(=O)NEt ₂	neat liquid	+248	(a)
HC(=O)NHCH ₂ Ph	8 M in CDCl ₃	+256.5	(g)
MeC(=O)NH ₂ (acetamide)	1.5 M in CHCl ₃	+275.2	(h)
	1:3 v/v in acetone	+274.7	(i)
	in H ₂ O	+270	(j)
	1 M in H ₂ O	+268.0	(l)
	in MeOH	+267	(a)
MeC(=O)NHMe	neat liquid	+273.9	(i)
		+273	(a)
		+272.8	(k)
	1:1 v/v in acetone	+275.3	(i)
	1:3 v/v in acetone	+272.8	(i)
	inf. dil. in acetone	+277.7	(h)
	2 M in CCl ₄	+273.2	(k)
	2 M in H ₂ O	+266.4	(k)
	neat liquid	+284	(a)
		+281.6	(i)
MeC(=O)NMe ₂	2 M in Et ₂ O	+282.8	(i)
	1 M in Et ₂ O	+286.1	(i)
	0.5 M in Et ₂ O	+287.6	(i)
	1:1 v/v in acetone	+282.1	(i)

TABLE 47—*cont.*

Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
	1:3 v/v in acetone	+281.3	(i)
	inf. dil. in acetone	+282.2	(h)
$\text{MeC}=\text{NMe}$	1:1 v/v in acetone	+155.5	(i)
$\begin{array}{c} \text{OMe} \\ \\ \text{MeC}=\text{NMe} \end{array}$	1:3 v/v in acetone	+155.8	(i)
(isoamide structure)	inf. dil. in acetone	+155.2	(h)
	neat liquid	+155.8	(i)
$\text{EtC}(=\text{O})\text{NHMe}$	neat liquid	+275.6	(k)
	2 M in CCl_4	+275.8	(k)
	2 M in H_2O	+268.8	(k)
$\text{Pr}^i\text{C}(=\text{O})\text{NHMe}$	neat liquid	+277.5	(k)
	2 M in CCl_4	+277.7	(k)
	2 M in H_2O	+270.8	(k)
$\text{Bu}^t\text{C}(=\text{O})\text{NHMe}$	2 M in CCl_4	+282.3	(k)
	2 M in H_2O	+274.1	(k)
$\text{HN} \begin{array}{c} \diagup \diagdown \\ \triangle \end{array} \text{C}(=\text{O})\text{NH}_2$	50% in CDCl_3	+273.3 (CONH_2)	(m)
$\text{MeC}(=\text{O})\text{NH}(\text{aryl})$	in DMSO	+242 to +249	(c)
	satd. in CH_2Cl_2	+273.0	(n)
	satd. in CH_2Cl_2	+267.0	(n)
	satd. in CH_2Cl_2	+274.0	(n)

For additional data see footnote (c)

(a) Data from ref. 636; ^{14}N PFT spectra, 13.0 MHz, field parallel to sample tube, originally referred to aqueous NH_3 , +376 ppm from neat nitromethane (Table 11), conversion scheme II (Table 4).

(b) Data from ref. 433; ^{15}N natural abundance spectra with spin-polarization transfer from ^1H , 10.14 MHz, originally referred to neat nitromethane + 10% DMSO-d_6 , uncorrected for bulk susceptibility effects; ^1H -coupled spectra.

(c) See ref. 1, Tables 57–61, and references therein.

TABLE 47—*cont.*

- (d) See Table 6, and references therein.
- (c) Data from ref. 619; ^{15}N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NO_3^- standard calibrated (+1.5 ppm) against neat nitromethane, conversion scheme IV (Table 4); $\text{Cr}(\text{acac})_3$ added as relaxation reagent.
- (f) Data from ref. 32; ^{15}N -labelled compounds, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to satd. aqueous KNO_2 (−228.9 ppm from neat nitromethane, Table 6), conversion scheme II (Table 4); originally reported relative to what was supposed to be aqueous NH_4Cl standard at +590.7 ppm from the standard employed, but this value corresponds to NH_4NO_3 (Table 6).
- (g) Data from ref. 118; ^{15}N -enriched (30%) compound, ^{15}N spectra with spin-population transfer (SPT), 25.32 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.
- (h) Data from ref. 259; ^{15}N natural-abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.
- (i) Data from ref. 259; high-precision ^{14}N CW spectra, 4.3342 MHz, concentric spherical sample containers in order to eliminate bulk-susceptibility effects, differential-saturation technique with full lineshape fitting; referred to neat nitromethane, $+35.0 \pm 0.2^\circ\text{C}$.
- (j) Data from ref. 408; ^{15}N -labelled compound, ^{15}N spectrum, 18.24 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.
- (k) Data from ref. 431; double-resonance ^1H - ^{15}N spectra, AISEFT technique, 90/9.12 MHz, field parallel to sample tube, originally referred to neat MeCONHMe and originally recalibrated to neat nitromethane, uncorrected for bulk-susceptibility effects; natural abundance of ^{15}N .
- (l) Data from ref. 215; ^{15}N natural abundance spectrum, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO_3 , +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).
- (m) Data from ref. 607; ^{15}N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.
- (n) Data from refs. 435 and 624; ^{15}N -labelled compounds, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to liquid NH_3 , +380.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

Table 48

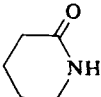
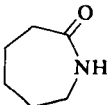
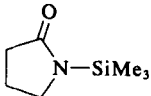
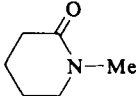
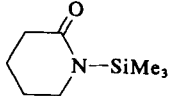
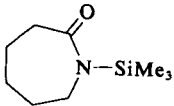
Nitrogen shieldings of some amide structures in protonating media

Compound	Concentration	Nitrogen shielding (in ppm, referred to neat nitromethane) in solvent specified								
		FSO ₃ H	MeSO ₃ H	TFA + 20 % MeSO ₃ H	TFA + 5 % MeSO ₃ H	TFA	Cl ₂ CHCOOH	MeCOOH	H ₂ O	MeOH
MeCONH ₂	4.000 M	+251.7	+249.1	+255.8	+260.6	+261.6	+262.7	+268.6	+267.7	+272.0
	0.001 M	+251.8	+248.8	+251.4	+252.1	+254.0	+260.0	+268.4	+267.3	+272.6
Polyglycine, (Gly) _n , n = ca. 50	2.00 M	+257.3	+262.1	-	+268.2	+271.3	+270.6	-	-	-
	0.01 M	+258.0	+261.6	-	+265.1	+271.3	+270.2	-	-	-
Polyalanine, (L-Ala) _n , n = ca. 50	1.50 M	-	-	+250.9	+253.0	+256.6	-	-	-	-
	0.01 M	-	-	+250.4	+251.7	+256.7	-	-	-	-

Data from ref. 299, ¹⁵N enriched (99%) compounds, ¹⁵N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NO₃⁻ in aqueous NH₄NO₃, +4.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

TABLE 49

Nitrogen shieldings in some simple lactams

Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
	neat liquid	+263.3	(a)
	2 M in CCl ₄	+263.8	(a)
	2 M in H ₂ O	+256.8	(a)
	2 M in CCl ₄	+264.7	(a)
	2 M in H ₂ O	+257.7	(a)
	2 M in CCl ₄	+261.1	(a)
	2 M in H ₂ O	+254.1	(a)
	75% v/v in C ₆ D ₆	+262.7	(b)
	75% v/v in C ₆ D ₆	+270.6	(b)
	75% v/v in C ₆ D ₆	+263.6	(b)
	75% v/v in C ₆ D ₆	+261.7	(b)

For additional data see ref. 1, Table 62 therein

(a) Data from ref. 431; double-resonance ^1H - ^{15}N spectra, AISEFT technique, 90/9.12 MHz, field perpendicular to sample tube, originally referred to neat MeCONHMe and originally recalibrated to neat nitromethane, uncorrected for bulk susceptibility effects; natural abundance of ^{15}N .

(b) Data from ref. 350; ^{15}N natural abundance spectra, 20.28 MHz, field parallel to sample tube, originally referred to neat formamide, +268.6 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

TABLE 50

Nitrogen shieldings in conjugated cyclic lactams, thiolactams and amidines
(tautomeric or isomeric forms of OH-, SH- and NH₂-substituted azines and azoles)

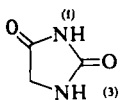
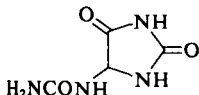
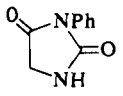
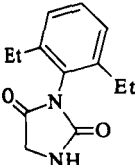
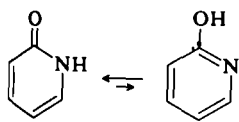
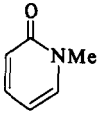
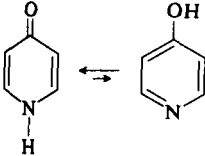
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
 (hydantoin)	powdered solid	+233 (1-N) +298 (3-N)	(a) (a)
 (allantoin)	powdered solid	+237 (1-N) +283 (3-N) +294 (exocyclic)	(a) (a) (a)
	satd. in DMSO-d ₆	+216.8 (NPh) +299.2 (NH)	(b) (b)
	satd. in DMSO-d ₆	+266.2 (NH)	(b)
	satd. in DMSO-d ₆ various	+207.8 +209 to +212	(c) (d)
	various	ca. +215	(d)
	various	+222 to +227	(d)
	various	+240 to +248	(d)

TABLE 50—*cont.*

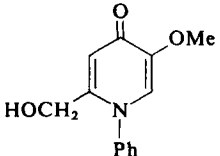
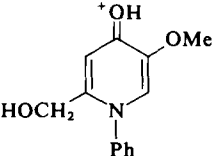
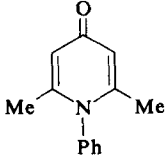
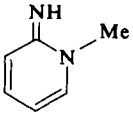
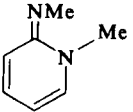
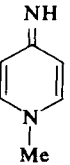
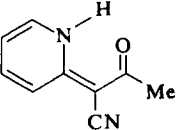
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
	3% in DMSO-d ₆	+231	(e)
	3% in DMSO-d ₆ +HCl	+196	(e)
	satd. in CDCl ₃	+214	(e)
	in acetone-d ₆	+242.6 (NMe) +194.2 (=NH)	(f) (f)
	in acetone-d ₆	+239.3 (NMe) +191.3 (=NMe)	(f) (f)
	in acetone	ca. +260 (NMe) ca. +168 (=NH)	(d) (d)
	satd. in CHCl ₃	+200 (NH)	(g)

TABLE 50—*cont.*

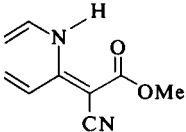
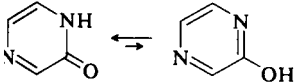
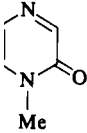
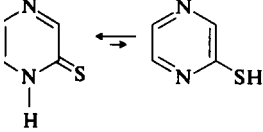
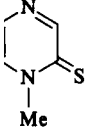
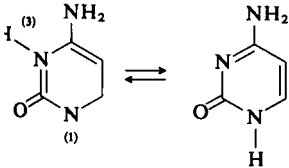
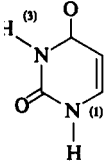
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
	satd. in CHCl_3	$+230 \pm 3$ (NH)	(g)
	in DMSO-d_6	$+198.3$ (NH) $+35.6$ ($=\text{N}$)	(h) (h)
	in DMSO-d_6	$+211.8$ (NMe) $+38.9$ ($=\text{N}$)	(h) (h)
	in DMSO-d_6	$+179.7$ (NH) $+51.2$ ($=\text{N}$)	(h) (h)
	in DMSO-d_6	$+180.1$ (NMe) $+58.3$ ($=\text{N}$)	(h) (h)
	in H_2O , pH = 2	$+294 \pm 4$ (NH_3^+)	(i)
	pH = 8	$+257 \pm 4$ (1-N, 3-N) $+306 \pm 4$ (NH_2) $+257 \pm 4$ (1-N) $+191 \pm 4$ (3-N)	(i) (i) (i) (i)
cytosine)	pH = 14	$+324 \pm 4$ (NH_2) $+186 \pm 4$ (1-N, 3-N)	(i) (i)
	in DMSO-d_6	$+245.2$ (1-N) $+217.7$ (3-N)	(j) (j)
	in DMSO-d_6 $+\text{Et}_4\text{N}^+\text{F}^-$ (1 equiv.)	not observed (1-N) $+215.6$ (3-N)	(j) (j)
	in DMSO-d_6 $+\text{Et}_4\text{N}^+\text{F}^-$ (4 equiv.)	$+235.8$ (1-N) $+217.0$ (3-N)	(j) (j)
uracil)	in DMSO-d_6	$+228.1$ (1-N)	(j)
1-N-cyclohexyluracil	$+\text{Et}_4\text{N}^+\text{F}^-$ (54 equiv.)	$+218.7$ (3-N)	(j)

TABLE 50—*cont.*

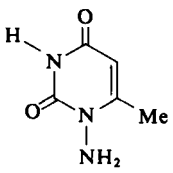
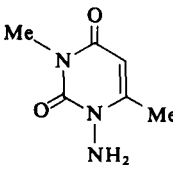
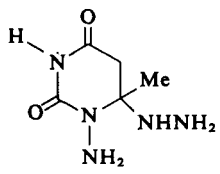
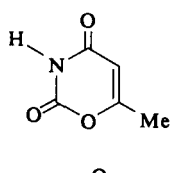
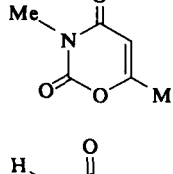
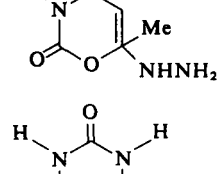
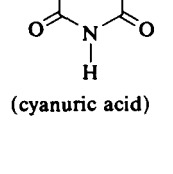
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
 <chem>Cc1c[nH]c(=O)[nH]c1=O</chem>	in DMSO-d ₆	+221.7 (NH)	(k)
 <chem>Cc1c[nH]c(=O)[nH]c1C=O</chem>	in DMSO-d ₆	+224.6 (NMe)	(k)
 <chem>Cc1c[nH]c(=O)[nH]c1C(=O)NHNH2</chem>	in DMSO-d ₆	+228.0 (NH, ring)	(k)
 <chem>Cc1c[nH]c(=O)[nH]c1=O</chem>	in DMSO-d ₆	+230.5	(k)
 <chem>Cc1c[nH]c(=O)[nH]c1=O</chem>	in DMSO-d ₆	+233.5	(k)
 <chem>Cc1c[nH]c(=O)[nH]c1=O</chem>	in DMSO-d ₆	+233.8	(k)
 <chem>O=C1NC(=O)NC(=O)N1</chem> (cyanuric acid)	powdered solid	+ 250	(l)

TABLE 50—cont.

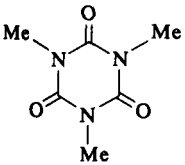
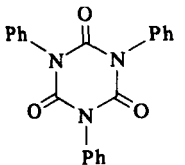
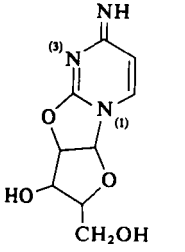
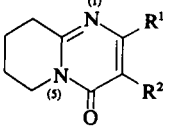
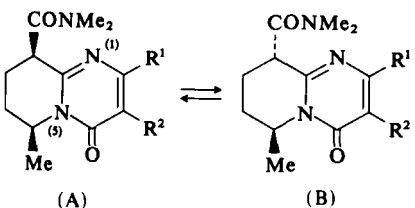
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
	TFA	+291.5	(m)
	TFA	+277.2	(m)
	in DMSO-d ₆	+320.2 (1-N) +213.6 (3-N)	(n) (n)
	in CDCl ₃		
R ¹ = H, R ² = COOEt		+183.5 (5-N) +144.9 (1-N)	(o, p) (o, p)
R ¹ = Me, R ² = Et		+196.3 (5-N) +139.1 (1-N)	(o) (o)
	in CDCl ₃		
(A)			
(B)			
R ¹ = R ² = H		{ +281.8 (NMe ₂ , A) +188.4 (5-N, A) +140.2 (1-N, A) +283.2 (NMe ₂ , B) +188.4 (5-N, B) +140.2 (1-N, B)	(o) (o) (o) (o) (o) (o)

TABLE 50—*cont.*

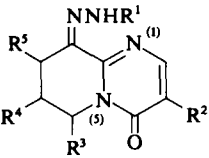
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes				
$R^1 = H, R^2 = CN$		+280.6 (NMe ₂ , A)	(o)				
		+188.4 (5-N, A)	(o)				
		+141.8 (1-N, A)	(o)				
		+283.4 (NMe ₂ , B)	(o)				
		+188.1 (5-N, B)	(o)				
		+141.8 (1-N, B)	(o)				
$R^1 = H, R^2 = Ph$		+280.2 (NMe ₂ , A)	(o)				
		+183.9 (5-N, A)	(o)				
		+140.3 (1-N, A)	(o)				
		+282.6 (NMe ₂ , B)	(o)				
		+183.9 (5-N, B)	(o)				
		+139.1 (1-N, B)	(o)				
$R^1 = H, R^2 = COOEt$		+280.6 (NMe ₂ , A)	(o)				
		+181.9 (5-N, A)	(o)				
		+143.9 (1-N, A)	(o)				
		+283.2 (NMe ₂ , B)	(o)				
		+181.6 (5-N, B)	(o)				
		+143.0 (1-N, B)	(o)				
$R^1 = Me, R^2 = Et$		+280.9 (NMe ₂ , A)	(o)				
		+195.3 (5-N, A)	(o)				
		+135.3 (1-N, A)	(o)				
		+283.6 (NMe ₂ , B)	(o)				
		+195.0 (5-N, B)	(o)				
		+134.6 (1-N, B)	(o)				
	in CDCl ₃						
R^1	R^2	R^3	R^4	R^5			
Ph	COOEt	Me	H	H	<i>Z</i> -isomer	+194.7 (5-N)	(q)
					<i>E</i> -isomer	+154.9 (1-N)	(q)
						+190.4 (5-N)	(q)
						(?) (1-N)	(q)
Ph	COOEt	H	Me	H	<i>Z</i> -isomer	+200.8 (5-N)	(q)
						+155.7 (1-N)	(q)
Ph	COOEt	H	H	Me	<i>Z</i> -isomer	+206.0 (5-N)	(q)
						+155.3 (1-N)	(q)

TABLE 50—*cont.*

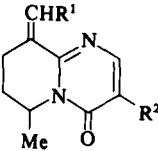
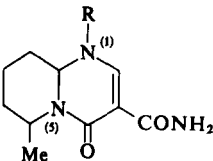
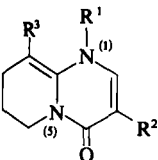
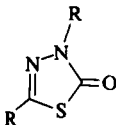
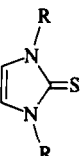
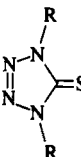
Compound				Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
α -MeOC ₆ H ₄	COOEt	Me	H	H	<i>Z</i> -isomer	+193.3 (5-N) (q)
					<i>E</i> -isomer	+149.0 (1-N) (q)
						+189.0 (5-N) (q)
						+151.6 (1-N) (q)
Ph	H	Me	H	H	<i>Z</i> -isomer	+196.0 (5-N) (q)
						+150.1 (1-N) (q)
						
					in CDCl ₃	
						+193.5 (5-N) (p)
						+161.2 (1-N) (p)
						+204.0 (5-N) (p)
						+164.2 (1-N) (p)
						+199.1 (5-N) (p)
						+162.1 (1-N) (p)
						
					in CDCl ₃	
						+281.9 (1-N) (p)
						+287.1 (1-N) (p)
						
						+221.9 (5-N) (p)
						+251.6 (1-N) (p)
						+222.5 (5-N) (p)
						+268.3 (1-N) (p)
						+245.0 (5-N) (p)
						+164.2 (1-N) (p)

TABLE 50—*cont.*

Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
Tetrahydropterin derivatives			
(6-<i>rs</i>-tetrahydrofolic acid)	in H ₂ O/D ₂ O, pH = 7 0.7 M in 6 M aqueous HCl	+206.8 (1-N) +302.0 (2-N) +240.4 (3-N) +337.6 (5-N) +309.8 (8-N) +312.0 (10-N) +258.8 (NH, side chain) +267.7 (1-N) +295.5 (2-N) +242.8 (3-N) +335.5 (5-N) +303.6 (8-N) +319.7 (10-N) +261.4 (NH, side chain)	(r) (r) (r) (r) (r) (r) (r) (r) (s) (s) (s) (s) (s) (s) (s)
	in H ₂ O/D ₂ O, pH = 7	+207.7 (1-N) +298.5 (2-N) +240.5 (3-N) +334.5 (5-N) +308.4 (8-N) +308.4 (10-N) +260.8 (NH, side chain)	(r) (r) (r) (r) (r) (r) (r)

TABLE 50—*cont.*

Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
		see Table 87	
		see Table 87	
		see Table 87	
Nucleoside structures		see Table 104	
For additional data see footnote (d)			

(a) Data from ref. 182; ^{15}N natural abundance CP-MASS spectra, 9.12 MHz, originally referred to $(\text{NH}_4)_2\text{SO}_4$ (solid) standard calibrated (+360 ppm) against neat liquid nitromethane, uncorrected for bulk-susceptibility effects.

(b) Data from ref. 250; ^{15}N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NH_4^+ in aqueous NH_4NO_3 , +359.6 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); gated decoupling in order to obtain ^1H -coupled spectra with NOE retained.

(c) Data from ref. 350; ^{15}N natural abundance spectra, 20.28 MHz, field parallel to sample tube, originally referred to neat formamide, +268.6 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4); originally reported relative to liquid NH_3 .

(d) See ref. 1, Table 64 therein, and ref. 4, pp. 172 and 190.

(e) Data from ref. 639; ^{15}N -labelled compounds, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; originally reported relative to liquid NH_3 standard taken at +380.2 ppm from nitromethane.

(f) Data from ref. 348; ^{15}N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(g) Data from ref. 257; ^{14}N PFT spectra, 21.7 MHz, field parallel to sample tube, uncorrected for bulk-susceptibility effects.

(h) Data from ref. 256; ^{15}N natural abundance spectra, 40.53 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk susceptibility effects.

(i) Data from ref. 238; low-precision ^{14}N PFT spectra, 13.0 MHz, originally referred to aqueous NH_3 , +378 ppm from neat nitromethane (Table 11).

(j) Data from ref. 359; ^{15}N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to liquid NH_3 , +380.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

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TABLE 50—*cont.*

(k) Data from ref. 635, ^{15}N natural abundance spectra, 10.05 and 9.03 MHz, field perpendicular to sample tube, originally referred to formamide in DMSO, +264.7 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(l) Data from ref. 182; ^{15}N natural abundance CP-MASS spectra, 9.12 MHz, originally referred to solid $(\text{NH}_4)_2\text{SO}_4$ standard calibrated (+360 ppm) against neat liquid nitromethane, uncorrected for bulk-susceptibility effects.

(m) Data from ref. 280; ^{15}N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NO_3^- in aqueous NH_4NO_3 , +4.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

(n) Data from ref. 640; ^{15}N -labelled 1-N and 3-N sites, ^{15}N spectra, 40.5 MHz, field parallel to sample tube, originally referred to NO_3^- in aqueous NH_4NO_3 , +4.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

(o) Data from ref. 641; ^{15}N natural abundance spectra, 10.04 MHz, field perpendicular to sample tube, originally referred to aqueous KNO_3 , +3.5 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); 0.5–1.0 M solutions.

(p) Data from refs. 642, 643, details as in footnote (o).

(q) Data from ref. 254, details as in footnote (o); originally recalculated to nitromethane standard.

(r) Data from ref. 286; ^{15}N -labelled and unlabelled compounds, ^{15}N spectra, 10.1 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(s) See ref. 1, Table 64, footnote (e) therein.

TABLE 50A

Nitrogen shieldings in some flavins

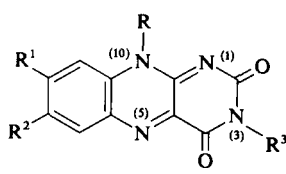
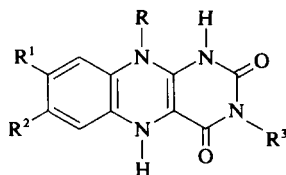
Compound	Solvent	Nitrogen shielding referred to neat nitromethane
		
(oxidized form)		
		
(reduced form)		

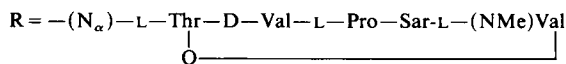
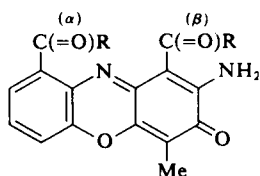
TABLE 50A—*cont.*

Compound	Solvent	Nitrogen shielding referred to neat nitromethane			
		N-1	N-3	N-5	N-10
Riboflavin 5'-phosphate R = ribosyl-5'-phosphate R ¹ = R ² = Me R ³ = H					
oxidized	H ₂ O (pH = 6, 9)	+190.1	+221.0	unlabelled	
reduced	H ₂ O (pH = 7.0)	+218.0	+231.5	unlabelled	
Tetraacetylriboflavin R = ribosyl-2',3',4',5'-tetraacetate R ¹ = R ² = Me R ³ = H					
oxidized	CHCl ₃	+182.0	+221.9	unlabelled	
reduced	CHCl ₃	+265.5	+236.?	unlabelled	
3-Methyl-tetraacetylriboflavin R = ribosyl-2',3',4',5'-tetraacetate R ¹ = R ² = R ³ = Me					
oxidized	CHCl ₃	+180.8	+221.3	unlabelled	
reduced	CHCl ₃	+265.3	+236.2	unlabelled	
3,7-Dimethyl-10-tetraacetylribitylisoalloxazin R = ribityl-2',3',4',5'-tetraacetate R ¹ = H R ² = R ³ = Me					
oxidized	CHCl ₃	+180.8	+221.3	+26.9	+231.5
reduced	CHCl ₃	+265.2	+236.2	+321.2	+309.7
7-Methyl-10-ribityl-isoalloxazine-5'-phosphate R = ribityl-5'-phosphate R ¹ = R ³ = H R ² = Me					
oxidized	H ₂ O (pH = 5.5)	+190.9	+221.3	+46.3	+217.?
reduced	H ₂ O (pH = 5.4)	+253.8	+231.2	+321.3	+294.6
	H ₂ O (pH = 8.0)	+195.0	+231.2	+321.3	+284.?
Protein-bound <i>Megasphaera elsdenii</i> flavodoxim					
oxidized	H ₂ O (pH = 7.0)	+195.8	+220.0	+31.5	+216.3
reduced	H ₂ O (pH = 6.7)	+198.9	+231.2	+318.0	+283.5
	H ₂ O (pH = 7.6)	+198.3	+232.0	+318.0	+283.6

Data from ref. 287; ¹⁵N-labelled flavins, ¹⁵N spectra; 27.36 MHz, field parallel to sample tube, originally referred to 4 M ¹⁵NH₄NO₃ in 2 M HNO₃ + 359.1 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

TABLE 51

Nitrogen shieldings in actinomycin-D



Nitrogen shielding referred to neat nitromethane in moieties specified
(for abbreviations of amino-acid residues see Table 56)

Solution	L-(NMe)Val	Sar	L-Pro	D-Val	L-Thr	NH ₂	=N—	Notes
0.012 M in DMSO	+270.2	+278.4 +278.6	+238.6	+260.7	+265.8 +265.9	+294.1	?	(a)
0.017 M in CDCl ₃	+271.1	+278.6	+238.3 +238.8	+259.3 +259.9	+265.1 +266.8	+298.1	?	(b)
0.012 M in MeOH	+269.2	+275.9	+237.3 +237.9	+260.1 +261.2	+265.8 +265.5	+298.2	?	(a)
0.0037 M in H ₂ O	+264.9	+271.6	+233.2	+258.8 +259.7	+262.7 +269.9	+300.9	?	(a)
0.01 M in H ₂ O/MeOH (93:7)	+270.2	+275.9	+237.0 +237.9	+260.1 +261.2	+265.8 +266.5	+298.2	?	(c)
0.0015 M in aqueous buffer, pH = 7.0	+263.9	+271.5	+233.0 +233.4	+258.8 +259.5	+262.6 +263.2	+300.9	?	(c)
in aqueous buffer + dinucleotide d(pGpC)	+263.2	+271.0 +271.5	+232.0	+257.3 +257.9	+264.1 +265.3	+301.0	?	(c)
in aqueous buffer + calf thymus DNA	+263.9	?	+231.7 +232.9	+258.1 +260.2	? ?	?	?	(d)

(a) Data from ref. 242; fully ¹⁵N-labelled compound, ¹⁵N spectra, 10.14 MHz, field perpendicular to sample tube, originally referred to neat formamide, +267.7 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(b) As in note (a), but 20.47 MHz spectra, field parallel to sample tube.

(c) Data from ref. 307; details as in note (a).

(d) Data from ref. 307; 50.66 MHz ¹⁵N spectra, field parallel to sample tube, other details as in note (a).

Table 52

Nitrogen shieldings in some polyamide and polypeptide polymers ("Nylons")

Structure	Nitrogen shielding referred to neat nitromethane in solvent specified				Notes
	H ₂ SO ₄	TFA	HCOOH	(CF ₃) ₂ CHOH	
-[-(CH ₂) _n CONH-]-					
"Nylon(n+1)"					
n = 5 (Nylon-6)	+232.9	+239.5	+251.0	+255.3	(a)
n = 10 (Nylon-11)	+232.6	+236.7	-	-	(a)
n = 11 (Nylon-12)	+232.5	+236.7	-	-	(a)
-[-(CH ₂) ₆ -NH-CO-(CH ₂) _m -CO-NH-]-					
"Nylon 6, (m+2)"					
m = 4 (Nylon-6,6)	+232.0	+239.3	+250.9	+254.8	(a)
	-	+238.7	-	+253.1 (6% w/w)	(b)
	-	+239.0	-	+253.5 (12% w/w)	(b)
	-	+240.9	-	+253.5 (25% w/w)	(b)
	-	+243.2	-	+253.9 (30% w/w)	(b)
m = 6 (Nylon-6,8)	+233.3	+237.8	+250.4	+254.4	(a)
m = 8 (Nylon-6,10)	+233.4	+238.4	+249.8	+254.8	(a)
m = 10 (Nylon-6,12)	+233.3	+236.6	+249.1	+255.3	(a)
See also Table 74					

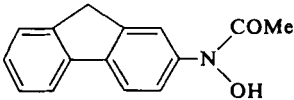
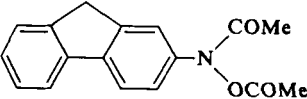
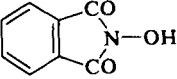
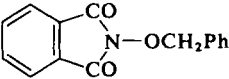
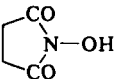
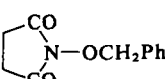
Table 52 (continued)

(a) Data from ref. 115, ^{15}N natural abundance JCP spectra (J-cross-polarization technique), 10.1 MHz, field perpendicular to sample tube, originally referred to MeCONH_2 (satd. in H_2O), +268.0 ppm from neat nitromethane (Table 47, conversion scheme IV (Table 4); originally reported relative to aqueous acidified NH_4NO_3 (NH_4^+ ion) standard taken at +89.5 ppm from the standard employed.

(b) Data from ref. 644, details as above.

TABLE 53

Nitrogen shieldings in some *N*-hydroxy derivatives of amides and related structures

Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	in CD ₃ OD, -50 °C	+199.4 (<i>cis</i> -amide)	(a)
		+201.2 (<i>trans</i> -amide)	(a)
	in CD ₃ OD, 32 °C	+199.5 (averaged)	(a)
	in CD ₃ OD, -50 °C	+190.3 (<i>cis</i> -amide)	(a)
		+194.0 (<i>trans</i> -amide)	(a)
	in CD ₃ OD, 32 °C	+191.9 (averaged)	(a)
	0.5 M in DMSO	+165.8	(b)
	0.5 M in DMSO	+167.5	(b)
	0.5 M in DMSO	+165.8	(b)
	0.5 M in DMSO	+153.4	(b)

(a) Data from ref. 645; ¹⁵N natural abundance spectra, 40.55 MHz, field parallel to sample tube, originally referred to neat HCONMe₂, +277.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); originally reported relative to liquid NH₃ standard taken at +103.8 ppm from the standard employed.

(b) Data from ref. 252; ¹⁵N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; Cr(acac)₃ added as relaxation reagent.

Table 54

Nitrogen shieldings in some thioamides and thioureas

Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
MeC(=S)NH_2	1 M in H_2O	+224.2	(a)
various RC(=S)NR_2 structures	various	+219 to +237	(b)
$(\text{H}_2\text{N})_2\text{C=S}$ (thiourea)	1 M in H_2O satd. in H_2O + EtOH	+272.9 +273.3	(a) (c)
$\text{H}_2\text{NC(=S)NHMe}$	satd. in EtOH	+277.3 (NH_2) +277.8 (NHMe)	(c) (c)
$\text{H}_2\text{NC(=S)NHC(=O)Me}$	satd. in CDCl_3 + acetone	+258.8 (NH_2) +220.2 (NH)	(c) (c)
$\text{H}_2\text{NC(=S)NMe}_2$	satd. in H_2O + EtOH	+276.0 (NH_2) +277.8 (NMe_2)	(c) (c)
$(\text{MeNH})_2\text{C=S}$	satd. in EtOH	+278.9	(c)
MeNHC(=S)NMe_2	satd. in CDCl_3	+281.4 (NH) +287.3 (NMe_2)	(c) (c)
$\text{pMeC}_6\text{H}_4\text{NHC(=S)NMe}_2$	satd. in CDCl_3	+286.6 (NH) +279.3 (NMe_2)	(c) (c)
$(\text{Me}_2\text{N})_2\text{C=S}$	satd. in CDCl_3 in CDCl_3 + BF_3 in CDCl_3 + BF_3 (2:3 mol ratio)	+287.6 +271.6 +280.6	(c) (c) (c)
$(\text{Et}_2\text{N})_2\text{C=S}$	satd. in CDCl_3	+258.8	(c)
$(\text{Pr}^i_2\text{N})_2\text{C=S}$	satd. in CDCl_3	+243.3	(c)

For additional data, see footnote (b); N-nitrosothioureas, see Table 120

Table 54 (continued)

(a) Data from ref. 215, ^{15}N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO_3 , +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(b) See ref. 1, Table 68 therein, and references therein.

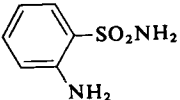
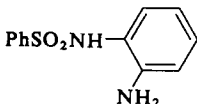
(c) Data from ref. 239, ^{15}N natural abundance spectra, 9.12 and 6.03 standard calibrated (+2.6 ppm) against neat nitromethane, conversion scheme IV (Table 4); $\text{Cr}(\text{acac})_3$ added as relaxation reagent to compounds without NH or NH_2 moieties.

Table 55

Nitrogen shieldings in some sulphonamides and sulphamic acid derivatives

Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
$\text{H}_2\text{N-SO}_3\text{H}$	satd. in H_2O , pH = 0.15	+287.9	(a)
$(\text{H}_2\text{N-SO}_3)^- \text{NH}_4^+$	satd. in H_2O , pH = 4.3-6.2	+288.6 (NH_2) +357.8 (NH_4^+)	(a) (a)
$\text{HN}(\text{SO}_3)_2^{2-} (\text{NH}_4^+)_2$	satd. in H_2O , pH = 8.3	+227.3 (NH) +358.8 (NH_4^+)	(a) (a)
$\text{N}(\text{SO}_3)_3^{3-} (\text{NH}_4^+)_3$	10% in aqueous NH_3 , pH) 9.0	+154.8 (N) +358.5 (NH_4^+)	(a) (a)
$\text{HN}(\text{SO}_2\text{F})_2$	neat liquid, 24°C	+249.2	(b)
$(\text{FO}_2\text{S})_2\text{N-N}(\text{SO}_2\text{F})_2$	in BrF_5 , 24°C	+213.1	(b)
	in SO_2ClF , -40°C	+212.3	(c)
$\text{FXeN}(\text{SO}_2\text{F})_2$	in BrF_5 , -58°C	+250.4	(b,d)
	in SO_2ClF , -40°C	+247.9	(c)
$\text{F}[\text{XeN}(\text{SO}_2\text{F})_2]^+ \text{AsF}_6^-$	in BrF_5 , -59°C	+261.7	(c)
MeSO_2NH_2	0.2 M in DMSO	+286.0	(e)
$(\text{MeSO}_2)_2\text{NH}$	0.2 M in DMSO	+222.8	(e)
PhSO_2NH_2	in H_2O	+289.1	(f)
		+275.1 (anion)	(f)
	in DMSO	+285.9	(f)
	in toluene	+289.4	(f)
	in H_2O , bound to native human carbonic anhydrase	+299.0	(f)

Table 55 (continued)

	in DMSO	+285.4 (SNH ₂)	(f)
		+277.4 (anion, SNH ⁻)	(f)
	in DMSO + 1 eq. ZnCl ₂	+289.2 (SNH ₂)	(f)
	in dioxane	+272.6 (SNH)	(f)
		+254.6 (anion, SN ⁻)	(f)
	in dioxane + 1 eq. ZnCl ₂	+273.9 (SNH)	(f)
	in dioxane + 2 eq. ZnCl ₂	+268.3 (SNH)	(f)
		+253.4 (anion, SN ⁻)	(f)
	in dioxane/H ₂ O		
	pH = 2.4	+272.3 (SNH)	(f)
	4.4	+273.5	(f)
	6.0	+273.5	(f)
	8.6	+271.7	(f)
	10.5	+259.1 (anion, SN ⁻)	(f)
	11.4	+253.8 (anion)	(f)
	in dioxane/H ₂ O + 1 eq. ZnCl ₂		
	pH = 5.5	+273.0 (SNH)	(f)
	6.0	+272.0	(f)
	7.7	+272.8	(f)
	11.0	+253.4 (anion)	(f)
pMeC ₆ H ₄ SO ₂ NH ₂	0.2 M in DMSO	+284.5	(e)
(pMeC ₆ H ₄ SO ₂) ₂ NH	0.2 M in DMSO	+220.9	(e)
(pMeC ₆ H ₄ SO ₂) ₃ N	0.2 M in DMSO	+159.8	(e)

For additional data, see ref. 1, Table 69 therein

(a) Data from ref. 631, ¹⁵N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NO₃⁻ standard calibrated (+1.5 ppm) against neat nitromethane, conversion scheme IV (Table 4).

Table 55 (continued)

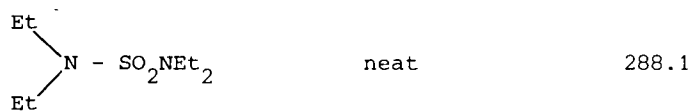
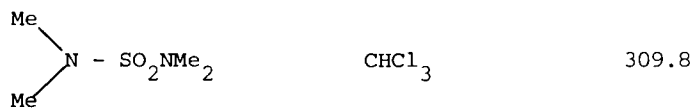
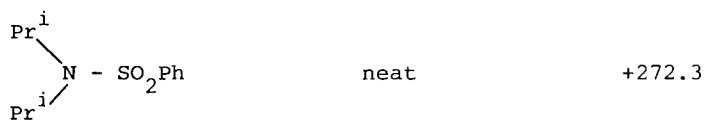
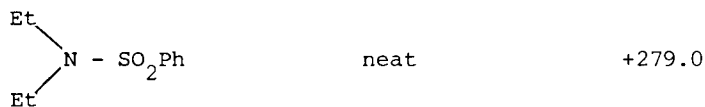
- (b) Data from ref. 105, ^{15}N labelled compounds, ^{15}N spectra, 40.55 MHz, field parallel to sample tube, originally referred to what was termed as NH_4Cl , -90 ppm from liquid NH_3 , probably NH_4NO_3 , +359.7 ppm from neat nitromethane (see data in Table 6), conversion scheme II (Table 4).
- (c) Data from ref. 291, details as in footnote (b), but referred directly to neat nitromethane.
- (d) Data from ref. 292, details as in footnote (b).
- (e) Data from ref. 634, ^{15}N natural abundance spectra, 18.24 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk susceptibility effects.
- (f) Data from ref. 291, ^{15}N labelled compounds, ^{15}N spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO_3 , +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4); ^1H coupled and decoupled spectra.

Table 55A

Some additional data on nitrogen shieldings in sulphonamides,
sulphinamides and sulphenamides

Compound	Solvent	Nitrogen shielding referred to neat nitromethane (ppm)
Sulphonamides		
$\begin{array}{c} \text{Me} \\ \diagdown \\ \text{N} - \text{SO}_2\text{Cl} \\ \diagup \\ \text{Me} \end{array}$	CHCl_3	+273.4
$\begin{array}{c} \text{Et} \\ \diagdown \\ \text{N} - \text{SO}_2\text{Cl} \\ \diagup \\ \text{Et} \end{array}$	CHCl_3	+253.2
$\begin{array}{c} \text{Pr}^i \\ \diagdown \\ \text{N} - \text{SO}_2\text{Cl} \\ \diagup \\ \text{Pr}^i \end{array}$	neat	+239.8
$\begin{array}{c} \text{Me} \\ \diagdown \\ \text{N} - \text{SO}_2\text{Me} \\ \diagup \\ \text{Me} \end{array}$	CHCl_3	+302.0
$\begin{array}{c} \text{Et} \\ \diagdown \\ \text{N} - \text{SO}_2\text{Me} \\ \diagup \\ \text{Et} \end{array}$	neat	+281.0
$\begin{array}{c} \text{Pr}^i \\ \diagdown \\ \text{N} - \text{SO}_2\text{Me} \\ \diagup \\ \text{Pr}^i \end{array}$	neat	269.0

Table 55A (continued)



Sulphinamides

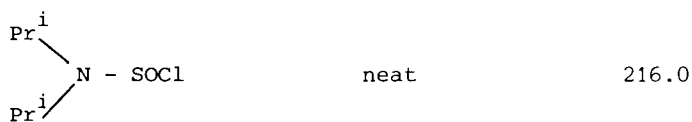
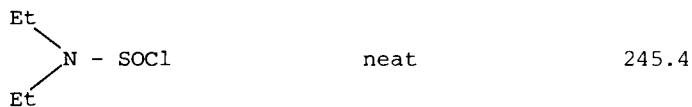
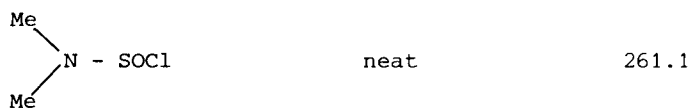


Table 55A (continued)

$\begin{array}{c} \text{Bu}^{\text{S}} \\ \diagdown \\ \text{N} - \text{SOCl} \\ \diagup \\ \text{Bu}^{\text{S}} \end{array}$	neat	218.5 (diastereo 219.9 isomers)

$\begin{array}{c} \text{Me} \\ \diagdown \\ \text{N} - \text{SOCl} \\ \diagup \\ \text{PhCH}_2 \end{array}$	CHCl_2	251.4

$\begin{array}{c} \text{Me} \\ \diagdown \\ \text{N} - \text{SONMe}_2 \\ \diagup \\ \text{Me} \end{array}$	CHCl_3	307.2

$\begin{array}{c} \text{Et} \\ \diagdown \\ \text{N} - \text{SONEt}_2 \\ \diagup \\ \text{Et} \end{array}$	neat	283.2

$\begin{array}{c} \text{Pr}^{\text{i}} \\ \diagdown \\ \text{N} - \text{SONPr}^{\text{i}} \\ \diagup \\ \text{Pr}^{\text{i}} \end{array}$	neat	272.2

$\begin{array}{c} \text{Et} \\ \diagdown \\ \text{N} - \text{SONPr}^{\text{i}} \\ \diagup \\ \text{Et} \end{array}$	neat	269.2 (N-Pr_2^{i}) 288.2 (N-Pr_2^{i})

$\begin{array}{c} \text{Me} \\ \diagdown \\ \text{N} - \text{S} = \text{O} \\ \diagup \\ \text{N} - \text{Me} \end{array}$	neat	289.0

Sulphenamides

$\begin{array}{c} \text{Me} \\ \diagdown \\ \text{N} - \text{SCl} \\ \diagup \\ \text{Me} \end{array}$	neat	304.2

Table 55A (continued)

$\begin{array}{c} \text{Et} \\ \diagdown \\ \text{N} - \text{SCl} \\ \diagup \\ \text{Et} \end{array}$	neat	274.7
$\begin{array}{c} \text{Pr}^i \\ \diagdown \\ \text{N} - \text{SCl} \\ \diagup \\ \text{Pr}^i \end{array}$	neat	249.7
$\begin{array}{c} \text{Me} \\ \diagdown \\ \text{N} - \text{SCl} \\ \diagup \\ \text{PhCH}_2 \end{array}$	neat	292.8
$\begin{array}{c} \text{Me} \\ \diagdown \\ \text{N} - \text{SNMe}_2 \\ \diagup \\ \text{Me} \end{array}$	neat	327.2
$\begin{array}{c} \text{Et} \\ \diagdown \\ \text{N} - \text{SEt}_2 \\ \diagup \\ \text{Et} \end{array}$	neat	304.9
$\begin{array}{c} \text{Pr}^i \\ \diagdown \\ \text{N} - \text{SNPr}_2^i \\ \diagup \\ \text{Pr}^i \end{array}$	neat	289.9

Data from ref. 646, ^{15}N natural abundance spectra, 25.4 MHz, field parallel to sample tube, originally referred to 1M NaNO_3 in $\text{D}_2\text{O}/\text{HNO}_3$, according to authors +5.1 ppm from neat nitromethane.

TABLE 56

Structural formulae, abbreviations and nitrogen shielding data for amino acids

Conventional formula, common name and abbreviation for corresponding residue	Solution	Nitrogen shielding referred to neat nitromethane			Notes
		cation	anion	anion	
$\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$ Glycine (Gly)	various H_2O	+349 to +354	+347 to +350 +350.2	+355 to +363	(a) (b)
$\text{H}_2\text{N}-\text{CH}(\text{Me})-\text{COOH}$ Alanine (Ala)	various H_2O	+337 to +341	ca. +337 +338		(a) (c)
$\text{H}_2\text{N}-\text{CH}(\text{Me})-\text{CH}(\text{Me})-\text{COOH}$ Valine (Val)	H_2O	ca. +344	ca. +344		(a)
$\text{H}_2\text{N}-\text{CH}_2-\text{CH}(\text{Me})-\text{CH}_2-\text{COOH}$ Leucine (Leu)	H_2O	ca. +339	ca. +342		(a)
$\text{H}_2\text{N}-\text{CH}(\text{Me})-\text{CH}(\text{Me})-\text{COOH}$ Isoleucine (Ile)	various	+343 to +348	ca. +340		(a)
$\text{H}_2\text{N}-\text{CH}(\text{C}_6\text{H}_5)-\text{COOH}$ Phenylglycine (Phg)	TFA	ca. +337			(a)
$\text{MeHN}-\text{CH}_2-\text{COOH}$ Sarcosine (Sar)	various	ca. +350	ca. +348		(a)
$\text{H}_2\text{N}-\text{CH}(\text{OH})-\text{COOH}$ Serine (Ser)	H_2O	ca. +344	ca. +346		(a)

TABLE 56—*cont.*

Conventional formula, common name and abbreviation for corresponding residue	Solution	Nitrogen shielding referred to neat nitromethane			Notes
		cation	amphion	anion	
$\begin{array}{c} \text{HO} \quad \text{Me} \\ \quad \diagdown \quad / \\ \text{C} \\ / \quad \backslash \\ \text{H}_2\text{N} \quad \text{COOH} \end{array}$ Threonine (Thr)	H ₂ O		ca. +348		(a)
$\begin{array}{c} \text{HS} \\ \\ \text{C} \\ / \quad \backslash \\ \text{H}_2\text{N} \quad \text{COOH} \end{array}$ Cysteine [Cys(SH)]	H ₂ O H ₂ O, pH = 4-6	ca. +338	ca. +341 +342.8		(a) (d)
$\begin{array}{c} \text{COOH} \\ \\ \text{S} \quad \text{S} \\ \quad \\ \text{C} \quad \text{C} \\ / \quad \backslash \quad / \quad \backslash \\ \text{H}_2\text{N} \quad \text{COOH} \quad \text{NH}_2 \end{array}$ Cysteine (Cys-Cys)			ca. +342		(a)
$\begin{array}{c} \text{MeS} \\ \\ \text{C} \\ / \quad \backslash \\ \text{H}_2\text{N} \quad \text{COOH} \end{array}$ Methionine (Met)	H ₂ O		+341.1		(c)
$\begin{array}{c} \text{HOOC} \\ \\ \text{C} \\ / \quad \backslash \\ \text{H}_2\text{N} \quad \text{COOH} \end{array}$ Aspartic acid (Asp)	H ₂ O/HCl H ₂ O, pH = 9.0	ca. +340	+337.4		(a) (c)
$\begin{array}{c} \text{COOH} \\ \\ \text{C} \\ / \quad \backslash \\ \text{H}_2\text{N} \quad \text{COOH} \end{array}$ Glutamic acid (Glu)	H ₂ O H ₂ O	ca. +339	ca. +338 +341		(a) (c)
$\begin{array}{c} \text{NH}_2 \\ \\ \text{C} \\ // \quad \backslash \\ \text{O} \quad \text{C} \\ \quad \\ \text{H}_2\text{N} \quad \text{COOH} \end{array}$ Asparagine (Asn)	H ₂ O (ammonium) (amide) powdered solid	ca. +338 ca. +268	ca. +340 ca. +268 +342 (ammonium) +265 (amide)		(a) (a) (f)

TABLE 56—*cont.*

Conventional formula, common name and abbreviation for corresponding residue	Solution	Nitrogen shielding referred to neat nitromethane			Notes
		cation	amphion	anion	
<chem>NC(=O)CCC(N)C(=O)O</chem> Glutamine (Gln)	various	ca. +341 (ammonium)			(a)
	powdered solid	ca. +268 (amide)	+342 (ammonium)		(a) (f)
	H ₂ O		+265 (amide)		(f)
			+340.5 (ammonium)		(c)
			+270 (amide)		(c)
<chem>NC(CCCC(N)C(=O)O)C(=O)O</chem> Lysine (Lys)	in H ₂ O, pH = 4-6		+340.8 (N _α)		(d)
			+348.4 (N _ε)		(d)
		+338.7 (N _α)			(g)
		+345.9 (N _ε)			(g)
		see also Table 57			
<chem>NC(O)CCC(N)C(=O)O</chem> Hydroxylysine (Hyl)	various	ca. +340	ca. +342 (N _α)		(a)
		ca. +347	ca. +354 (N _ε)		(a)
<chem>NC(=N)NCCC(N)C(=O)O</chem> Arginine (Arg)	various	ca. +340	ca. +340	ca. +349 (N _α)	(a)
		ca. +297	ca. +296	ca. +289 (N _δ)	(a)
		ca. +309	ca. +308	ca. +293 (N _ε)	(a)
	H ₂ O, pH = 4-6		+340.5 (N _α)		(d)
			+296.6 (N _δ)		(d)
			+308.5 (N _ε)		(d)
<chem>NC(CCCC(N)C(=O)O)C(=O)O</chem> Ornithine (Orn)	H ₂ O, pH = 4-6		+340.9 (N _α)		(d)
			+346.6 (N _δ)		(d)
<chem>NC1=CN=C(CCN1C(=O)O)N</chem> Histidine (His)		see Table 59			
<chem>NC(Cc1ccccc1)C(=O)O</chem> Phenylalanine (Phe)	H ₂ O/HCl	+339.4			(e)
	H ₂ O		ca. +341		(a)

TABLE 56—*cont.*

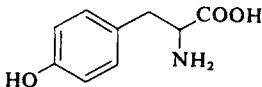
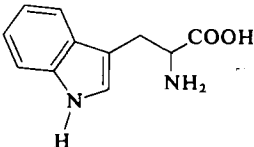
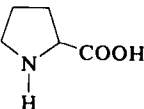
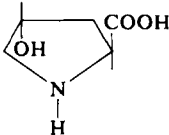
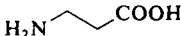
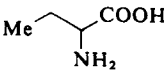
Conventional formula, common name and abbreviation for corresponding residue	Solution	Nitrogen shielding referred to neat nitromethane			Notes
		cation	anion	anion	
 Tyrosine (Tyr)	H ₂ O/HCl	ca. +341			(a)
 Tryptophan (Trp)	H ₂ O		ca. +249 (ammonium) ca. +299 (NH)		(a) (a)
 Proline (Pro)	various	+325 to +328	ca. +324		(a)
 Hydroxyproline (Hyp)	H ₂ O		ca. +329		(a)
 β-Alanine (β-Ala)	various	ca. +348	ca. +348		(a)
 α-Aminobutyric acid (α-Abu)	H ₂ O/HCl	+350.2			(c)

TABLE 56—*cont.*

Conventional formula, common name and abbreviation for corresponding residue	Solution	Nitrogen shielding referred to neat nitromethane			Notes
		cation	amphion	anion	
$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{COOH}$ γ -Aminobutyric acid (γ -Abu)	various	ca. +347	ca. +348		(a)
$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH}$ δ -Aminovaleric acid (δ -Ava)	various	ca. +347	ca. +348		(a)
$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH}$ ϵ -Aminocaproic acid (ϵ -Aca)	various	ca. +348	ca. +348		(a)

For additional data see footnote (a)

(a) See ref. 1, Tables 70–73 therein; also ref. 4, p. 165, and references therein.

(b) Data from ref. 304; ^{15}N natural abundance spectra, 27.36 MHz, field parallel to sample tube, originally referred to NH_4^+ in 5 M NH_4NO_3 in 2 M HNO_3 , +359.0 ppm from neat nitromethane (Table 6), and originally recalculated to liquid NH_3 standard taken at +380.2 ppm from nitromethane, conversion scheme II (Table 4).

(c) Data from ref. 295; ^{15}N -labelled amino acids from biosynthesis *in vivo*, ^{15}N spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO_3 , +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(d) Data from ref. 647; ^{15}N natural abundance spectra, 25.35 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(e) Data from ref. 404; ^{15}N natural abundance spectra, 10.09 MHz, field perpendicular to sample tube, originally reported relative to liquid NH_3 , but actually referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(f) Data from ref. 182; ^{15}N natural abundance CP-MASS spectra, 9.12 MHz, originally referred to solid $(\text{NH}_4)_2\text{SO}_4$ standard calibrated (+360 ppm) against liquid nitromethane, uncorrected for bulk-susceptibility effects.

(g) Data from ref. 293; ^{15}N natural abundance spectra, 9.04 MHz, field perpendicular to sample tube, originally referred to aqueous urea, +303.6 ppm from neat nitromethane (Table 43), conversion scheme IV (Table 4).

TABLE 57

Nitrogen shieldings in various species of lysine and
 ϵ -*N*-hydroxymethyllysine calculated from ^{15}N NMR titration
 curves for aqueous solutions

$\text{R}-\text{H}_2\text{N}^+ \text{---} \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{COOH})\text{NH}_3^+$		(A)			
$\text{R}-\text{H}_2\text{N}^+ \text{---} \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{COO}^-)\text{NH}_3^+$		(B)			
$\text{RHN}^+ \text{---} \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{COO}^-)\text{NH}_3^+$		(C)			
$\text{RHN} \text{---} \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{COO}^-)\text{NH}_2$		(D)			
		Nitrogen shielding referred to neat nitromethane			
Compound		A	B	C	D
Lysine (R = H)	α -N	+341.8	+340.8	+347.3	+348.8
	ϵ -N	+347.4	+348.4	+350.4	+356.4
ϵ -N-hydroxymethyllysine (R = CH ₂ OH)	α -N	+341.8	+340.8	+341.0	+348.8
	ϵ -N	+322.9	+322.9	+333.8	+333.8
		pK_a values obtained from ^{15}N shielding changes			
		A $\rightleftharpoons$ B	B $\rightleftharpoons$ C	C $\rightleftharpoons$ D	
R = H		2.2	9.6	11.5	
R = CH ₂ OH		2.3	5.8	9.7	

Data from ref. 647: ^{15}N natural abundance spectra, 25.35 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

Table 58

Nitrogen shieldings in an amorphous polymer of
lysine-formaldehyde-urea

Compound	Solvent	Nitrogen shielding referred to neat nitromethane
Lysine monohydrochloride	H ₂ O, pH=6.4	+338.2 (N _α) +345.8 (N _ε) see also Table 57
Lysine-formaldehyde-urea polymer	H ₂ O	+338.0 (N _α , Lys) +339.1 (N _ε , Lys) +303.2 +302.6 substituted +298 urea +285 moieties

Data from ref. 293, ¹⁵N natural abundance spectra, 9.04 MHz, field perpendicular to sample tube, originally referred to aqueous urea, +303.6 ppm from neat nitromethane (Table 43), conversion scheme IV (Table 4).

TABLE 59

Nitrogen shieldings in various species of histidine

$ \begin{array}{c} \begin{array}{ccc} \begin{array}{c} (\tau) \text{HN} \text{---} \text{C}_5\text{H}_3\text{N}^+ \text{---} \text{CH}_2\text{CH}(\text{NH}_3^+)\text{COO}^- \\ (\pi) \end{array} & \xrightleftharpoons{pK_a = 6.3} & \begin{array}{c} \text{HN} \text{---} \text{C}_5\text{H}_3\text{N} \text{---} \text{CH}_2\text{CH}(\text{NH}_3^+)\text{COO}^- \\ \text{(B)} \end{array} \\ \text{(A)} & & \updownarrow \\ & & \begin{array}{c} \text{N} \text{---} \text{C}_5\text{H}_3\text{N} \text{---} \text{CH}_2\text{CH}(\text{NH}_3^+)\text{COO}^- \\ \text{(C)} \end{array} \\ & & \updownarrow \\ & & \begin{array}{c} \text{HN} \text{---} \text{C}_5\text{H}_3\text{N} \text{---} \text{CH}_2\text{CH}(\text{NH}_2)\text{COO}^- \\ \text{(D)} \end{array} \\ & & \updownarrow \\ & & \begin{array}{c} \text{N} \text{---} \text{C}_5\text{H}_3\text{N} \text{---} \text{CH}_2\text{CH}(\text{NH}_2)\text{COO}^- \\ \text{(E)} \end{array} \\ & \xrightleftharpoons{pK_a = 9.0} & \end{array} \end{array} $				
Nitrogen shielding referred to neat nitromethane				
Solution or state	Cation A	Amphions B, C	Anions D, E	Notes
in H ₂ O + HCl	+338 (NH ₃ ⁺)			(a)
or NaOH	+206 (τ -N)	+201 (τ -N)	+186 (τ -N)	(a)
	+203 (π -N)	+148 (π -N)	+162 (π -N)	(a)
solid state	+208 (τ -N)	+213 (τ -N)	+213 (τ -N)	(b)
	+205 (π -N)	+138 (π -N)	+132 (π -N)	(b)
hydrochloride monohydrate	+324.9			
single crystal	+189.9			(c)
	+108.7			
	↓			
	+208 (isotropic)			(c)
	+321.2			
	+161.9			(c)
	+99.5			
	↓			
	+194 (isotropic)			(c)

(a) Averaged data from ref. 1, p. 264 and references therein.

(b) Data from ref. 186; ¹⁵N-labelled histidine at π -N and τ -N, ¹⁵N CP-MASS spectra, 29.82 MHz, originally referred to solid (NH₄)₂SO₄ standard calibrated (+360 ppm) against neat liquid nitromethane, uncorrected for bulk-susceptibility effects; solid samples obtained from lyophilization of solutions at various pH.

(c) Data from ref. 191; details as in footnote (b), but single-crystal spectra yielding nitrogen shielding anisotropy effects.

Table 60

Nitrogen shieldings in some amino acid ester hydrochlorides

Formula	Nitrogen shielding referred to neat nitromethane	
	in H ₂ O, pH = 3-4	in DMSO
H ₂ ⁺ Gly-OMe	+351.9	+347.1
H ₂ ⁺ Gly-OEt	+351.7	+347.6
H ₂ ⁺ Ala-OMe	+338.8	+335.1
H ₂ ⁺ β-Ala-OMe	+347.8	+343.9
H ₂ ⁺ α-Aibu-OMe	+327.5	+324.3
H ₂ ⁺ γ-Abu-OMe	+346.3	+342.8
H ₂ ⁺ Val-OMe	+344.5	+338.8
H ₂ ⁺ Leu-OMe	+340.9	+336.2
H ₂ ⁺ Ile-OMe	+343.3	+338.7
H ₂ ⁺ Phg-OMe	+336.6	+333.6
H ₂ ⁺ Phe-OMe	+341.9	+336.8
H ₂ ⁺ Tyr-OMe	+342.0	+337.9
H ₂ ⁺ Ser-OMe	+345.7	+342.0
H ₂ ⁺ Thr-OMe	-	+344.9
H ₂ ⁺ Met-OMe	+341.3	+337.3
H ₂ ⁺ Cys(SH)-OMe	+342.2	+338.7
H ₂ ⁺ Cys-CysH ₂ ⁺ OMe OMe	+342.4	+337.6
H ₂ ⁺ γ-OMe-Glu-OMe	+340.6	+337.4

Table 60 (continued)

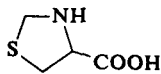
$H_2^+ \beta\text{-OMe-Asp-OMe}$	+341.7	+337.2
	+307.7	
$H_2^+ \text{Arg-OMe}$	+340.8	-
	+295.6	
$H_2^+ \text{Lys-OMe}$	+341.0	+336.6
($\epsilon\text{-N}$ protonation)	+345.9	+341.8
$H_2^+ \text{His-OMe}$	+340.6	
	+204.2	-
(ring protonation)	+206.2	
$H_2^+ \text{Trp-OMe}$	+342.0	+337.4
	+249.8	+245.8
$H_2^+ \text{Pro-OMe}$	+326.3	+322.5
$H_2^+ \text{Hyp-OMe}$	+330.0	+326.7
$H_2^+ \text{Sar-OMe}$	+350.0	+347.6
$pN^+H_3C_6H_4COOMe$	+328.3	+320.6

Data from ref. 296, ^{15}N enriched (1%) compounds, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NO_3^- in aqueous NH_4NO_3 , +4.0 ppm from neat nitromethane, Table 6, Conversion scheme II (Table 4).

For abbreviations of amino acid residues, see Table 56.

Table 61

Effects on nitrogen shieldings of N-hydroxymethylation of some amino acids with aqueous formaldehyde

Compound	Nitrogen atom	Nitrogen shielding referred to neat nitromethane	
		in unreacted	in its N-CH ₂ OH derivative
Ornithine	α-N	+341.2	+341.2
	δ-N	+347.0	+323.0 (N-CH ₂ OH)
Lysine	α-N	+340.8	+340.8
	ε-N	+348.5	+322.9 (N-CH ₂ OH)
Arginine	α-N	+341.2	+341.2
	δ-N	+296.8	+296.3
	ε-N	+308.7	+286.1 (N-CH ₂ OH)
Cysteine	α-N	+342.8	+319.1
			
α-N-Acetyl-lysine	α-N	+251.2	+251.2
	ε-N	+349.4	+323.3 (N-CH ₂ OH)
α-N-Acetylarginine	α-N	+251.0	+251.0
	δ-N	+297.0	+296.3
	ε-N	+310.5	+287.3 (N-CH ₂ OH) +309.6
α-N-Acetylcysteine	α-N	+256.3	+256.3 (no reaction)

Data from ref. 647, ¹⁵N natural abundance spectra, 25.35 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk susceptibility effects, pH = 4-6.

For structural formulae of amino acids, see Table 56.

Table 62

Nitrogen shieldings in amide and carbamate (urethane) moieties of some N-acyl amino acids and their derivatives

Formula	Solution	Nitrogen shielding referred to neat nitromethane	Notes
$N_{\alpha} - (\text{COMe}) - \text{Lys} - \text{OH}$	in H_2O	+250.1 (N_{α})	(a)
		+349.3 (N_{δ})	(a)
$N_{\alpha} - (\text{COMe}) - \text{Arg} - \text{OH}$	in H_2O	+250.2 (N_{α})	(a)
		+296.8 (N_{δ})	(a)
		+310.5 (N_{ϵ})	(a)
$N_{\alpha} - (\text{COMe}) - \text{Cys}(\text{SH})\text{OH}$	in H_2O	+257.6	(a)
$N_{\alpha} - (\text{COMe}) - \text{Gly} - \text{OMe}$	in DMSO	+271.3	(b)
$N_{\alpha} - (\text{COMe}) - \text{Ala} - \text{OMe}$	in DMSO	+255.8	(b)
$N_{\beta} - (\text{COMe}) - \beta - \text{Ala} - \text{OMe}$	in DMSO	+263.6	(b)
$N_{\alpha} - (\text{COMe}) - \alpha - \text{Aibu} - \text{OMe}$	in DMSO	+245.3	(b)
$N_{\gamma} - (\text{COMe}) - \gamma - \text{Abu} - \text{OMe}$	in DMSO	+262.1	(b)
$N_{\alpha} - (\text{COMe}) - \text{Val} - \text{OMe}$	in DMSO	+261.9	(b)
$N_{\alpha} - (\text{COMe}) - \text{Leu} - \text{OMe}$	in DMSO	+258.3	(b)

N_{α} -(COMe)-Ile-OMe	in DMSO	+260.2	(b)
N_{α} -(COMe)-Phg-OMe	in DMSO	+256.5	(b)
N_{α} -(COMe)-Phe-OMe	in DMSO	+259.2	(b)
N_{α} -(COMe)-Tyr-OMe	in DMSO	+258.6	(b)
N_{α} -(COMe)-Met-OMe	in DMSO	+259.9	(b)
γ -OMe- N_{α} -(COMe)-Glu-OMe	in DMSO	+259.3	(b)
β -OMe- N_{α} -(COMe)-Asp-OMe	in DMSO	+257.5	(b)
N_{α} -(COMe)-Trp-OMe	in DMSO	+257.8; +249.0	(b)
N_{α} -(COMe)-Sar-OMe	in DMSO	+277.6; +277.3 (<u>cis</u> , <u>trans</u>)	(b)
pMeCONHC ₆ H ₄ COOMe	in DMSO	+274.2	(b)
N_{α} -(COOPh)-Gly-OH	in DMSO	+303.5	(b)
N_{α} -(COOPh)-Ala-OH	in DMSO	+289.1	(b)
N_{β} -(COOPh)- β -Ala-OH	in DMSO	+298.2	(b)
N_{α} -(COOPh)- α -Aibu-OH	in DMSO	+279.6	(b)
N_{γ} -(COOPh)- γ -Abu-OH	in DMSO	+297.3	(b)

Table 62 (continued)

N_{α} -(COOPh)-Val-OH	in DMSO	+295.2	(b)
N_{α} -(COOPh)-Leu-OH	in DMSO	+291.7	(b)
N_{α} -(COOPh)-Ile-OH	in DMSO	+294.1	(b)
N_{α} -(COOPh)-Phg-OH	in DMSO	+289.7	(b)
N_{α} -(COOPh)-Phe-OH	in DMSO	+292.5	(b)
N_{α} -(COOPh)-Tyr-OH	in DMSO	+292.6	(b)
N_{α} -(COOPh)-Ser-OH	in DMSO	+295.5	(b)
N_{α} -(COOPh)-Thr-OH	in DMSO	+299.7	(b)
N_{α} -(COOPh)-Met-OH	in DMSO	+292.9	(b)
N_{α} -(COOPh)-Asp-OH	in DMSO	+292.8	(b)
N_{α} -(COOPh)-Asn-OH	in DMSO	+292.0 (N_{α}); +270.5	(b)
N_{α} -(COOPh)-Glu-OH	in DMSO	+292.7	(b)
N_{α} -(COOPh)-Gln-OH	in DMSO	+292.2 (N_{α}); +271.5	(b)
N_{α} -(COOPh)-Trp-OH	in DMSO	+191.1 (N_{α}); +249.5	(b)

N_{α} -(COOPh)-Arg-OH	in DMSO	+292.0 (N_{α}); +294.7 (N_{δ}); +304.9	(b)
N_{α} -(COOPh)-Lys-OH·HCl	in DMSO	+291.8 (N_{α}); +343.2	(b)
N_{α} -(COOPh)-N-(OCOBu ^t)-Orn-OH	in DMSO	+291.9 (N_{α}); +295.4	(b)
N_{α} -(COOPh)-Pro-CH	in DMSO	+282.2	(b)
N_{α} -(COOPh)-Hyp-OH	in DMSO	+285.8	(b)
N_{α} -(COOPh)-pyroglutamic acid	in DMSO	+230.4	(b)
pPhOOCNHC ₆ H ₄ COOH	in DMSO	+272.2	(b)

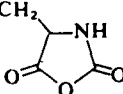
For abbreviations of amino acid residues, see Table 56

(a) Data from ref. 647, ¹⁵N natural abundance spectra, 25.35 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk susceptibility effects.

(b) Data from ref. 296, ¹⁵N enriched (1%) compounds, ¹⁵N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NO₃⁻ in aqueous NH₄NO₃, +4.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

TABLE 63

Concentration and temperature effects on nitrogen shieldings in some amino acid derivatives

Compound	Solvent	Concentration	Temperature (°C)	Nitrogen shielding referred to neat nitromethane
	CH ₂ Cl ₂	1.00 M	30	+292.7
		0.01 M	30	+294.5
	dioxane	1.00 M	30	+294.2
		0.10 M	30	+294.8
		0.01 M	30	+294.8
		0.10 M	95	+294.6
	DMSO	1.00 M	30	+289.9
		0.01 M	30	+289.8
L-Phe- <i>N</i> -carboxyanhydride (L-Phe-NCA)				
MeCONHCH ₂ CONHPh <i>N</i> -Acetylglycine anilide	DMSO	1.00 M	130	+251.0
		1.00 M	80	+250.0
		1.00 M	30	+250.0
		0.01 M	30	+251.0
	TFA	1.00 M	30	+247.1
		0.01 M	30	+246.1
(Gly) _n Polyglycine	TFA	3.00 M	30	+271.3
		1.00 M	30	+271.3
		0.03 M	30	+271.3
	CF ₃ COOH +5% MeSO ₃ H	3.00 M	30	+268.8
		1.00 M	30	+266.5
		0.03 M	30	+265.2
(Leu) _n Polyleucine	TFA	2.00 M	30	+252.8
	+5% MeSO ₃ H	1.00 M	30	+252.2
		0.03 M	30	+251.7

Data from ref. 296; ¹⁵N-enriched (10–40%) compounds, ¹⁵N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NO₃⁻ in aqueous NH₄NO₃, +4.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

Table 64

Substituent effects on nitrogen shieldings in amino acid derivatives referred to shieldings in corresponding glycine derivatives

Amino acid moiety (Abbreviations explained in Table 56)	Nitrogen shielding referred to that in corresponding Gly moiety in same solvent			
	Ammonium group in methyl ester hydrochloride		Amido group in N-COOPh derivative	Amido group in N-acetyl derivative of methyl ester
	in H ₂ O	in DMSO	in DMSO	in DMSO
Ala	-13.1	-12.3	-14.4	-15.5
β-Ala	-4.1	-3.5	-5.3	-7.7
α-Aibu	-24.4	-23.1	-23.9	-26.0
γ-Abu	-5.6	-4.6	-6.2	-9.2
Val	-7.4	-8.6	-8.3	-9.4
Leu	-11.0	-11.0	-11.7	-13.0
Ile	-8.6	-8.7	-9.4	-11.1
Phg	-15.3	-13.7	-13.8	-14.8
Phe	-10.0	-10.6	-11.0	-12.1
Tyr	-9.9	-9.5	-10.9	-13.7
Ser	-6.2	-5.4	-8.0	-
Thr	-	-3.1	-3.8	-
Met	-10.6	-10.1	-10.6	-11.4
Cys(SH)	-9.7	-8.7	-	-
β-Me-Asp	-10.2	-9.7	-	-13.8
Lys	-10.9	-10.8	-11.7	-
Trp	-9.9	-10.0	-12.4	-13.5
Pro	-25.6	-24.9	-21.3 (cis)	-
Hyp	-21.9	-20.7	-17.7 (cis)	-

Data from ref. 296, based on ¹⁵N spectra of ¹⁵N enriched compounds.

TABLE 65

Nitrogen shieldings in some complexes of Co(III) with amines and amino acids

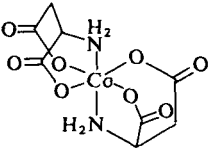
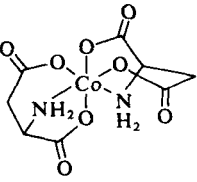
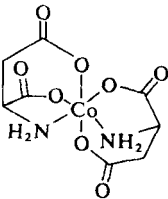
Structure (en = ethylenediamine ox = oxalate anion gly = glycine anion asp = aspartate anion)	Solution	Nitrogen shielding referred to neat nitromethane	Complexation shift of nitrogen shielding relative to free ligand in H ₂ O (amphion)	Notes
Isomeric species of Co(III)(asp) ₂ ⁻				
 (<i>trans-N</i> isomer)	in H ₂ O	+380.2	+43	(a)
 (<i>trans-O₅</i> isomer)	in H ₂ O	+400.8	+63	(a)
 (<i>trans-O₆</i> isomer)	in H ₂ O	+398.0	+61	(a)
[Co(en) ₃]Cl ₃	in aqueous 5 M LiBr	+395.2 (en <i>trans</i> to N)	+35	(b)
[Co(gly)(en) ₂]Cl ₂	in aqueous 5 M LiBr	+391.5 (en <i>trans</i> to N)	+31	(b)
		+407.2 (en <i>trans</i> to O)	+47	(b)
		+413.6 (gly <i>trans</i> to N)	+53	(b)

TABLE 65—*cont.*

Structure (en = ethylenediamine ox = oxalate anion gly = glycine anion asp = aspartate anion)	Solution	Nitrogen shielding referred to neat nitromethane	Complexation shift of nitrogen shielding relative to free ligand in H ₂ O (amphion)	Notes
<i>trans</i> -(O)-[Co(gly) ₂ (en)]Cl	in aqueous 5 M LiBr	+385.9 (en <i>trans</i> to N) +408.8 (gly <i>trans</i> to N)	+26 +49	(b) (b)
<i>cis</i> -(O)-[Co(gly) ₂ (en)]Cl	in aqueous 5 M LiBr	+385.3 (en <i>trans</i> to N) +399.2 (en <i>trans</i> to O) +403.8 (gly <i>trans</i> to N) +421.3 (gly <i>trans</i> to O)	+25 +39 +44 +61	(b) (b) (b) (b)
[Co(ox)(en) ₂]Cl	in aqueous 5 M LiBr	+379.5 (en <i>trans</i> to N) +401.5 (en <i>trans</i> to O)	+19 +41	(b) (b)
<i>mer</i> -[Co(gly) ₃]	in aqueous 5 M LiBr	+402.9 (gly <i>trans</i> to N) +403.7 (gly <i>trans</i> to N) +419.4 (gly <i>trans</i> to O)	+43 +44 +59	(b) (b) (b)
<i>mer</i> -[Co(ox)(gly)(en)]	in aqueous 5 M LiBr	+379.1 (en <i>trans</i> to N) +396.8 (en <i>trans</i> to O) +400.7 (gly <i>trans</i> to N)	+19 +37 +41	(b) (b) (b)
<i>fac</i> -[Co(gly) ₃]	in aqueous 5 M LiBr	+422.6 (gly <i>trans</i> to O)	+62	(b)
[Co(ox) ₂ (en)]Na	in aqueous 5 M LiBr	+397.6 (en <i>trans</i> to O)	+37	(b)
<i>cis</i> -(N)-[Co(ox)(gly) ₂]K	in aqueous 5 M LiBr	+416.7 (gly <i>trans</i> to O)	+56	(b)
<i>trans</i> -(N)-[Co(ox)(gly) ₂]K	in aqueous 5 M LiBr	+396.2 (gly <i>trans</i> to N)	+36	(b)
[Co(ox) ₂ (gly)]K ₂	in aqueous 5 M LiBr	+419.4 (gly <i>trans</i> to O)	+59	(b)
λ- <i>cis</i> -(NO ₂)- <i>trans</i> -(NH ₂)-[Co(NO ₂) ₂ R ₂] ^{+/-}	1 M in H ₂ O			

TABLE 65—*cont.*

Structure (en = ethylenediamine ox = oxalate anion gly = glycine anion asp = aspartate anion)	Solution	Nitrogen shielding referred to neat nitromethane	Complexation shift of nitrogen shielding relative to free ligand in H ₂ O (amphion)	Notes
R				
glycine anion		+391.0	+42	(c)
α -aminobutyrate anion		+384.2	+34	(c)
valine anion		+381.7	+39	(c)
leucine anion		+378.4	+41	(c)
isoleucine anion		+380.2	+39	(c)
phenylalanine anion		+376.6	+37	(c)
proline anion		+361.6	+36	(c)
methionine anion		+375.5	+34	(c)
lysine anion		+375.2 (α -N)	+38	(c)
		+346.8 (ϵ -N)	+2	(c)
arginine anion		+372.0 (α -N)	+34	(c)
		+304.3 (ϵ -N)	-2	(c)
		+291.0 (δ -N)	-3	(c)
β -alanine anion		+370.4	+24	(c)

(a) Data from ref. 405; ¹⁵N-enriched complexes, ¹⁵N spectra, 8.059 MHz, field perpendicular to sample tube, originally referred to aqueous NH₄Cl, +352.9 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); free ligand shielding can be found in Table 56.

(b) Data from ref. 406; ¹⁵N natural abundance spectra, 10.09 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; originally reported relative to liquid NH₃ standard taken at +380.2 ppm from neat nitromethane.

(c) Data from ref. 404; details as in note (b).

Table 66
Nitrogen shieldings in some oligopeptides

Compound (for abbreviations of amino acid residues, see Table 56)	Solvent or state	Nitrogen shielding referred to neat nitromethane (assignments in order of amino acid residues, if not stated otherwise)	Notes
Ala-Gly Gly-Ala	H ₂ O	+271.9 (Gly)	(a)
Bu ^t OCO-Ala-Gly-OMe	H ₂ O	+274.0 (Gly)	(a)
Pro-Phe-Gly-Phe-Gly	H ₂ O	(?); +270.1; +272.3; +256.7; +275.1	(b)
pMeC ₆ H ₄ SO ₂ -Gly-Gly-Gly-OEt	HCOOH	+289.0; +271.2; +271.8	(c)
	ClCH ₂ CH ₂ OH	+289.6; +272.9; +274.2	(c)
	DMSO	+288.7; +274.8; +276.6	(c)
	pyridine	+288.9; +275.0; +277.6	(c)
PhCH ₂ OCO-β-Ala-Gly-Gly-OH	HCOOH	+296.0; +266.9; +271.9	(c)
	DMSO	+297.6; +270.6; +275.3	(c)

Table 66 (continued)

PhCH ₂ OCO-β-Ala-Gly-Gly-OEt	HCOOH	+296.0; +267.3; +272.0	(c)
	ClCH ₂ CH ₂ OH	+297.1; +267.1; +274.2	(c)
	DMSO	+297.5; +271.0; +276.5	(c)
	pyridine	+298.5; +271.4; +277.5	(c)
PhCH ₂ OCO-Ala-Gly-Gly-OEt	HCOOH	+285.5; +273.2; +271.9	(c)
	ClCH ₂ CH ₂ OH	+288.8; +274.4; +274.0	(c)
	DMSO	+288.9; +276.9; +276.9	(c)
	pyridine	+289.2; +276.2; +277.0	(c)
PhCH ₂ OCO-α-Abu-Gly-Gly-OEt	HCOOH	+291.8; +271.4; +271.8	(c)
	ClCH ₂ CH ₂ OH	+291.9; +272.6; +274.2	(c)
	DMSO	+292.2; +275.1; +277.0	(c)
PhCH ₂ OCO-Val-Gly-Gly-OEt	HCOOH	+294.7; +269.7; +271.9	(c)
	ClCH ₂ CH ₂ OH	+294.5; +270.8; +274.2	(c)
	DMSO	+294.7; +273.1; +276.9	(c)
	CH ₂ Cl ₂	+296.2; +272.9; +277.3	(c)
	pyridine	+294.5; +272.5; +277.8	(c)
PhCH ₂ OCO-Ile-Gly-Gly-OEt	HCOOH	+292.2; +268.2; +271.7	(c)
	DMSO	+292.9; +272.4; +276.8	(c)

PhCH ₂ OCO-Leu-Gly-Gly-OEt	HCOOH	+291.1; +271.5; +272.0	(c)
	DMSO	+291.8; +275.6; +277.0	(c)
	CH ₂ Cl ₂	+292.0; +275.4; +276.9	(c)
	pyridine	+291.8; +276.3; +277.7	(c)
α,ε-(PhCH ₂ OCO) ₂ -Lys-Gly-Gly-OEt	HCOOH	(?) +293.5; +271.9; +271.9	(c)
	ClCH ₂ CH ₂ OH	+292.1; +295.4; +271.8; +272.5	(c)
	DMSO	+291.6; +296.4; +275.4; +276.8	(c)
	pyridine	+292.5; +297.7; +276.3; +278.2	(c)
PhCH ₂ OCO-Gly-Met-Gly-OH	HCOOH	+303.3; +261.4; +270.6	(c)
	DMSO	+303.5; +265.0; +274.3	(c)
	pyridine	+304.3; +264.5; +273.9	(c)
PhCH ₂ OCO-Gly-Met-Gly-Gly-OEt	HCOOH	+303.7; +261.3; +271.2; +271.8	(c)
	ClCH ₂ CH ₂ OH	+304.0; +262.7; +273.0; +274.2	(c)
	DMSO	+303.5; +264.4; +274.7; +276.8	(c)
	pyridine	+304.4; +263.5; +274.2; +277.5	(c)
PhCH ₂ OCO-Phg-Gly-Gly-OEt	HCOOH	+294.4; +270.3; +272.1	(c)
	DMSO	+291.8; +273.5; +276.5	(c)

Table 66 (continued)

PhCH ₂ OCO-Tyr-Gly-Gly-OEt	HCOOH	+290.9; +270.7; +271.8	(c)
	ClCH ₂ CH ₂ OH	+292.0; +271.9; +274.3	(c)
	DMSO	+291.9; +275.0; +276.7	(c)
	pyridine	+292.8; +273.7; +277.9	(c)
PhCH ₂ OCO-Trp-Gly-Gly-OEt	HCOOH	+290.6; +254.4; +270.7; +271.1	(c)
	ClCH ₂ CH ₂ OH	+290.8; +252.4; +272.9; +274.0	(c)
	DMSO	+292.8; +249.5; +275.6; +277.1	(c)
	pyridine	+292.2; +250.7; +271.3; +277.6	(c)
PhCH ₂ OCO-Gly-Pro-Gly-Gly-OEt	HCOOH	+303.8; (?) +271.7; +272.0	(c)
	ClCH ₂ CH ₂ OH	+304.7; (?) +273.2; +273.8	(c)
	DMSO	+304.7; (?) +275.2; +277.3	(c)
PhCH ₂ OCO-γ-Abu-Gly-Gly-OEt	HCOOH	+294.8; +268.0; +272.2	(c)
	DMSO	+297.0; +271.7; +276.7	(c)
	pyridine	+297.7; +272.3; +277.4	(c)
CF ₃ CO-Gly-Gly-Ala-OMe	DMSO	+271.7; +274.3; +261.4	(d)
CF ₃ CO-Gly-Gly-Val-Ala-OMe	DMSO	+271.7; +274.3; +266.2; +257.6	(d)

PhCH ₂ OCO-Gly-Ala-Ala-OH	HCOOH	+303.3; +257.5; +257.5	(c)
	ClCH ₂ CH ₂ OH	+304.1; +259.0; +259.8	(c)
	DMSO	+303.5; +261.3; +260.9	(c)
	pyridine	+304.4; +261.2; +260.9	(c)
PhCH ₂ OCO-Gly-Ala-Ala-OMe	HCOOH	+303.3; +257.5; +257.5	(c)
	ClCH ₂ CH ₂ OH	+304.0; +259.7; +259.7	(c)
	DMSO	+303.6; +261.7; +261.7	(c)
	pyridine	+304.4; +261.4; +262.2	(c)
PhCH ₂ OCO-β-Ala-Ala-Ala-OMe	HCOOH	+296.1; +251.2; +257.6	(c)
	ClCH ₂ CH ₂ OH	+297.3; +251.7; +259.9	(c)
	DMSO	+298.0; +255.6; +262.0	(c)
PhCH ₂ OCO-Val-Ala-Ala-OMe	HCOOH	+294.7; +254.5; +257.3	(c)
	DMSO	+295.1; +258.8; +262.0	(c)
	pyridine	+294.9; +257.1; +262.2	(c)
PhCH ₂ OCO-Ile-Ala-Ala-OMe	HCOOH	+293.7; +253.9; +257.2	(c)
	DMSO	+293.9; +258.3; +262.0	(c)

Table 66 (continued)

PhCH ₂ OCO-Leu-Ala-Ala-OMe	HCOOH	+291.0; +256.8; +257.4	(c)
	ClCH ₂ CH ₂ OH	+291.2; +258.5; +259.9	(c)
	DMSO	+291.6; +261.6; +262.1	(c)
	pyridine	+291.6; +259.9; +262.5	(c)
PhCH ₂ OCO-Phe-Ala-Ala-OH	HCOOH	+292.8; +255.6; +257.3	(c)
	ClCH ₂ CH ₂ OH	+292.5; +257.5; +259.1	(c)
	DMSO	+293.0; +261.3; +261.3	(c)
PhCH ₂ OCO-Phe-Ala-Ala-OMe	HCOOH	+292.7; +255.8; +257.3	(c)
	DMSO	+292.7; +261.2; +262.0	(c)
	pyridine	+293.0; +259.4; +262.3	(c)
PhCH ₂ OCO-Gly-Pro-Ala-Ala-OMe	HCOOH	+303.5; (?) +257.5; +257.5	(c)
	ClCH ₂ CH ₂ OH	+304.1; (?) +259.9; +259.9	(c)
	DMSO	+304.2; (?) +262.6; +262.1	(c)
	pyridine	+304.9; +251.7; +261.3; +262.0	(c)
PhCH ₂ OCO-Gly-Val-Val-OMe	HCOOH	+304.5; +261.8; +258.9	(c)
	ClCH ₂ CH ₂ OH	+304.2; +263.8; +261.2	(c)
	DMSO	+303.5; +267.6; +263.7	(c)
	CH ₂ Cl ₂	+306.2; +264.4; +263.1	(c)

	pyridine	+304.7; +265.6; +263.1	(c)
PhCH ₂ OCO-β-Ala-Val-Val-OMe	HCOOH	+296.4; +255.6; +259.5	(c)
	ClCH ₂ CH ₂ OH	+297.7; +256.2; +261.6	(c)
	DMSO	+297.8; +260.8; +263.8	(c)
	CH ₂ Cl ₂	+299.3; +259.7; +263.7	(c)
	pyridine	+298.7; +259.3; +263.0	(c)
PhCH ₂ OCO-Ala-Val-Val-OMe	HCOOH	+288.4; +264.9; +259.1	(c)
	DMSO	+289.0; +268.5; +264.4	(c)
	pyridine	+289.7; +263.7; +263.1	(c)
PhCH ₂ OCO-Phe-Val-Val-OMe	HCOOH	+291.5; +258.6; +259.1	(c)
	ClCH ₂ CH ₂ OH	+292.7; +260.3; +261.2	(c)
	DMSO	+292.7; +263.9; +263.9	(c)
	pyridine	+293.0; +262.8; +262.8	(c)
PhCH ₂ OCO-Met-Val-Val-OMe	HCOOH	+292.3; +260.5; +259.0	(c)
	DMSO	+292.6; +267.1; +264.1	(c)
	CH ₂ Cl ₂	+293.4; +263.3; +263.3	(c)
	pyridine	+293.2; +263.7; +263.0	(c)

Table 66 (continued)

PhCH ₂ OCO-Gly-Pro-Val-Val-OMe	HCOOH	+303.2; (?) +260.5; +259.0	(c)
	ClCH ₂ CH ₂ OH	+304.7; (?) +262.9; +261.6	(c)
	DMSO	+304.3; (?) +265.5; +264.5	(c)
	CH ₂ Cl ₂	+306.9; (?) +264.2; +265.3	(c)
	pyridine	+305.7; (?) +264.2; +264.2	(c)
	DMSO/MeOH	+304.2; (?) +266.5; +264.5	(c)
PhCH ₂ OCO-Gly-Leu-Leu-OMe	HCOOH	+301.8; +259.5; +257.9	(c)
	ClCH ₂ CH ₂ OH	+304.0; +260.7; +259.9	(c)
	DMSO	+303.5; +263.5; +262.9	(c)
	CH ₂ Cl ₂	+305.7; +261.8; +261.3	(c)
	pyridine	+304.7; +262.9; +262.4	(c)
PhCH ₂ OCO-β-Ala-Leu-Leu-OMe	HCOOH	+296.3; +253.0; +258.1	(c)
	ClCH ₂ CH ₂ OH	+297.7; +253.2; +260.2	(c)
	DMSO	+297.8; +257.6; +263.1	(c)
	CH ₂ Cl ₂	+299.6; +256.9; +262.1	(c)
	pyridine	+298.7; +257.2; +262.2	(c)
PhCH ₂ OCO-Ala-Leu-Leu-OMe	HCOOH	+288.1; +260.0; +257.5	(c)
	ClCH ₂ CH ₂ OH	+289.3; +261.4; +259.9	(c)

	DMSO	+289.2; +264.0; +262.9	(c)
	CH ₂ Cl ₂	+290.6; +260.8; +260.8	(c)
	pyridine	+289.8; +262.6; +262.2	(c)
PhCH ₂ OCO-Phe-Leu-Leu-OMe	HCOOH	+292.0; +257.5; +257.5	(c)
	DMSO	+292.7; +262.9; +262.9	(c)
	CH ₂ Cl ₂	+293.0; +259.5; +261.1	(c)
	pyridine	+293.1; +260.6; +262.1	(c)
PhCH ₂ OCO-Gly-Pro-Leu-Leu-OMe	HCOOH	+304.0; (?) +259.0; +257.9	(c)
	DMSO	+304.3; (?) +263.9; +263.6	(c)
	CH ₂ Cl ₂	+305.7; (?) +260.3; +261.3	(c)
PhCH ₂ OCO-Gly-Met-Met-OMe	HCOOH	+303.9; +261.1; +259.4	(c)
	DMSO	+303.5; +265.1; +263.9	(c)
	pyridine	+305.0; +264.4; +263.5	(c)
PhCH ₂ OCO-Gly-Phe-Phe-OH	HCOOH	+303.9; +261.1; +259.8	(c)
	ClCH ₂ CH ₂ OH	+304.2; +263.1; +263.1	(c)
	DMSO	+303.9; +265.2; +263.5	(c)
	pyridine	+304.8; +264.6; +262.8	(c)

Table 66 (continued)

PhCH ₂ OCO-Gly-Phe-Phe-OMe	HCOOH	+304.0; +261.0; +259.4	(c)
	DMSO	+303.8; +265.2; +263.7	(c)
	pyridine	+304.8; +264.2; +263.0	(c)
PhCH ₂ OCO-Gly-Phe-Phe-Gly-OEt	HCOOH	+303.8; +261.1; +258.2; +270.6	(c)
	ClCH ₂ CH ₂ OH	+304.1; +262.2; +261.3; +273.6	(c)
	DMSO	+303.8; +264.8; +263.8; +275.6	(c)
	pyridine	+304.7; +263.8; +261.9; +275.7	(c)
PhCH ₂ OCO-Gly-Phe-Phe-Gly-Gly-OEt	HCOOH	+303.4; +261.0; +258.9; +270.7; +272.1	(c)
	ClCH ₂ CH ₂ OH	+304.0; +262.5; +261.3; +272.9; +274.5	(c)
	DMSO	+303.8; +264.7; +263.0; +274.7; +276.8	(c)
	CH ₂ Cl ₂	+307.8; +264.3; +260.7; +276.2; +278.3	(c)
	pyridine	+304.4; +263.6; +261.1; +274.1; +277.5	(c)
PhCH ₂ OCO-Ala-Phe-Phe-OMe	HCOOH	+288.5; +262.0; +259.4	(c)
	DMSO	+289.4; +266.5; +263.9	(c)
	pyridine	+289.8; +264.9; +263.4	(c)
PhCH ₂ OCO-Ala-Phe-Phe-Ala-OMe	HCOOH	+288.2; +262.1; +258.8; +253.0	(c)
PhCH ₂ OCO-β-Ala-Phe-Phe-OH	HCOOH	+296.2; +254.8; +259.8	(c)
	ClCH ₂ CH ₂ OH	+297.2; +255.9; +261.2	(c)

	DMSO	+297.9; +259.4; +264.3	(c)
	pyridine	+298.6; +258.9; +263.0	(c)
PhCH ₂ OCO-β-Ala-Phe-Phe-OMe	HCOOH	+296.2; +254.8; +259.4	(c)
	ClCH ₂ CH ₂ OH	+297.5; +259.0; +263.9	(c)
	pyridine	+298.6; +258.4; +262.8	(c)
PhCH ₂ OCO-Gly-Pro-Phe-Phe-OMe	DMSO	+304.1; (?) +266.0; +263.9	(c)
	pyridine	+306.3; (?) +264.0; +265.1	(c)
PhCH ₂ OCO-Ile-Val-OH	DMSO	+292.8; +263.2	(e)
PhCH ₂ OCO-Ile-Val-Glu(O-Bu ^t)-Gln-OH	DMSO	+292.3; +262.1; +261.6; +260.1 +273.5(CONH ₂ , side chain)	(e)
PhCH ₂ OCO-Glu(O-Bu ^t)-Gln-O ⁻ (dicyclohexylammonium salt)	DMSO	+292.5; +258.6; +311.9 (ammonium)	(e) (e)
PhCH ₂ OCO-Tyr(O-Bu ^t)-Gln-OH	DMSO	+291.9; +262.9; +271.4 (CONH ₂ , side chain)	(e)
PhCH ₂ OCO-Gln-Leu-OMe	DMSO	+291.6; +262.5; +271.5 (CONH ₂ , side chain)	(e)
PhCH ₂ OCO-Leu-Tyr(O-Bu ^t)-Gln-Leu-OMe	DMSO	+291.8; (?) +263.1; +261.7; +271.5 (CONH ₂ , side chain)	(e)

Table 66 (continued)

$\text{PhCH}_2\text{OCO-Glu(O-Bu}^t\text{)-Asn-Tyr-OBu}^t$	DMSO	+291.5; +264.7; (?); +270.2 (CONH ₂ , side chain)	(e)
$\text{PhCH}_2\text{OCO-Gly-Ser-OMe}$	TFA	+305.2; +269.2	(c)
	$\text{ClCH}_2\text{CH}_2\text{OH}$	+304.1; +267.8	(c)
	MeOH	+305.4; +269.2	(c)
	DMSO	+303.9; +269.2	(c)
	pyridine	+304.8; +269.9	(c)
$\text{PhCH}_2\text{OCO-Ala-Ser-OMe}$	TFA	+289.8; +269.3	(c)
	$\text{ClCH}_2\text{CH}_2\text{OH}$	+289.2; +268.1	(c)
	MeOH	+290.5; +269.2	(c)
	DMSO	+288.4; +269.5	(c)
$\text{PhCH}_2\text{OCO-Val-Ser-OMe}$	TFA	+295.3; +265.0	(c)
	DMSO	+295.3; +265.4	(c)
$\text{PhCH}_2\text{OCO-Phe-Ser-OMe}$	TFA	+293.1; +266.8	(c)
	$\text{ClCH}_2\text{CH}_2\text{OH}$	+292.5; +266.5	(c)
	MeOH	+293.6; +267.2	(c)
	DMSO	+292.9; +268.0	(c)
	pyridine	+293.0; +267.3	(c)

PhCH ₂ OCO-Gly-Thr-OMe	TFA	+305.2; +272.3	(c)
	ClCH ₂ CH ₂ OH	+304.1; +271.3	(c)
	MeOH	+305.3; +272.7	(c)
	DMSO	+303.8; +273.1	(c)
	pyridine	+304.6; +273.7	(c)
PhCH ₂ OCO-Ala-Thr-OMe	TFA	+290.0; +272.8	(c)
	DMSO	+289.4; +273.8	(c)
	pyridine	+289.8; +274.0	(c)
MeCO-D-Phe-L-Pro-OMe	DMSO/MeOH	+249.6(cis); +257.0(<u>trans</u>)	(c)
	(4:1)	+250.6(trans); +257.5 (<u>cis</u>)	(c)
MeCO-Leu-D-Phe-OMe	DMSO/MeOH	+257.5; +264.4	(c)
	HCOOH	+252.9; +260.2	(c)
PhOCO-Orn(N _δ ·HCl)-Leu-OMe	DMSO/MeOH	+293.1; +262.8	(c)
		+344.6; (N _δ , Orn)	(c)
	HCOOH	+291.8; +259.9	(c)
		+347.0 (N _δ , Orn)	(c)
MeOCO-Val-Orn(N _δ ·HCl)-OMe	DMSO/MeOH	+296.0; +261.5	(c)
		+344.8 (N _δ , Orn)	(c)

Table 66 (continued)

	HCOOH	(?) +259.5 +347.0 (N_δ , Orn)	(c) (c)
MeOCO-Val-Orn($N_\delta \cdot HCl$)-Leu-OMe	DMSO/MeOH	+296.2; +260.8; +262.5 +344.7 (N_δ , Orn)	(c) (c)
H_2^+ Gly-Ala-Ala-OH (CF_3COO^-)	TFA	+354.1; +255.7; +256.7	(c)
	HCOOH	+353.7; +257.4; +257.4	(c)
H_2^+ Gly-Ala-Ala-OMe (CF_3COO^-)	TFA	+354.8; +255.9; +256.3	(c)
	HCOOH	+355.0; +257.5; +257.5	(c)
	H_2O	+353.6; +256.4; +256.4	(c)
	DMSO	+353.1; +261.4; +261.4	(c)
H_2^+ Ala-Gly-Gly-OEt (CF_3COO^-)	TFA	+340.8; +272.3; +270.9	(c)
	HCOOH	+340.4; +273.2; +272.0	(c)
	H_2O	+339.8; +272.1; +271.2	(c)
	$ClCH_2CH_2OH$	+339.6; +273.6; +274.0	(c)
	DMSO	+339.6; +277.0; +276.3	(c)
H_2^+ Phe-Gly-Gly-OEt	TFA	+342.8; +270.9; +271.0	(c)
	HCOOH	+342.8; +270.0; +272.0	(c)
	H_2O	+342.0; +267.5; +272.0	(c)

H_2^+ Val-Gly-Gly-OEt	ClCH ₂ CH ₂ OH	+341.5; +269.8; +273.9	(c)
	DMSO	+341.6; +271.0; +276.0	(c)
	TFA	+346.0; +269.2; +271.9	(c)
	HCOOH	+345.7; +269.2; +271.9	(c)
	H ₂ O	+344.9; +267.5; +271.7	(c)
	ClCH ₂ CH ₂ OH	+344.5; +269.0; +273.9	(c)
H_2^+ Gly-Val-Val-OMe	DMSO	+344.3; +269.7; +276.2	(c)
	TFA	+354.7; +259.8; +257.6	(c)
	HCOOH	+354.1; +262.2; +259.2	(c)
	H ₂ O	+354.1; +261.3; +257.8	(c)
	ClCH ₂ CH ₂ OH	+353.6; +265.2; +261.4	(c)
	DMSO	+353.1; +269.8; +264.1	(c)
H_2^+ Ala-Val-Val-OMe	TFA	+350.8; +259.6; +257.5	(c)
	HCOOH	+354.1; +262.1; +259.2	(c)
	H ₂ O	+354.1; +261.3; +257.6	(c)
	ClCH ₂ CH ₂ OH	+353.6; +265.2; +261.4	(c)
	DMSO	+353.1; +269.3; +264.1	(c)

Table 66 (continued)

H_2^+ Val-Ala-Ala-OMe	TFA	+347.2; +252.5; +255.8	(c)
	HCOOH	+346.5; +253.7; +257.1	(c)
	H ₂ O	+345.4; +252.5; +256.7	(c)
	ClCH ₂ CH ₂ OH	+345.4; +254.5; +259.7	(c)
	DMSO	+344.5; +254.8; +261.8	(c)
PhCH ₂ OCO-Gly-L-Pro-L-Leu-L-Ala-L-Pro-OH (cis,trans isomerism around Gly-Pro and Ala-Pro bonds)	DMSO	+260	
		+261 (Pro)	(f)
		+268	
		+267 (Ala)	(f)
		+269	
		+273 (Leu)	(f)
		+313 (Gly)	(f)

For additional data, see ref. 1, Tables 78-81

(a) Data from ref. 114, ¹⁵N labelled glycine moiety, ¹⁵N spectra with JCP (J-cross-polarization), 10.13 MHz, field perpendicular to sample tube, originally referred to acidified aqueous NH₄Cl, +352.5 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4)

(b) Data from ref. 441, ¹⁵N natural abundance INEPT spectra, 20.28 MHz, field parallel to sample tube, originally referred to 80% formamide + 10% acetone, +267.7 ppm from neat nitromethane (Table 6) conversion scheme IV (Table 4); originally reported relative to liquid NH₃ standard, taken at

+108.5 ppm from standard used.

(c) Data from ref. 296, ^{15}N enriched compounds, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NO_3^- in aqueous NH_4NO_3 , +4.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

(d) Data from ref. 240, ^{15}N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to NH_4^+ in 5 M NH_4NO_3 in 2 M HNO_3 , +359.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

(e) Data from ref. 311, ^{15}N natural abundance spectra, 40.55 MHz, field parallel to sample tube, originally referred to NO_3^- in aqueous NH_4NO_3 , +4.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); inverse-gated decoupling in order to remove NOE.

(f) Data from ref. 131, ^{15}N natural abundance spectrum, 20.3 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk susceptibility effects.

TABLE 67

Nitrogen shieldings and differentiation thereof in *cis*- and *trans*-amide isomers of *N*-acylproline moiety in some oligopeptides

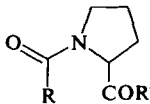
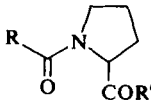
		Nitrogen shielding referred to neat nitromethane	
		 <i>cis</i> isomer	 <i>trans</i> isomer
Compound (<i>cis</i> / <i>trans</i> isomer ratio in parentheses)	Solvent	(assignments in order of residues)	
Bu ¹ OCO-Gly-Pro-Gly-Gly-OEt (1:9 ± 1)	CH ₂ Cl ₂	+304.3	+305.1
		+251.5	+248.7
		+274.8	+274.5
		+277.3	+277.3
	acetone +DMSO (85:15 v/v)	+302.8	+303.4
		+252.3	+249.8
		+274.3	+274.7
		+276.9	+277.7
PhCH ₂ OCO-Gly-Pro-Ala-Ala-OMe (1:10 ± 1)	CH ₂ Cl ₂	(?)	+306.0
		(?)	(?)
		(?)	+261.6
		(?)	+263.3
	acetone +DMSO (85:15 v/v)	+304.2	+304.0
		+251.9	+250.7
		+259.3	+262.2
		+261.8	+263.0
PhCH ₂ OCO-Gly-Pro-Leu-Leu-OMe (1:8 ± 1)	CH ₂ Cl ₂	(?)	+305.6
		(?)	(?)
		(?)	+260.7
		+261.7	+261.4
	acetone +DMSO (70:30 v/v)	(?)	+304.3
		+251.6	+250.9
		+261.2	+263.8
		+262.5	+263.3
PhCH ₂ OCO-Gly-Pro-Val-Val-OMe (1:7.0 ± 0.5)	CH ₂ Cl ₂	(?)	+306.9
		(?)	(?)
		(?)	+264.8
		(?)	+265.8
	acetone	+305.5	+305.7
		(?)	(?)
		(?)	+266.0
		+265.4	+265.3

TABLE 67—*cont.*

		Nitrogen shielding referred to neat nitromethane	
Compound (<i>cis</i> / <i>trans</i> isomer ratio in parentheses)	Solvent	<i>cis</i> isomer (assignments in order of residues)	<i>trans</i> isomer
(1:2.4±0.1)	acetone +DMSO (70:30 v/v)	(?) +251.7 (?) +263.6	+304.2 +251.8 +265.7 +264.1
PhCH ₂ OCO-Gly-Pro-Phe-Phe-OMe (1:7.0±0.5)	CH ₂ Cl ₂	(?) (?) (?) (?)	+306.3 (?) +264.1 +265.2
(1:2.5±0.1)	acetone +DMSO (70:30 v/v)	(?) +252.3 +263.2 +264.3	+303.9 +250.3 +265.7 +263.8
PhCH ₂ OCO-Pro-Pro-OH (<i>cis</i> - <i>trans</i> isomerism at PhOCO-Pro)	H ₂ O acetone +DMSO (70:30 v/v)	+276.8 +239.9 +281.7 +252.2	(?) (?) +281.3 +252.3
			
(70:30 v/v)	acetone +DMSO	+281.9 +260.5 (+275.1; +275.4; +275.7) (Gly) +250.8 +262.4	+280.9 +258.9 +251.0 +261.9
(D,L-Pro) _n)	H ₂ O		+294.0 (N _s , Arg) +305.3 (N _e , Arg) +244-+259 (broad resonance)
	acetone		+249.5 (<i>meso</i>) +250-+267 (broad resonance)
	+DMSO (70:30 v/v)		+256 } (<i>meso</i>) +257.5 }

Data from ref. 648; ¹⁵N-labelled last residue in sequence; ¹⁵N spectra taken at natural abundance for other residues, 36.48 MHz, field parallel to sample tube, originally referred to NO₃⁻ in aqueous NH₄NO₃, +4.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

Table 68

Nitrogen shieldings in oxytocin and 8-arginine-vasopressin

Molecule (for abbreviations, see Table 56)	Nitrogen shieldings referred to neat nitromethane (aqueous solutions, pH = 4.0)
$ \begin{array}{c} \text{Cys}^1 \text{H}_2^+ \\ \\ \text{Tyr}^2 \\ \\ \text{Ile}^3 \\ \\ \text{Gln}^4 \\ \\ \text{Asn}^5 \\ \\ \text{Cys}^6 \\ \\ \text{Pro}^7 \\ \\ \text{Leu}^8 \\ \\ \text{Gly}^9 \text{-NH}_2 \end{array} $	$ \begin{array}{c} +342.0 \text{ (NH}_3^+) \\ +256.4 \\ +260.3 \\ +260.3 \text{ (NH); } +268.0 \text{ (NH}_2) \\ +263.7 \text{ (NH); } +268.3 \text{ (NH}_2) \\ +260.3 \\ \text{not observed} \\ +257.8 \\ +269.7 \text{ (NH); } +273.2 \text{ (terminal CONH}_2) \end{array} $
"Oxytocin"	
$ \begin{array}{c} \text{Cys}^1 \text{H}_2^+ \\ \\ \text{Tyr}^2 \\ \\ \text{Phe}^3 \\ \\ \text{Gln}^4 \\ \\ \text{Asn}^5 \\ \\ \text{Cys}^6 \\ \\ \text{Pro}^7 \\ \\ \text{Arg}^8 \\ \\ \text{Gly}^9 \text{-NH}_2 \end{array} $	$ \begin{array}{c} +342.2 \text{ (NH}_3^+) \\ +256.5 \\ +259.2 \\ +261.1 \text{ (NH); } +267.9 \text{ (NH}_2) \\ +263.5 \text{ (NH); } +268.3 \text{ (NH}_2) \\ +260.0 \\ \text{not observed} \\ +258.4 \text{ (}\alpha\text{-NH); } +294.4 \text{ (}\delta\text{-NH); } +308.1 \\ \text{(terminal NH, NH}_2) \\ +269.3 \text{ (NH); } +273.2 \text{ (terminal CONH}_2) \end{array} $
"8-Arginine-vasopressin"	

Table 68 (continued)

Data from ref. 300, ^{15}N specifically labelled and unlabelled molecules, ^{15}N spectra, 20.27 MHz, field parallel to sample tube, originally referred to NH_4^+ in 5 M NH_4NO_3 in 2 M HNO_3 , +359.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); see also ref. 1, Table 82 therein, and reference therein.

Table 69
Nitrogen shieldings in enkaphalin and its derivatives

Compound	Solution	Nitrogen shielding referred to neat nitromethane (ppm) (assignments in order of amino acid residues)	Notes
H-Tyr-Gly-Gly-Phe-OH	0.02 M in H ₂ O	(?); +272.3; 274.9; +262.1	(a)
	in H ₂ O		
	cation	(?); +267.2; +271.3; +259.9	(b)
	amphion	(?); +268.0; +270.9; +255.4	(b)
	anion	(?); +267.4; +271.5; +255.4	(b)
	in DMSO		
	cation	(?); +269.6; +273.2; +262.8	(b)
	amphion	(?); +269.7; +273.7; +260.8	(b)
	anion	(?); +271.0; +273.7; +258.1	(b)
Bu ^t OCO-Tyr-Gly-Gly-Phe-OH	in H ₂ O		
	neutral		
	molecule	(?); +269.2; +271.2; +259.0	(b)
	anion	(?); +269.2; +271.4; +255.3	(b)
	in DMSO		
	neutral		
	molecule	(?); +274.0; +273.6; +263.3	(b)
	anion	(?); +273.4; +273.9; +259.1	(b)

H-Tyr-Gly-Gly-Phe-Leu-OH 0.02 M in H₂O (?); +272.2; +275.1; +261.6; +260.7 (a)

For additional data, see ref. 1, Table 85 therein

(a) Data from ref. 447, ¹⁵N labelled residues except Tyr; ¹⁵N spectra, 27.4 MHz, field parallel to sample tube, originally referred to NH₄⁺ in NH₄NO₃ in DMSO, +358.1 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); there seem to be systematic differences with respect to data corresponding to note (b), probably due to unreliable calibration procedures in either case.

(b) Data from ref. 301, details as in note (a), but referred originally to NH₄⁺ in 1 M NH₄NO₃ in 0.4 M HNO₃, +359.0 ppm from neat nitromethane (Table 6); see also comments above.

Table 70
Nitrogen shieldings in gramicidin S

L-Val-L-Orn-L-Leu-D-Phe-L-Pro L-Pro-D-Phe-L-Leu-L-Orn-L-Val				for abbreviations of amino acid residues, see Table 56			
"gramicidin-S"							
Sample	Nitrogen shielding (in ppm, referred to neat nitromethane) for amino acid residues specified						Notes
	L-Val	L-Orn (N _α)	L-Orn (N _δ)	L-Leu	D-Phe	L-Pro	
<u>gramicidin-S</u>							
solid	+249	+259	+340	+249	+259	+269	(a)
in HCOOH	+259.5	+255.8	+347.2	+252.3	+255.8	+252.8	(b)
0.15 M in MeOH	+261.9	+254.2	+348.4	+252.5	+253.0	+244.7	(c)
in MeOH	+262.3	254.2	+347.8	+252.7	+253.1	+243.5	(d)
0.001 M in MeOH	+262.1	+254.2	?	+252.9	+253.1	?	(e)
in DMSO/MeOH (4:1)	+266.4	+254.9	+344.6	+257.6	+252.7	+245.8	(b)
in DMSO	+267.3	+255.2	+343.6	+257.4	+252.9	+246.3	(d)
in DMSO (80°C)	+267.3	+255.0	+342.9	+257.1	+253.5	?	(d)
0.001 M in DMSO	+267.3	+255.0	?	+257.2	+253.2	?	(d)

in $\text{CF}_3\text{CH}_2\text{OH}$	+260.5	+255.4	+348.1	+249.9	+254.5	+241.3	(d)
0.001 M in $\text{CF}_3\text{CH}_2\text{OH}$	+259.4	+255.0	?	+249.1	+254.1	?	(e)
+ 5% CD_3OD							
0.001 M in H_2O	+260.2	+254.9	?	+252.0	+250.5	?	(e)
2,2',N ₀ -Trimethylornithyl derivative of gramicidin-S							
0.15 M in MeOH	+263.0	+255.0	+332.0	+252.4	+253.3	+247.2	(c)

For additional data, see ref. 1, Table 88 therein

- (a) Data from ref. 180, ^{15}N natural abundance CP-MASS spectra, 30.41 MHz, originally referred to NO_3^- in solid NH_4NO_3 , +5 ppm from neat liquid nitromethane (Table 6); low-precision measurements, assignments tentative.
- (b) Data from ref. 296, ^{15}N enriched compound, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NO_3^- in aqueous NH_4NO_3 , +4.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

Table 70 (continued)

- (c) Data from ref. 241, ^{15}N natural abundance spectra, 50.68 MHz, field parallel to sample tube, originally referred to neat HCONMe_2 , +277.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); originally reported to " NH_4^+ standard" taken at +82.2 ppm from the standard employed.
- (d) Data from ref. 240, ^{15}N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to NH_4^+ in 5 M NH_4NO_3 in 2 M HNO_3 , +359.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).
- (e) Data from ref. 302, ^{15}N natural abundance INEPT spectra, 30.4 MHz, originally referred to neat nitromethane via proton resonance frequency of SiMe_4 in order to eliminate bulk susceptibility effects; however, this introduces solvent effects on proton shielding of internal SiMe_4 standard which was added to neat nitromethane sample as well as to the solutions involved; the effects are thus transmitted to the nitrogen shieldings.

Table 71
Nitrogen shieldings in angiotensin amide

Formula	Nitrogen shielding referred to neat nitromethane under conditions specified	
	¹⁵ N natural abundance, 0.3 M solution in H ₂ O, pH = 4.5	¹⁵ N labelled compound, 0.02 M solution in H ₂ O, pH = 4.5
H ₂ ⁺ Asn ¹	+341.7(NH ₃ ⁺), +267.7(NH ₂)	unlabelled
Arg ²	+258.2(N _α), +294.6 (N _δ), +307.7(N _ε)	+304.4 (N _ε -labelled)
Val ³	+258.2	+257.9
Tyr ⁴	+255.7	+254.9
Val ⁵	+258.2	+256.2
His ⁶	+203.7(N _τ), +206.4 (N _π)	unlabelled
Pro ⁷	+243.5	unlabelled
Phe ⁸	+258.2	+256.2
OH		

Data from ref. 237, ¹⁵N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk susceptibility effects.

Table 72

Nitrogen shieldings in amino acid residues in some proteins and in free amino acids produced by bacterial cells

Sample	Nitrogen shieldings referred to neat nitromethane	Notes
^{15}N -enriched	+345.1 (N_ϵ -Lys), free amino acid	(a)
Bacterium lactofermentum	+344.3 (N_δ -Orn), free amino acid	(a)
cells grown under high	+336.7 (Glu), free amino acid	(a)
oxygen supply in normal	+334.6 (Ala), free amino acid	(a)
(2.5 $\mu\text{g}/\text{l}$) biotin	+321.0 (Pro), free amino acid	(a)
concentration	+306.1 (N_ϵ -Arg), free amino acid	(a)
	+304.3 (N_δ -Arg), free amino acid	(a)
	+265.4 (N_δ -Gln), free amino acid	(a)
	+249.4 (N_α -MeCO-Gln), free amino acid	(a)
^{15}N -enriched	+351.6 (NH_4^+)	(a)
Bacterium lactofermentum	+341.2 (Val), free amino acid	(a)
cells grown under low	+339.5 (N_α -Asp), free amino acid	(a)
oxygen supply in	+268.1 (N_γ -Asn), free amino acid	(a)

normal and high	+258.1 (Glu), peptide	(a)
(25 µg/l) biotin	+252.8 (N-MeCO-glucosamine)	(a)
concentration	+246.8 (Ala), peptide	(a)

¹⁵ N-glycine residue		
incorporated into		
reduced glutathione	+260.9 (Gly)	(b)
of intact human		
erythrocytes,		
H-Glu-Cys)SH)-Gly-OH		

Amino acid residues	+346 (N _ε -Lys)	(c)
in coat protein of	+339 (terminal Ala)	(c)
bacteriophage fd virus	+310 (N _ε -Trp)	(d)
(solid pellets)	+268 to +271 (Gly and side-chain Gln)	(c)
	+260 (various amide groups)	(c)
	+241 (Pro)	(c)

Table 72 (continued)

Amino acid residues	+342, +343 (NH_2 in free amino acids and N $^\epsilon$ -Lys)	(e)
of storage protein in	+298, +308 (N_δ and N_ϵ in Arg)	(e)
soybean cotyledons and	+207 (His, ring)	(e)
leaves (solid samples)	+260 (various peptide linkages)	(e)
Amino acid residues	+360.7 (NH_4^+)	(f)
in tact mycelia of	+346.8 (N_ϵ -Lys, N_δ -Orn)	(f)
Neurospora crassa	+345.1 (free Val and Ser)	(f)
and some free amino	+340.2 (free Gln, Glu, Lys, Arg)	(f)
acids	+338.5 (free Ala)	(f)
(suspension in H_2O)	+328.1 (free Pro)	(f)
	+309.7 (N_ϵ -Arg)	(f)
	+297.2 (N_δ -Arg)	(f)
	+293.9 (N_α -citrulline)	(f)
	+306.8 (N_ω -citrulline)	(f)
	+266.6 (N_δ -Gln)	(f)

For additional data, see ref. 1, Tables 90-93 therein

(a) Data from ref. 207, ^{15}N spectra, 30.4 MHz, field parallel to sample tube, originally referred to 4 M NH_4Cl in 2 M HCl , +352.5 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); originally reported relative to " HNO_3 " standard at -350.9 ppm from standard employed; temperature maintained at $+18 \pm 2^\circ\text{C}$.

(b) Data from ref. 304, ^{15}N labelled solid samples, ^{15}N CP-MASS spectra, 27.37 MHz, originally referred to 5 M NH_4NO_3 in 2 M HNO_3 , +359.0 ppm (NH_4^+) from neat nitromethane (Table 6), conversion scheme II (Table 4), but reported relative to liquid NH_3 standard taken at +380.2 ppm from nitromethane.

(c) Data from ref. 178, ^{15}N labelled samples of Escherichia Coli bacteria infected with filamentous bacteriophage fd; ^{15}N CP-MASS spectra, 15.24 MHz, originally referred to NH_4^+ in solid NH_4NO_3 , +358.4 ppm from neat liquid nitromethane (Table 6), uncorrected for bulk susceptibility effects.

(d) Data from ref. 179, ^{15}N labelled N-Trp, details as in note (c).

(e) Data from refs. 175, 176, 184, 649, samples grown on ^{15}N labelled amide group of glutamine, ^{15}N labelled amide group of glutamine, ^{15}N CP-MASS spectra, 9.12 MHz, originally referred to solid $(\text{NH}_4)_2\text{SO}_4$ standard calibrated against neat nitromethane (+360 ppm).

(f) Data from refs. 177, 650, ^{15}N labelled cultures, ^{15}N spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO_3 , +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

Table 73

Nitrogen shieldings in some solid polypeptides

Polymer (for abbreviations, see Table 56)	Solid state structure	Nitrogen shielding referred to neat nitromethane
(Gly) _n	α-helix	+267.7
	β-sheet	+272.2
(Ala) _n	α-helix	+257.1
(D,L-Ala) _n	β-sheet	+248.3
(Leu) _n	α-helix	+259.7
	β-sheet	+248.9
(D,L-Leu) _n	α-helix	+258.8
	β-sheet	+249.1
(Val) _n	β-sheet	+250.7; +251.7, minor peak
(Phe) _n	α-helix	+262.9
	β-sheet	+248.4
(γ-OMe-Glu) _n	α-helix	+259.7
(Pro) _n	α-helix	+248.8
Copolymers		
¹⁵ N-Gly + (Ala) _n	α-helix	+257.1 (Ala) +271.9 (Gly)
¹⁵ N-Gly + (γ-OMe-Glu) _n	α-helix	+259.7 (γ-OMe-Glu) +269.7 (Gly)
¹⁵ N-Gly + (Val) _n	β-sheet	+251.7 (Val) +264.2 (Gly) +267.1; +272.5 (Gly, minor components)

Table 73 (continued)

$^{15}\text{N-Gly} + (\beta\text{-Ala})_n$	β -sheet	+258.1 (β -Ala) +263.2 (Gly)
$^{15}\text{N-Gly} + (\text{Leu})_n$	β -sheet	+258.0 (Leu)
$^{15}\text{N-Leu} + (\text{Ala})_n$	α -helix	+257.3 (Ala) +260.4 (Leu)
$^{15}\text{N-Leu} + (\text{Val})_n$	β -sheet	+249.1 (Leu)
$^{15}\text{N-Val} + (\text{Ala})_n$	α -helix	+259.1 (Val)
$^{15}\text{N-Val} + (\text{Leu})_n$	α -helix	+260.1 (Leu)

For additional data, see Table 74

Data from ref. 180, ^{15}N labelled and unlabelled polymers, ^{15}N CP-MASS spectra, 30.41 MHz, originally referred to NO_3^- in solid NH_4NO_3 , +4.0 ppm from neat nitromethane (Table 6), uncorrected for bulk susceptibility effects.

Table 74
Nitrogen shieldings in some polypeptides

Formula (for abbreviations, see Table 56; Abe = aminobenzoic acid; 4-Amc = 4-H ₂ NCH ₂ - <u>trans</u> - cyclohexanoic acid; 4-Apa = 4-aminophenyl acetic acid)	Solvent or state	Nitrogen shielding referred to neat nitromethane (ppm) (assignments in order of amino acid residues)	Notes
(Gly) _n , "Nylon-2"	powdered solid	+276	(a)
	TFA	+270.3	(b)
		+270.2	(c)
(β-Ala) _n , "Nylon-3"	TFA	+251.9	(b)
		+250.8	(c)
(γ-Abu) _n , "Nylon-4"	TFA	+247.7	(b)
		+246.6	(c)
(δ-Ava) _n , "Nylon-5"	TFA	+243.9	(b)
		+242.8	(c)
(ε-Aca) _n , "Nylon-6"	TFA	+240.2	(b)
		+239.1	(c)

Nylon-type peptide polymers see also Table 52

(Ala) _n	powdered solid	+261	(a)
(D,L-β-Abu) _n	TFA	+236.0	(c)
(3-Abe-Gly) _n	TFA	+248.9; +271.1 +247.8; +270.1	(b) (c)
(3-Abe-β-Ala) _n	TFA	+244.2; +256.0 +243.1; +254.9	(b) (c)
(3-Abe-γ-Abu) _n	TFA	+243.5; +254.2 +242.4; +253.1	(b) (c)
(3-Abe-δ-Ava) _n	TFA	+244.2; +248.6 +243.1; +247.5	(b) (c)
(3-Abe-ε-Aca) _n	TFA	+244.8; +246.7 +243.7; +245.6	(b) (c)
(3-Abe-γ-Abu) _n	TFA	+243.6; +242.4 +242.5; +241.3	(b) (c)
(4-Abe-β-Ala) _n	TFA	+243.5; +256.2 +242.4; +255.1	(b) (c)
(4-Abe-ε-Aca) _n	TFA	+242.8; +245.7	(c)
(Gly-β-Ala) _n	TFA	+258.9; +266.8 +257.8; +265.7	(b) (c)

Table 74 (continued)

(Gly- γ -Abu) _n	TFA	+257.1; +263.4	(b)
		+256.0; +262.3	(c)
(Gly- δ -Ava) _n	TFA	+254.0; +264.0	(b)
		+252.9; +262.4	(c)
(Gly- ϵ -Aca) _n	TFA	+252.8; +264.7	(b)
		+251.7; +263.6	(c)
(β -Ala- γ -Abu) _n	TFA	+249.6; +251.2	(b)
		+248.5; +250.0	(c)
(β -Ala- δ -Ava) _n	TFA	+246.8; +250.9	(b)
		+245.7; +249.8	(c)
(β -Ala- ϵ -Aca) _n	TFA	+245.2; +250.5	(b)
		+244.1; +249.4	(c)
(γ -Abu- δ -Ava) _n	TFA	+243.7; +250.5	(b)
		+242.6; +249.4	(c)
(γ -Abu- ϵ -Aca) _n	TFA	+240.8; +248.3	(c)
(δ -Ava- ϵ -Aca) _n	TFA	+240.6; +241.9	(c)
(ϵ -Aca- β -Abu) _n	TFA	+235.3; +243.9	(c)
(ϵ -Aca-Gly-Gly) _n	TFA	+252.3; +264.5; +271.8	(b)
		+251.2; +263.4; +270.7	(c)

$(\epsilon\text{-Aca-}\beta\text{-Ala-Gly})_n$	TFA	+247.2; +253.7; +267.0	(b)
		+246.1; +252.6; +265.9	(c)
$(\epsilon\text{-Aca-Gly-}\beta\text{-Ala})_n$	TFA	+242.0; +259.6; +265.6	(b)
		+240.6; +258.5; +264.5	(c)
$(D,L\text{-Leu})_n$	TFA + MeSO_3H	+253.6 ($L_N\text{LL}$, $D_N\text{DD}$, isotactic)	(d)
		+254.4 ($D_N\text{LL}$, $L_N\text{DD}$, $L_N\text{LD}$,	
		+255.5 and $D_N\text{DL}$, heterotactic)	(d)
	TFA	+257.6 ($D_N\text{LD}$, $L_N\text{DL}$, syndiotactic) to +256.3	(d)
$(\gamma\text{-OMe-D,L-Glu})_n$	TFA	+256.7 ($L_N\text{LL}$, $D_N\text{DD}$, isotactic)	(d)
		+257.6 ($D_N\text{LL}$, $L_N\text{DD}$, $L_N\text{LD}$ and	
		+258.5 $D_N\text{DL}$, heterotactic)	(d)
		+259.5 ($D_N\text{LD}$, $L_N\text{DL}$, syndiotactic)	(d)
$(D,L\text{-}\beta\text{-Abu})_n$	TFA	+237.1	(b)
$(\epsilon\text{-Aca-4-Amc})_n$	TFA	+243.5; (?)	(b)
$(3\text{-Abe-4-Amc})_n$	TFA	+247.6; +249.0	(b)
$(4\text{-Apa-}\epsilon\text{-Aca})_n$	TFA	+246.8; +251.1	(b)
$(3\text{-Abe-4-Abe})_n$	TFA	+240.5; +242.2	(b)

Table 74 (continued)

(Gly-Gly-Ala) _n	TFA	+272.0; +271.6; +255.4	(e)
	HCOOH	+273.0; +272.3; +257.0	(e)
(Gly-Ala-Ala) _n	TFA	+272.1; +255.4; +256.2	(e)
	HCOOH	+272.9; +257.0; +257.6	(e)
(Gly/Val) _n	TFA	+271.4 (Gly-Gly)	(e)
		+270.1 (Val-Gly)	(e)
		+254.0 (Val-Val)	(e)
		+259.0 (Gly-Val)	(e)
(Gly-Gly-Val) _n	TFA	+267.9; +271.1; +259.5	(e)
	HCOOH	+269.2; +272.1; +262.3	(e)
(Gly/Leu) _n	TFA	+271.1 (Gly-Gly)	(e)
		+270.6 (Leu-Gly)	(e)
		+254.7 (Leu-Leu)	(e)
		+257.2 (Gly-Leu)	(e)
(Gly-Gly-Pro) _n	TFA	+270.2; +271.1; +241.9	(e)
(Gly/ε-(PhOCO)-Lys) _n	HCOOH	+272.3 (Gly-Gly)	(e)
		+271.3 (Gly-Lys)	(e)
		+257.8 (Lys-Lys)	(e)
		+259.8 (Gly-Lys)	(e)
(Gly/D,L-α-Abu) _n	TFA	+271.3 (Gly-Gly)	(e)
		+270.1 (α-Abu-Gly)	(e)
		+255.6 (α-Abu-α-Abu)	(e)
		+257.8 (Gly-α-Abu)	(e)

(Gly/ γ -Me-Glu) _n	TFA	+271.3 (Gly-Gly)	(e)
		+270.1 (γ -Me-Glu-Gly)	(e)
		+258.1 (γ -Me-Glu- γ -Me-Glu)	(e)
		+259.8 (Gly- γ -Me-Glu)	(e)
	HCOOH	+272.3 (Gly-Gly)	(e)
		+271.3 (γ -Me-Glu-Gly)	(e)
		+261.1 (γ -Me-Glu- γ -Me-Glu)	(e)
		+259.8 (Gly- γ -Me-Glu)	(e)
(Gly/Met) _n	TFA	+271.2 (Gly-Gly)	(e)
		+269.7 (Met-Gly)	(e)
		+257.2 (Met-Met)	(e)
		+259.1 (Gly-Met)	(e)
(Gly/Cys(SCH ₂ Ph)) _n	TFA	+271.2 (Gly-Gly)	(e)
		+268.7 (CysSR-Gly)	(e)
		+257.1 (CysSR-CysSR)	(e)
		+259.4 (Gly-CysSR)	(e)
(Gly-Gly-Phe) _n	TFA	+268.5; +271.6; +258.5	(e)
	HCOOH	+270.5; +272.4; +260.7	(e)
(Gly/Phg) _n	TFA	+271.4 (Gly-Gly)	(e)
		+269.8 (Phg-Gly)	(e)
		+254.9 (Phg-Phg)	(e)
		+257.2 (Gly-Phg)	(e)
(Gly-Gly- β -Ala) _n	TFA	+265.6; +272.1; +259.0	(e)
	HCOOH	+267.4; +272.2; +262.7	(e)

Table 74 (continued)

(Gly- β -Ala- β -Ala) _n	TFA	+266.5; +259.6; +249.3	(e)
(Gly-Gly- γ -Abu) _n	TFA	+265.1; +271.0; +256.6	(e)
	HCOOH	+267.7; +271.8; +260.5	(e)
(Ala/Gly) _n	TFA	+270.1 (Gly-Gly)	(e)
		+278.8 (Ala-Gly)	(e)
		+254.6 (Ala-Ala)	(e)
		+254.2 (Gly-Ala)	(e)
(Ala/Val) _n	TFA	+254.7 (Ala-Ala)	(e)
		+250.4 (Val-Ala)	(e)
		+252.9 (Val-Val)	(e)
		+258.8 (Ala-Val)	(e)
(Ala/Leu) _n	TFA	+254.7 (Ala-Ala)	(e)
		+252.7 (Leu-Ala)	(e)
		+253.6 (Leu-Leu)	(e)
		+255.5 (Ala-Leu)	(e)
(Ala/Phe) _n	TFA	+254.5 (Ala-Ala)	(e)
		+251.6 (Phe-Ala)	(e)
		+254.5 (Phe-Phe)	(e)
(Ala/Gly/Val) _n	TFA	+254.6 (Ala-Ala)	(e)
		+254.1 (Gly-Ala)	(e)
		+251.2 (Val-Ala)	(e)
		+269.9 (Gly-Gly)	(e)
		+270.7 (Ala-Gly)	(e)

		+267.6 (Val-Gly)	(e)
		+254.1 (Val-Val)	(e)
		+257.3 (Ala-Val)	(e)
		+257.7 (Gly-Val)	(e)
(Ala/Gly/Phe) _n	TFA	+254.6 (Ala-Ala)	(e)
		+254.1 (Gly-Ala)	(e)
		+251.2 (Phe-Ala)	(e)
		+264.9 (Gly-Gly)	(e)
		+270.7 (Ala-Gly)	(e)
		+267.6 (Phe-Gly)	(e)
		+254.1 (Phe-Phe)	(e)
		+257.3 (Ala-Phe)	(e)
		+257.7 (Gly-Phe)	(e)

For additional data, see ref. 1, Tables 95-102 therein

(a) Data from ref. 182, ¹⁵N natural abundance CP-MASS spectra, 9.12 MHz, originally referred to solid (NH₄)₂SO₄ standard calibrated (+360 ppm) against neat liquid nitromethane, uncorrected for bulk susceptibility effects.

(b) Data from ref. 130, ¹⁵N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NO₃⁻ in aqueous NH₄NO₃, +4.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

(c) Data from ref. 309, and references therein; details as in note (b), but 40.55 MHz spectra, field parallel to sample tube.

(d) Data from ref. 313, ¹⁵N labelled compounds, ¹⁵N spectra, 40.55 MHz, details as in note (c); inverse-gated decoupling or INEPT technique.

(e) Data from ref. 296, details as in note (b).

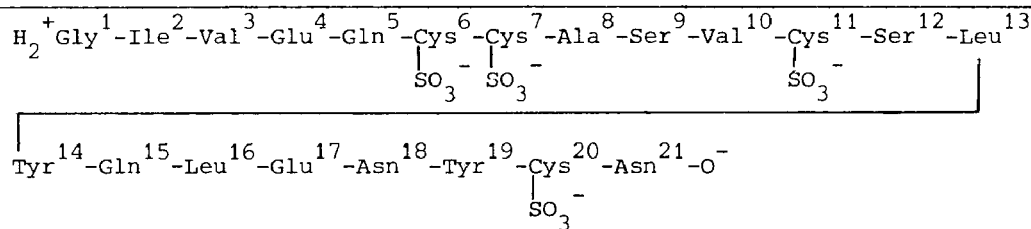
Table 75

Characteristic nitrogen shieldings for peptide linkages in polypeptides dissolved in CF_3COOH

Peptide linkage (for abbreviations, see Table 56)	Nitrogen shielding referred to neat nitromethane (in ppm) for measurements where field is parallel to sample tube (for field perpendicular to sample tube, add 1.1 ppm)
Gly-Gly	+270.1
Ala-Ala	+254.6
Val-Val	+252.7
Leu;Leu	+253.5
Phe-Phe	+254.4
(γ -Me)Glu-(γ -Me)Glu	+256.8
Met-Met	+255.9
Ala-Gly	+270.8
Val-Gly	+266.9
Leu-Gly	+269.0
Phe-Gly	+267.6
(γ -Me)Glu-Gly	+269.0
Val-Ala	+250.2
Leu-Ala	+252.5
(γ -Me)Glu-Ala	+252.3
Phe-Ala	+251.2
Leu-Val	+255.3
(γ -Me)Glu-Val	+254.3
(γ -Me)Glu-Leu	+254.3
Gly-Ala	+254.2
Gly-Val	+258.3
Gly-Leu	+255.9
Gly-Phe	+257.7
Gly-(γ -Me)Glu	+258.6
Ala-Val	+258.8
Ala-Leu	+255.5
Met-(γ -Me)Glu	+258.6
Ala-Phe	+257.3
Val-Leu	+251.2
Val-(γ -Me)Glu	+253.1
Met-Ala	+252.3

Data from refs. 309 and 310 originally referred to NO_3^- in aqueous NH_4NO_3 , +4.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

Nitrogen shieldings in Bunte salt form of bovine insulin-A chain



Peak numbering (not related to amino acid residue numbering)	Nitrogen shielding referred to neat nitromethane (ppm) under conditions specified					Tentative assignments
	in H ₂ O		in DMSO			
	25°C	35°C	29°C	40°C	40°C after 2 days	
1	+254.5	+250.5	+258.4	+258.5	+258.4	
2	+254.5	+250.6	+259.0	+259.2	+259.1	
3	+255.4	+255.8	+259.6	+259.8	+259.7	
4	+256.3	+257.0	+260.0	+261.0	+259.0	
5	+256.9	+257.1	+261.2	+261.3	+261.2	

Table 76 (continued)

6	+257.5	+257.7	+261.3	+261.5	+261.3	
7	+259.0	+259.5	+262.0	+262.0	+262.1	Val ³ (or peak 8)
8	+259.2	+259.5	+262.1	+262.1	+262.2	Val ³ (or peak 7)
9	+259.2	+259.6	+262.5	+262.6	+262.5	
10	+259.4	+259.6	+262.5	+262.6	+262.5	
11	+259.7	+259.9	+262.6	+262.8	+262.7	
12	+259.7	+260.2	+263.0	+263.1	+263.1	
13	+260.1	+260.3	+263.3	+263.4	+263.4	
14	+260.2	+260.7	+263.4	+263.6	+263.5	
15	+261.3	+261.5	+263.7	+263.8	+263.7	
16	+261.4	+261.5	+264.4	+264.4	+264.4	
17	+262.0	+262.4	+266.0	+266.1	+266.1	Asn ¹⁸ (NH)
18	+265.1	+265.4	+267.0	+267.1	+267.0	Ile ²
19	+267.3	+267.7	+269.4	+269.7	+269.5	Ser ⁹
20	+267.5	+268.0	+270.1	-	+270.2	Asn ¹⁸ , Asn ²¹ (NH ₂)

21	+270.0	+268.6	+270.9	+271.2	+271.0	Ser ¹²
22	+270.0	+268.6	+271.3	+271.6	+271.4	Gln ⁵ , Gln ¹⁵ (NH ₂)
23			+357.2			Gly ¹ (NH ₃ ⁺)

For abbreviations of amino acid residues, see Table 56; data from ref. 311, ¹⁵N natural abundance spectra, 40.55 MHz, field parallel to sample tube, originally referred to NO₃⁻ in aqueous NH₄NO₃, +4.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

TABLE 77

Nitrogen shieldings in some azides and their protonated forms

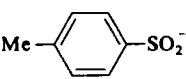
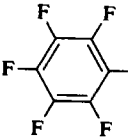
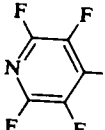
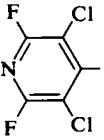
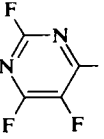
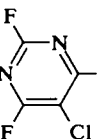
		Nitrogen shielding referred to neat nitromethane in nitrogen atoms specified				
Compound or ion	Solution	R—N= or RNH—	=N ⁺ = or —N ⁺ ≡	=N ⁻ or ≡N	other	Notes
Azide ion (⁻ N=N ⁺ =N ⁻)						
Na ⁺ N ₃ ⁻	0.3 M in H ₂ O	+280.6	+131.5	+280.6		(a)
	5.13 M in H ₂ O	+281.7	+132.2	+281.7		(a)
	in H ₂ O	+280.5	+131.7	+280.5		(b)
K ⁺ N ₃ ⁻ (labelled at terminal ¹⁵ N)	in CH ₂ Cl ₂	+282.0	?	+282.0		(c)
	+18-crown-6 ether					
Li ⁺ N ₃ ⁻	in H ₂ O	+280.4	+131.8	+280.4		(a)
Covalent azides, $\begin{array}{c} \text{R} \\ \diagdown \\ \text{N}=\text{N}^+=\text{N}^- \\ \diagup \\ \text{R} \end{array}$						
H	in Et ₂ O	+324.5	+134.1	+178.6		(a)
Cl	in CD ₂ Cl ₂	+273.1	+123.7	+114.1		(a)
Me	in benzene	+321.7	+130.2	+171.5		(a)
	neat liquid	+320.8	?	+172.3		(d)
Et	neat liquid	+307.7	+132.0	+169.2		(a)
		+306.1	?	+169.2		(d)
	0.3 M in CCl ₄	+306.4	+132.1	+166.6		(a)
Ph	in acetone	+288.5	+136.7	+147.4		(a)
	in CH ₂ Cl ₂ + 18-crown-6 ether	+242.7	+148.7	+139.4		(c)
	in CDCl ₃	+307.6	+145.5	+150.3	(unlabelled)	(e)
		+308.2	+145.4	+150.3	(labelled RN= and =N ⁻)	(e)
		+307.0	+144.7	+149.8	(fully labelled)	(e)
	in CDCl ₃	+296.2	+144.4	+147.9	+147.8 (ring)	(e)

TABLE 77—*cont.*

Compound or ion	Solution	Nitrogen shielding referred to neat nitromethane in nitrogen atoms specified				Notes
		R—N≡ or RNH—	=N ⁺ = or —N ⁺ ≡	=N ⁻ or ≡N	other	
	in CDCl ₃	+285.1	+150.3	+142.1 +142.6	+146.4 (ring) (=N ⁻ labelled)	(e) (e)
	in CDCl ₃	+272.9	+136.9	+148.8	+158.9 (N-1, ring) +149.9 (N-3, ring)	(e)
	in CDCl ₃	+266.2	+135.6	+148.5	+161.1 (N-1, ring) +152.7 (N-3, ring)	(e)
PhC(=O)—	in Et ₂ O -30 °C	+251.4	+142.0	+137.1		(b)

For additional data see ref. 1, Table 103 therein

Protonated azides
(aminodiazonium ions)

$$\begin{array}{c} \text{R} \\ \diagdown \\ \text{N}-\text{N}^+\equiv\text{N} \\ \diagup \\ \text{H} \\ \text{R} \end{array}$$

H	in SO ₂ Cl/ FSO ₃ H/SbF ₅	+311.6	?	+114.0		(f)
Me	in SO ₂ Cl/ FSO ₃ H/SbF ₅	+306.3	?	+106.3		(f)
Et	in SO ₂ Cl/ FSO ₃ H/SbF ₅	+294.6	?	+102.7		(f)

(a) See ref. 1, Table 103 therein, and references therein.

(b) Data from ref. 376; ¹⁵N-labelled compounds, ¹⁵N spectra, 8.927 MHz, field perpendicular to sample tube, originally referred to satd. aqueous NaNO₃, +3.7 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).(c) Data from ref. 315; ¹⁵N-labelled compounds, ¹⁵N spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO₃, +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

TABLE 77—*cont.*

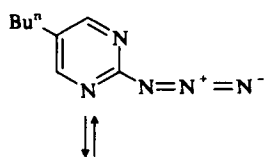
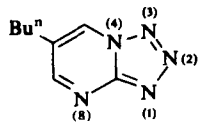
(d) Data from ref. 317; ^{15}N -labelled (RN and terminal N) compound, ^{15}N spectra, 8.06 MHz, field perpendicular to sample tube, originally referred to liquid NH_3 , +380.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(e) Data from ref. 316; ^{15}N -labelled and unlabelled compounds, ^{15}N spectra, 18.24 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(f) As in note (d), ^{15}N -labelled RNH and terminal N positions.

TABLE 78

Azidoazine—azoloazine valence tautomerism monitored by ^{15}N NMR

Structures	Nitrogen shieldings referred to neat nitromethane, and their assignments	
	15%	+270.0 (azide, $\text{R}-\text{N}=\text{}$) +141.1 } (azide, $=\text{N}^+=$ and $=\text{N}^-$) +142.3 } +111.1 (pyrimidine ring, ^1H -coupled doublet)
	neat liquid 85%	+69.0 (1-N) +32.0 (2-N) -23.3 (3-N) +142.4 (4-N) +103.4 (8-N) (^1H -coupled doublet)

Data from ref. 314; ^{15}N natural abundance spectra, 40.55 MHz, field parallel to sample tube, originally referred to NO_3^- in aqueous NH_4NO_3 , +4.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); ^1H -coupled spectra.

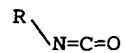
Table 79

Nitrogen shieldings in some cyanates, isocyanates, thiocyanates and isothiocyanates

Compound	Solution or state	Nitrogen shielding referred to neat nitromethane (ppm)	Notes
(Iso)cyanate ion (N=C=O) ⁻			
K ⁺ (NCO) ⁻	0.3 M in H ₂ O	+302.6	(a)
	6.2 M in H ₂ O (satd.)	+302.9	(a)
	in H ₂ O, pH = 8.8	+304.8	(b)
(NCO) ⁻ bound to native human carbonic anhydrase B	in H ₂ O, pH = 8.8	+337.8	(b)
	7.0	+338.0	(b)

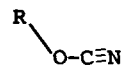
Table 79 (continued)

Covalent isocyanates



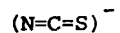
R = alkyl	neat liquids	+365 to +326	(a)
R = aryl	various	+338 to +335	(a)

Covalent cyanates



R = alkyl, aryl	various	+222 to +190	(a)

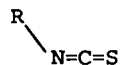
(Iso)thiocyanate ion



K^+ (NCS)	0.3 M in H_2O	+174.1	(a)
	9.5 M in H_2O (satd.)	+170.0	(a)

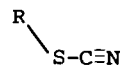
$\text{Li}^+ (\text{NCS})^-$	various	+163 to +203	(a)
$\text{NH}_4^+ (\text{NCS})^-$	solid state	+171.1 $(\text{NCS})^-$	(c)
$[(\text{Me}_2\text{NCH}_2\text{CH}_2)_3\text{NPd}(\text{NCS})]^+ (\text{NCS})^-$	in D_2O	+222.7 $(\text{NCS})^-$	(d)
		+302.1 (N-bound NCS)	(d)
$[(\text{Me}_2\text{NCH}_2\text{CH}_2)_3\text{NPd}(\text{SCN})]^+ (\text{NCS})^-$	in D_2O	+196.9 (S-bound NCS)	(d)

Covalent isothiocyanates



R = alkyl	various	+290 to +268	(a)
R = aryl	various	ca. +273	(a)

Covalent thiocyanates



R = alkyl	neat liquid	ca. +102	(a)

For additional data, see ref. 1, Tables 106 and 107 therein

Table 79 (continued)

- (a) See ref. 1, Table 106 therein, and references therein.
- (b) Data from ref. 289, ^{15}N labelled $(\text{NCO})^-$, ^{15}N spectra, 50.65 MHz, field parallel to sample tube, originally referred to 1 M HNO_3 , +6.2 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).
- (c) Data from ref. 264, ^{15}N labelled compound, ^{15}N CP-MASS spectrum, 18.25 MHz, originally referred to solid NH_4Cl (see Table 30, note (a) for conversion to nitromethane scale), uncorrected for bulk susceptibility effects.
- (d) Data from ref. 319, ^{15}N labelled NCS^- , ^{15}N spectra, 40.55 MHz, field parallel to sample tube, originally referred to aqueous KNO_3 , +3.5 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); original assignments to N- and S-bound NCS are reversed.

TABLE 80

Nitrogen shieldings in some cyanocarbenium ions

$R_2C^+-C\equiv N \leftrightarrow R_2C=C=N^+$	
Substituents R	Nitrogen shielding referred to neat nitromethane
MeO- 	+120.0
Me- 	+106.8
	+97.2
F- 	+101.0

Data from ref. 318; ^{15}N -labelled ions, solutions in $\text{CDCl}_3/\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$ at -80°C ; ^{15}N spectra, 8.06 MHz, field perpendicular to sample tube, originally referred to liquid NH_3 , +380.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

TABLE 81

Nitrogen shieldings in some cyanides, isocyanides and nitrilium ions

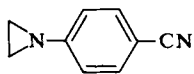
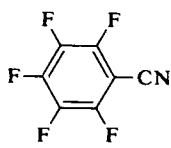
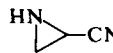
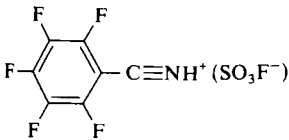
Compound or ion	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
Cyanide ion ($\text{C}\equiv\text{N})^-$			
K^+CN^-	0.3 M in H_2O	+106.1	(a)
	8.5 M in H_2O (satd)	+102.5	(a)
	in H_2O	+104.1	(b)
CN^- as ligand	various	see Table 83	
Covalent cyanides (nitriles)			
$\text{R}-\text{C}\equiv\text{N}$			
HCN	gaseous (300 K)	+115.4	(c)
	liquid	+129	(a)
MeCN	neat liquid	+135.8	(a)
	various solvents	+127 to +153	(a)
	adsorbed on zeolites	see Table 84	
EtCN	neat liquid	+136.7	(a)
Pr^nCN	neat liquid	+133.2	(a)
Pr^iCN	neat liquid	+135.6	(a)
Bu^iCN	neat liquid	+135.9	(a)
PhCN	1.9 M in dioxane	+123.4	(d)
	1.9 M in acetone	+124.0	(d)
	1.9 M in HCONMe_2	+124.7	(d)
	1.9 M in MeCN	+125.5	(d)
	1.9 M in CH_2Cl_2	+126.7	(d)
	1.9 M in MeNO_2	+127.4	(d)
	1.9 M in MeOH	+128.0	(d)
	4 M in CDCl_3	+125.8 (CN)	(e)
	satd. in CH_2Cl_2	+110.9	(f)
	50% in CDCl_3	+138.4 (CN)	(g)
$-\text{CMe}_2\text{CN}$ end groups in polystyrene and polymethylmethacrylate (polymerization initiated with azaisobutyronitrile)	in CDCl_3	+133.5; +135.2	(h)
$\text{Me}_3\text{Si}-\text{CN}$	2.5 M in CDCl_3	+130.5	(i)

TABLE 81—*cont.*

Compound or ion	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
Nitrilium ions			
$R-C\equiv N^+-R'$			
$R=H$ or Me , $R'=H$ or Me	various	+235 to +252	(a, j)
 $C\equiv NH^+ (SO_3F^-)$	in FSO_3H	+215.6	(f)
Isoyanides (isonitriles)			
$R-N^+\equiv C^-$			
$Me-NC$	neat liquid	+219.6	(a)
$Et-NC$	neat liquid	+205.1	(a)
Pr^a-NC	neat liquid	+206.0	(a)
Pr^i-NC	neat liquid	+193.4	(a)
Bu^i-NC	neat liquid	+184.9	(a)
$Ph-NC$	neat liquid	+204	(a)
Cyanamide structures			
$R_2N-C\equiv N$	see Table 46		
For additional data, see footnotes (a) and (j)			

(a) See ref. 1, Table 108 and references therein.

(b) Data from ref. 323; ^{15}N -labelled CN^- , ^{15}N spectrum, 36.5 MHz, field parallel to sample tube, originally referred to aqueous $NaNO_3$, +3.7 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

(c) Data from ref. 56; ^{15}N -labelled HCN , ^{15}N spectrum, 9.12 MHz, field perpendicular to sample tube, originally referred to gaseous N_2 at 300 K, calibrated (+74.7 ppm) against neat liquid nitromethane at 300 K; uncorrected for bulk-susceptibility effects.

(d) Data from ref. 320; ^{15}N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO_3 , +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(e) Data from ref. 600; ^{15}N natural abundance spectrum, 10.09 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk susceptibility effects; originally reported relative to liquid NH_3 standard taken at +380.2 ppm from nitromethane.

(f) Data from ref. 624; ^{15}N -labelled compounds, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to liquid NH_3 , +380.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(g) Data from ref. 607; ^{15}N natural abundance spectrum, 9.12 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

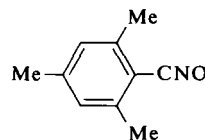
(h) Data from ref. 322; ^{15}N -labelled CN groups, ^{15}N spectrum, 10.09 MHz, field perpendicular to sample tube, originally referred to aqueous NH_3 , +378.4 ppm from neat nitromethane (Table 11) conversion scheme II (Table 4).

(i) Data from ref. 448; ^{14}N PFT spectra, 5.742 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(j) See ref. 3, p. 204 and references therein.

TABLE 82

Nitrogen shieldings in some fulminates (nitrile *N*-oxides)

Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
$\text{Na}^+(\text{CNO})^-$	in H_2O	+180	(a)
$\text{Bu}^t\text{—CNO}$	1.6 M in CDCl_3	+189.2	(b)
$\text{Ph}_3\text{C—CNO}$	1.7 M in CDCl_3	+184.2	(b)
	2.9 M in CDCl_3	+171.0	(b)
$\text{Me}_3\text{Si—CNO}$	2.9 M in CDCl_3	+164.6	(b)
$\text{Ph}_3\text{Si—CNO}$	1.5 M in CDCl_3	+160.2	(b)

For additional data see footnote (a)

(a) See ref. 1, Table 108 and references therein.

(b) Data from ref. 448; high-resolution ^{14}N PFT spectra, 5.742 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

Table 83

Nitrogen shieldings in some cyano complexes in H_2O

Structure	Nitrogen shielding referred to neat nitromethane	Notes
octahedral		
$[\text{Fe}(\text{CN})_6]^{4-}$	+99.6	(a)
$[\text{Ru}(\text{CN})_6]^{4-}$	+109.4	(a)
$[\text{Os}(\text{CN})_6]^{4-}$	+120.8	(a)
square-planar		
$[\text{Ni}(\text{CN})_4]^{2-}$	+89.6	(a)
	+90.2	(b)
$[\text{Pd}(\text{CN})_4]^{2-}$	+100.1	(a)
	+99.3	(b)
$[\text{Pt}(\text{CN})_4]^{2-}$	+109.2	(a)
	+109.6	(b)
linear		
$[\text{Ag}(\text{CN})_2]^-$	+103.7	(a)
$[\text{Au}(\text{CN})_2]^-$	+112.3	(a)
$\text{Hg}(\text{CN})_2$	+100.8	(a)
$[\text{Hg}_2(\text{CN})_2]^{2+}$	+98.5	(c)
tetrahedral		
$[\text{Cu}(\text{CN})_4]^{3-}$	+107.0	(a)
$[\text{Zn}(\text{CN})_4]^{2-}$	+105.1	(a)
	+106.0	(b)
$[\text{Cd}(\text{CN})_4]^{2-}$	+101.5	(a)
	+102.7	(b)
$[\text{Hg}(\text{CN})_4]^{2-}$	+101.8	(a)
	+102.1	(b)

Table 83 (continued)

(a) Data from ref. 323, ^{15}N labelled CN moiety, ^{15}N spectra, 36.5 MHz, field parallel to sample tube, originally referred to aqueous NaNO_3 , +3.7 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

(b) Data from refs. 399 and 651, ^{15}N enriched CN moiety, ^{15}N spectra 40.55 MHz, field parallel to sample tube, originally referred to aqueous 0.4 M KCN, +106.1 ppm from neat nitromethane (Table 81), conversion scheme II (Table 4).

(c) Data from ref. 416, ^{15}N labelled CN moiety, ^{15}N spectrum, 9.082 MHz, field perpendicular to sample tube, originally referred to satd. aqueous KCN, +102.5 ppm from neat nitromethane (Table 81), conversion scheme II (Table 4).

Table 84

Nitrogen shieldings in acetonitrile adsorbed on various zeolites

MeCN adsorbed in zeolite specified	Nitrogen shielding referred to neat nitromethane	Notes
Na-X	+159.7	(a)
K-X	+152.8	(a)
Na-X, 80% Na ⁺ exchanged for Li ⁺	+160.0	(a)
Na-X, 71% Na ⁺ exchanged for Rb ⁺	+148.5	(a)
Na-X, 50% Na ⁺ exchanged for Cs ⁺	+148.1	(a)
Na-X, 20% Na ⁺ exchanged for Ag ⁺	+171.8	(a)
60% Na ⁺ exchanged for Ag ⁺	+182.8	(a)
Na-Y, 88% Na exchanged for NH ₄ ⁺	+109	(b)
free MeCN (liquid)	+135.8	(c)

(a) Data from ref. 321, ¹⁵N labelled MeCN, ¹⁵N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to neat liquid MeCN, +135.8 ppm from neat nitromethane (Tables 6 and 81), conversion scheme II (Table 4).

(b) Data from ref. 262, details as in note (a), but originally referred to neat nitromethane, uncorrected for bulk susceptibility effects.

(c) See Table 81.

TABLE 85

Nitrogen shielding in some azoles

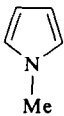
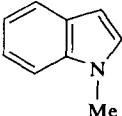
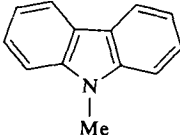
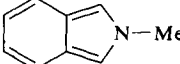
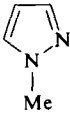
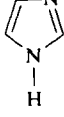
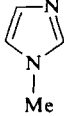
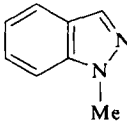
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	0.5 M in DMSO	+230.1	(a)
	in DMSO	+230.2	(c)
	2 M in acetone	+231.6	(b)
	in CDCl ₃	+230.9	(c)
	neat	+231.4	(b)
	0.5 M in DMSO	+253.6	(a)
	0.5 M in DMSO	+272.7	(a)
	satd. in Et ₂ O	+218 ± 2	(d)
	in CDCl ₃	+179.3 (N1)	(c)
		+73.7 (N2)	(c)
	in CDCl ₃	+180.8 (N1)	(e)
		+76.5 (N2)	(e)
	solid	+210 (N1)	(f)
		+138 (N3)	(f)
	0.5 M in DMSO	+218.5 (N1)	(a)
		+118.1 (N3)	(a)
	in DMSO	+218.0 (N1)	(c)
		+119.5 (N3)	(c)
	in DMSO	+219.2 (N1)	(e)
		+119.1 (N3)	(e)
	in CDCl ₃	+221.7 (N1)	(e)
		+124.1 (N3)	(e)
	in CDCl ₃	+219.5 (N1)	(c)
		+124.3 (N3)	(c)
	0.4 M in DMSO	+203.8 (N1)	(a)
		+57.6 (N2)	(a)
	0.5 M in DMSO	+202.8 (N1)	(g)
		+56.6 (N2)	(g)

TABLE 85—*cont.*

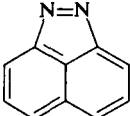
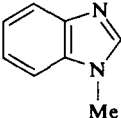
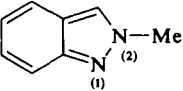
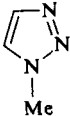
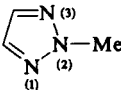
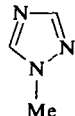
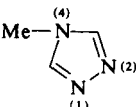
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	in THF	-75.6	(h)
	0.5 M in DMSO	+236.4 (N1) +136.3 (N3)	(a) (a)
	0.5 M in DMSO	+92.3 (N1) +162.1 (N2)	(a) (a)
	0.5 M in DMSO	+91.2 (N1) +161.0 (N2)	(g) (g)
	0.25 M in DMSO	+143.3 (N1) +16.2 (N2)	(a) (a)
	in DMSO	+28.4 (N3) +143.0 (N1) +16.2 (N2) +29.2 (N3)	(a) (c) (c) (c)
	in CDCl ₃	+145.0 (N1) +16.3 (N2) +30.7 (N3)	(c) (c) (c)
	0.5 M in DMSO	+54.0 (N1, 3) +135.0 (N2)	(a) (a)
	in DMSO	+50.1 (N1, 3) +131.4 (N2)	(c) (c)
	in CDCl ₃	+51.1 (N1, 3) +132.8 (N2)	(c) (c)
	0.5 M in DMSO	+171.3 (N1) +81.9 (N2) +127.4 (N4)	(a) (a) (a)
	in DMSO	+171.3 (N1) +82.2 (N2) +129.1 (N4)	(c) (c) (c)
	0.25 M in DMSO	+59.8 (N1, 2) +217.8 (N4)	(a) (a)
	in DMSO	+60.3 (N1, 2) +217.1 (N4)	(c) (c)

TABLE 85—*cont.*

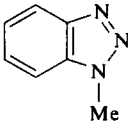
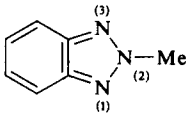
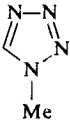
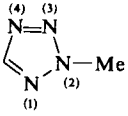
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	0.5 M in DMSO	+161.5 (N1) +1.1 (N2) +41.0 (N3)	(a) (a) (a)
	in DMSO	+161.8 (N1) +0.9 (N2) +40.8 (N3)	(c) (c) (c)
	in CDCl ₃	+164.1 (N1) +2.2 (N2) +42.2 (N3)	(c) (c) (c)
	0.5 M in MeOH	+167.0 (N1) +7.8 (N2) +55.0 (N3)	(i) (i) (i)
	0.5 M in acetone	+164.7 (N1) +1.5 (N2) +41.1 (N3)	(i) (i) (i)
	0.5 M in DMSO	+62.6 (N1, 3) +116.8 (N2)	(a) (a)
	in DMSO	+62.5 (N1, 3) +117.0 (N2)	(c) (c)
	in CDCl ₃	+63.1 (N1, 3) +119.2 (N2)	(c) (c)
	0.5 M in MeOH	+69.5 (N1, 3) +123.6 (N2)	(i) (i)
	0.5 M in acetone	+66.1 (N1, 3) +121.9 (N2)	(i) (i)
	0.5 M in DMSO	+151.1 (N1) +10.8 (N2) -12.7 (N3) +49.9 (N4)	(a) (a) (a) (a)
	in DMSO	+151.4 (N1) +10.8 (N2) -12.3 (N3) +50.2 (N4)	(c) (c) (c) (c)
	0.5 M in DMSO	+72.8 (N1) +101.8 (N2) +0.8 (N3) +46.8 (N4)	(a) (a) (a) (a)
	in DMSO	+73.2 (N1) +102.2 (N2) +0.9 (N3) +47.1 (N4)	(c) (c) (c) (c)

TABLE 85—*cont.*

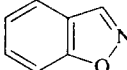
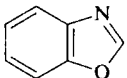
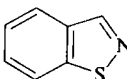
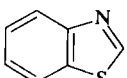
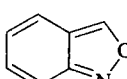
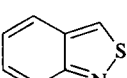
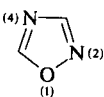
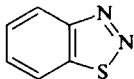
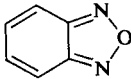
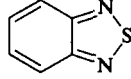
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	0.5 M in DMSO	-2.7	(a)
	in DMSO	-2.2	(e)
	in CDCl ₃	-0.6	(e)
	in DMSO	+123.7	(e)
	in CDCl ₃	+126.6	(e)
	in CCl ₄ (40%)	+123 ± 1.5	(j)
	in acetone	+81.8	(e)
	in acetone (90%)	+81.8	(k)
	in Et ₂ O	+82	(e)
	0.5 M in DMSO	+57.4	(a)
	in DMSO	+58.0	(e)
	in CDCl ₃	+62.2	(e)
	in D ₂ O/H ₂ O	+73.0	(e)
	0.5 M in DMSO	-3.3	(a)
	0.5 M in DMSO	+131.5	(a)
	satd. in Et ₂ O	+76 ± 2	(d)
	0.5 M in DMSO	+64.7	(a)
	0.5 M in DMSO	+7.5	(a)
	neat	+121 ± 2	(d)
	in Et ₂ O (1:1 v/v)	+20 ± 2 (N2)	(d)
		+140 ± 2 (N4)	(d)
	in Et ₂ O (1:1 v/v)	+81 ± 1	(d)

TABLE 85—*cont.*

Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	0.5 M in DMSO	-33.8	(a)
	0.5 M in DMSO	-30.3 (N2) -56.2 (N3)	(a) (a)
	in Et ₂ O (1:1 v/v)	+106 ± 1 (N2) +70 ± 1 (N4)	(d) (d)
	0.5 M in DMSO	+7.9	(a)
	in Et ₂ O (1:v/v)	+34 ± 1	(d)
	0.5 M in DMSO	-44.6 (N2) -59.2 (N3)	(a) (a)
	0.5 M in DMSO	-35.6	(a)
	0.5 M in DMSO	+49.1	(a)

(a) Data from ref. 26; ¹⁵N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO₃ in D₂O, +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4), Cr(acac)₃ added as relaxation reagent.

(b) Data from ref. 37; ¹⁴N CW spectrum, 4.3342 MHz, originally referred to neat nitromethane, high-precision differential-saturation technique with full lineshape fitting, concentric spherical sample standard containers in order to eliminate bulk-susceptibility effects.

(c) Data from ref. 249; ¹⁵N natural abundance spectra, 8.059 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; using solutions of 750 mg of the azole dissolved in 2 ml of solvent.

(d) See ref. 1, Table 112 and references therein.

(e) Data from ref. 120; ¹⁵N natural abundance spectra, 10.1 and 20.3 MHz field perpendicular and parallel respectively to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; since resonance frequencies were not specified for individual compounds, uncertainty in the shieldings can reach 1–2 ppm; Cr(acac)₃ added as relaxation reagent.

TABLE 85—*cont.*

(f) Data from ref. 186; ^{15}N -labelled imidazole, ^{15}N CP-MASS spectra, $(\text{NH}_4)_2\text{SO}_4$ standard calibrated (+360 ppm) against neat liquid nitromethane, uncorrected for bulk-susceptibility effects.

(g) Data from ref. 326; selectively ^{15}N -labelled compounds, ^{15}N spectra, 8.108 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(h) Data from ref. 652; ^{15}N -labelled compound, ^{15}N spectra, 40.56 MHz, field parallel to sample tube, originally referred to $^{15}\text{ND}_4^+$ line from 1.0 M $^{15}\text{ND}_4^{15}\text{NO}_3$ in D_2O , +359.6 ppm from neat nitromethane (Table 6), uncorrected for bulk-susceptibility effects.

(i) Data from ref. 253; ^{15}N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects, $\text{Cr}(\text{acac})_3$ added as relaxation reagent.

(j) Data from ref. 613; ^{14}N spectra, 6.5 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(k) Data from ref. 445; ^{15}N natural abundance spectra, 10.14 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

TABLE 86

Nitrogen shieldings in some azole derivatives

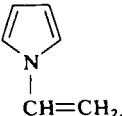
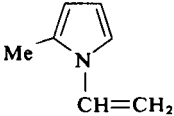
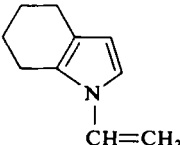
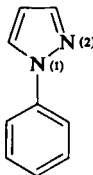
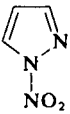
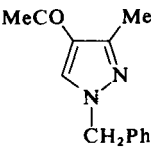
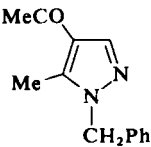
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	neat 2 M in acetone	+206.4 +205.6	(a) (a)
	neat 2 M in acetone	+208.5 +207.5	(a) (a)
	neat 2 M in acetone	+216.9 +212.9	(a) (a)
	2.4 M in benzene-d ₆ (37% w/w)	+160.1 (N1) +75.3 (N2)	(b) (b)
	in DMSO in CDCl ₃	+108.5 (N1) +84.6 (N2) +56.9 (NO ₂) +109.1 (N1) +86.1 (N2) +59.0 (NO ₂)	(c) (c) (c) (c) (c) (c)
	in DMSO in CDCl ₃	+168.9 (N1) +72.9 (N2) +173.1 (N1) +75.7 (N2)	(c) (c) (c) (c)
	in DMSO-d ₆ in CDCl ₃	+163.2 (N1) +75.5 (N2) +167.0 (N1) +91.4 (N2)	(c) (c) (c) (c)

TABLE 86—*cont.*

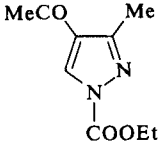
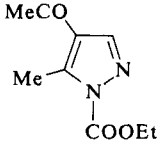
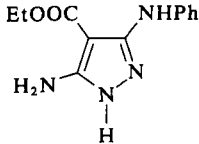
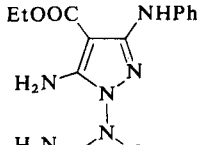
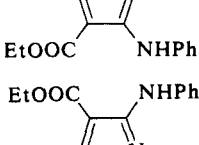
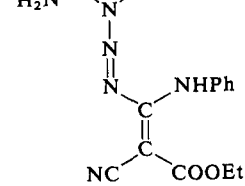
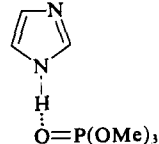
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	in DMSO-d ₆	+166.7 (N1)	(c)
	in CDCl ₃	+78.9 (N2)	(c)
		+167.9 (N1)	(c)
		+83.2 (N2)	(c)
	in DMSO-d ₆	+159.2 (N1)	(c)
	in CDCl ₃	+76.0 (N2)	(c)
		+159.9 (N1)	(c)
		+80.6 (N2)	(c)
	in DMSO	+218.7 (N1)	(d)
		+145.6 (N2)	(d)
	in DMSO	+211.5 (N1)	(d)
		+137.1 (N2)	(d)
	in CDCl ₃	+144.0 (N1)	(d)
		+154.5 (N2)	(d)
			
	neat	+214	(e)

TABLE 86—*cont.*

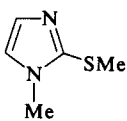
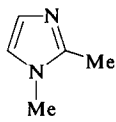
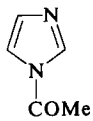
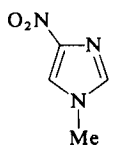
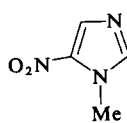
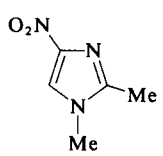
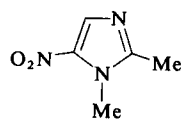
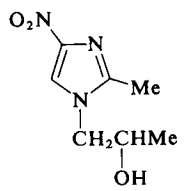
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	0.5 M in DMSO	+222.8 (N1) +121.3 (N3)	(f) (f)
	in DMSO-d ₆	+223.2 (N1) +121.5 (N3)	(c) (c)
	in CDCl ₃	+255.0 (N1) +127.3 (N3)	(c) (c)
	in DMSO-d ₆	+170.0 (N1) +110.3 (N3)	(c) (c)
	in CDCl ₃	+171.9 (N1) +113.9 (N3)	(c) (c)
	in DMSO	+208.5 (N1) +127.7 (N3) +18.0 (NO ₂)	(c) (c) (c)
	in DMSO	+219.4 (N1) ? (N3) +25 (NO ₂)	(c) (c) (c)
	in CDCl ₃	+222.3 (N1) ? (N3) +26 (NO ₂)	(c) (c) (c)
	in DMSO-d ₆	+210.3 (N1) +130.2 (N3)	(c) (c)
	in DMSO-d ₆	+224.1 (N1) +121.0 (N3)	(c) (c)
	in DMSO-d ₆	+203.3 (N1) +132.0 (N3)	(c) (c)

TABLE 86—*cont.*

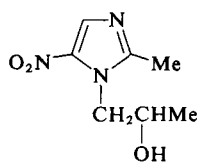
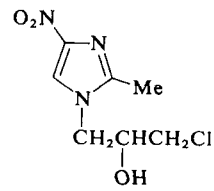
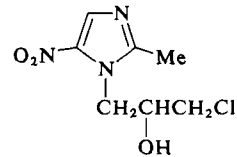
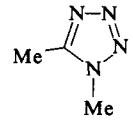
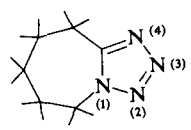
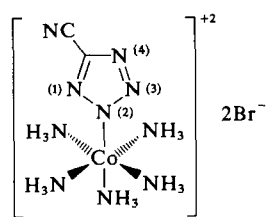
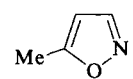
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	in DMSO-d ₆	+216.4 (N1) +120.5 (N3)	(c) (c)
	in DMSO-d ₆	+205.7 (N1) +131.7 (N3)	(c) (c)
	in DMSO-d ₆	+218.7 (N1) +120.4 (N3)	(c) (c)
	0.5 m in DMSO	+153.6 (N1) +9.5 (N2) -9.2 (N3) +52.6 (N4)	(g) (g) (g) (g)
	0.5 M in DMSO	+139.9 (N1) +8.5 (N2) -8.0 (N3) +57.4 (N4)	(g) (g) (g) (g)
	0.3 M in DMSO	+50.6 (N1) +81.7 (N2) -17.1 (N3) +33.5 (N4) +113.2 (CN) +423.7 (NH ₃ axial) +416.4 (NH ₃ equat.)	(h) (h) (h) (h) (h) (h) (h)
	in DMSO-d ₆ in CDCl ₃	-0.1 +2.4	(c) (c)

TABLE 86—*cont.*

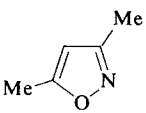
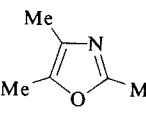
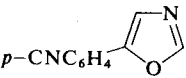
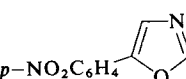
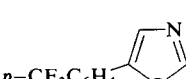
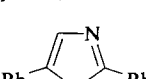
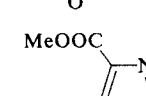
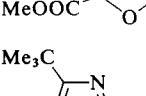
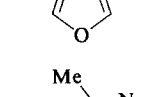
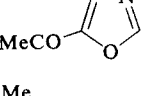
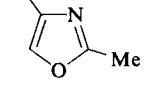
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	in DMSO-d ₆ in CDCl ₃	+9.2 +12.0	(c) (c)
	in DMSO-d ₆ in CDCl ₃ in CF ₃ CO ₂ H	+121.9 +126.2 +194.9	(c) (c) (c)
	in DMSO-d ₆	+118.9 +122.0 (CN)	(c) (c)
	in DMSO-d ₆	+117.7	(c)
	in DMSO-d ₆	+118.4	(c)
	in DMSO-d ₆	+122.0	(c)
	in DMSO-d ₆ in CDCl ₃	+119.2 +119.6	(c) (c)
	neat	+117 ± 5	(i)
	neat	+100 ± 10	(i)
	50% in CCl ₄	+117 ± 1.5	(i)
	neat	+128 ± 5	(i)

TABLE 86—*cont.*

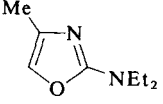
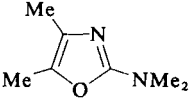
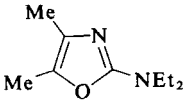
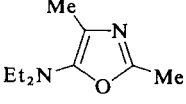
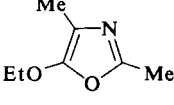
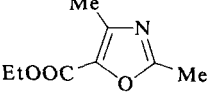
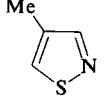
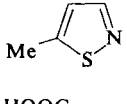
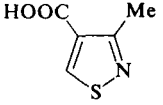
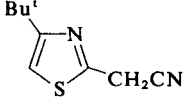
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	neat	+177 ± 5 +300 ± 15 (NEt ₂)	(i) (i)
	neat	+175 ± 5 +312 ± 15 (NEt ₂)	(i) (i)
	neat	+172 ± 5 +359 ± 15 (NEt ₂)	(i) (i)
	neat	+122 ± 5 +348 (NEt ₂)	(i) (i)
	neat	+117 ± 5	(i)
	neat	+100 ± 10	(i)
	in DMSO-d ₆ in CDCl ₃	+81.8 +87.0	(c) (c)
	in DMSO-d ₆ in CDCl ₃	+86.6 +90.6	(c) (c)
	in DMSO-d ₆	+89.6	(c)
	in DMSO-d ₆	+55.9	(c)

TABLE 86—*cont.*

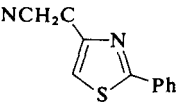
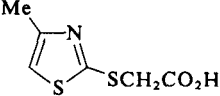
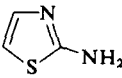
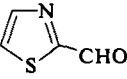
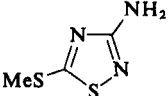
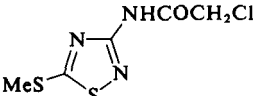
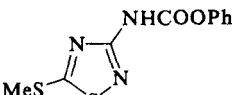
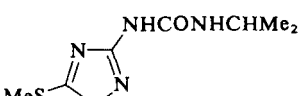
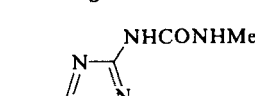
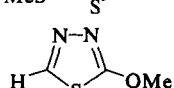
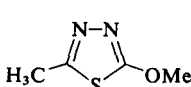
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	in DMSO-d ₆ in CDCl ₃	+66.4 +76.8	(c) (c)
	in DMSO-d ₆	+63.9	(c)
	in DMSO-d ₆	+129.9 +309.6 (NH ₂)	(c) (c)
	in acetone in acetone (90% v/v)	+38.1 +38.1	(c) (j)
	in DMSO-d ₆	+190.4 (N2) +310.3 (NH ₂)	(k) (k)
	in DMSO-d ₆	+244.8 (NH)	(k)
	in DMSO-d ₆	+267.8 (NH)	(k)
	in DMSO-d ₆	+262.2 (NHCO)	(k)
	in DMSO-d ₆	+174.3 (N2) +262.0 (NHCO) +300.5 (NHMe)	(k) (k) (k)
	in DMSO	+69.8 (N3) +18.0 (N4)	(l) (l)
	in DMSO in CDCl ₃	+69.7 (N3) +27.5 (N4) +72.8 (N3) +30.6 (N4)	(l) (l) (l) (l)

TABLE 86—*cont.*

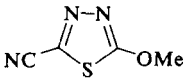
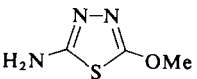
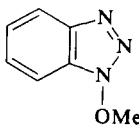
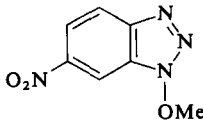
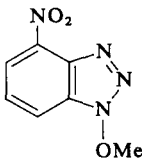
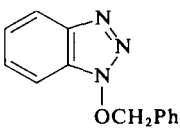
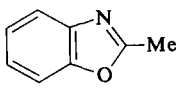
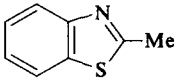
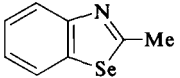
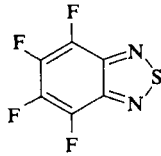
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	in DMSO	+64.7 (N3) +8.2 (N4)? +110.7 (CN)	(l) (l) (l)
	in DMSO	+81.1 (N3) +96.2 (N4) +318.8 (NH ₂)	(l) (l) (l)
	in MeOH	+116.7 (N1) +20.2 (N2) +63.2 (N3)	(m) (m) (m)
	in HCONH ₂ in acetone	+53.3 (N3) +116.1 (N1) +16.8 (N2)	(m) (m) (m)
	in DMSO	+52.9 (N3) +112.3 (N1) +14.7 (N2) +50.9 (N3)	(m) (m) (m) (m)
	in DMSO	+108.6 (N1) +11.8 (N2) +50.1 (N3) +1.9 (NO ₂)	(m) (m) (m) (m)
	in DMSO	+108.2 (N1) +7.4 (N2) +53.1 (N3) +13.1 (NO ₂)	(m) (m) (m) (m)
	0.5 M in DMSO	+115.6 (N1) +13.2 (N2) +50.1 (N3)	(n) (n) (n)
	in DMSO	+138.1	(g)
	in DMSO	+71.0	(g)
	in DMSO	+61.5	(g)

TABLE 86—*cont.*

Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	satd. in CH_2Cl_2	+60.1	(o)

(a) Data from ref. 37; ^{14}N CW spectra, 4.3342 MHz, referred originally to neat nitromethane, high-precision differential saturation technique with full lineshape fitting, concentric spherical sample/standard containers in order to eliminate bulk-susceptibility effects.

(b) Data from ref. 91; ^{15}N -labelled 1-phenyl[$^{15}\text{N}_2$]pyrazole, ^{15}N spectra, 10.14 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk susceptibility effects.

(c) Data from ref. 120; ^{15}N natural abundance spectra, 10.1 and 20.3 MHz field perpendicular and parallel respectively to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; since resonance frequencies were not specified for individual compounds, uncertainty in the shieldings can reach 1–2 ppm; $\text{Cr}(\text{acac})_3$ added as relaxation reagent.

(d) Data from ref. 330; ^{15}N -labelled compounds, ^{15}N spectra, 20.3 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(e) Data from ref. 329; ^{15}N natural abundance spectra, field not specified, originally referred to 0.1 M nitromethane in CDCl_3 , +3.8 ppm from neat nitromethane (Table 6), uncorrected for bulk-susceptibility effects.

(f) Data from ref. 248; ^{15}N natural abundance spectra, 18.28 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects, $\text{Cr}(\text{acac})_3$ added as relaxation reagent.

(g) Data from ref. 26; ^{15}N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO_3 in D_2O , +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4), $\text{Cr}(\text{acac})_3$ added as relaxation reagent.

(h) Data from ref. 333; details as in note (g).

(i) Data from ref. 613; ^{14}N spectra, 6.5 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(j) Data from ref. 445; ^{15}N natural abundance spectra, 10.14 MHz field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(k) Data from ref. 331; ^{15}N -labelled compounds, ^{15}N spectra, 9.12 and 20.28 MHz, field perpendicular and parallel respectively to sample tube, originally referred to 1 M HNO_3 in D_2O , +4.4 ppm from neat nitromethane (Table 6), uncorrected for bulk-susceptibility effects; since resonance frequencies were not specified for individual compounds, uncertainty in the shielding can reach 1–2 ppm.

(l) Data from ref. 255; ^{15}N natural abundance spectra, 40.55 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; using solutions of 1 g material in 3 ml of solvent.

(m) Data from ref. 253; details as in note (f).

(n) Data from ref. 252; details as in note (f).

(o) Data from ref. 624; ^{15}N -labelled compound, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to liquid NH_3 , +380.2 ppm uncorrected for bulk-susceptibility effects.

TABLE 87

Nitrogen shieldings in some tautomeric systems of azoles and their derivatives

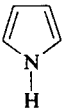
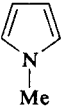
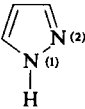
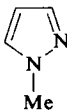
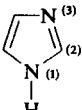
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	in CDCl ₃ in DMSO	+232.7 +224.6	(a) (a)
	in CDCl ₃ in DMSO 0.5 M in DMSO	+230.9 +230.2 +230.1	(a) (a) (b)
	in CDCl ₃ in CDCl ₃ in DMSO in CF ₃ CO ₂ H	+132.2 +134.0 +173.1 (N1) +79.8 (N2) +188.2	(a) (c) (c) (c) (c)
	in CDCl ₃ in CDCl ₃	+179.3 (N1) +73.7 (N2) +180.8 (N1) +76.5 (N2)	(a) (a) (c) (c)
	in CDCl ₃ in DMSO-d ₆ in CF ₃ CO ₂ H in HCl + DCl(2:1)	+133.4 (N1) +138.3 (N2) +133.4 (N1) +141.9 (N2) +195.6 (N1) +192.5 (N2) +190.4 (N1) +186.3 (N2)	(c) (c) (c) (c) (c) (c) (c) (c)
	in CDCl ₃ in CDCl ₃ in DMSO in DMSO	+170.7 +172.4 +167.6 +169.0	(a) (c) (a) (c)

TABLE 87—*cont.*

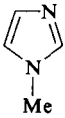
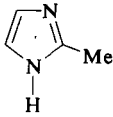
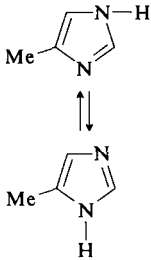
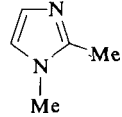
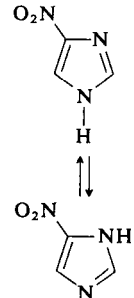
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	in CDCl ₃	+219.5 (N1)	(a)
		+124.3 (N3)	(a)
	in CDCl ₃	+221.7 (N1)	(c)
		+124.1 (N3)	(c)
	in DMSO	+218.0 (N1)	(a)
		+119.5 (N3)	(a)
	in DMSO	+219.2 (N1)	(c)
		+119.1 (N3)	(c)
	0.5 M in DMSO	+218.5 (N1)	(b)
		+118.1 (N3)	(b)
	in DMSO-d ₆	+171.6	(c)
	in CDCl ₃	+174.2	(c)
	in DMSO-d ₆	+172.8 (N1)	(c)
		+163.9 (N3)	(c)
	in CDCl ₃	+172.8 (N1)	(c)
		+167.0 (N3)	(c)
	in CF ₃ CO ₂ H	+213.2 (N1)	(c)
		+209.0 (N3)	(c)
	in DMSO-d ₆	+223.2 (N1)	(c)
		+121.5 (N3)	(c)
	in CDCl ₃	+225.0 (N1)	(c)
		+127.3 (N3)	(c)
	in DMSO/acetone (3 : 1 v/v)	+205.6 (N1)	(c)
		+128.9 (N3)	(c)
		+17.4 (NO ₂)	(c)

TABLE 87—*cont.*

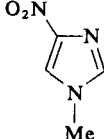
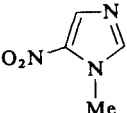
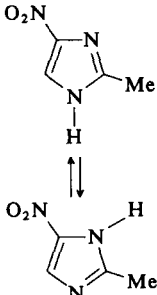
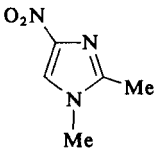
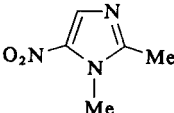
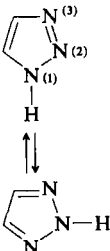
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	in DMSO	+208.5 (N1) +127.7 (N3) +18.0 (NO ₂)	(c) (c) (c)
	in CDCl ₃	+222.3 (N1) ? (N3)	(c) (c)
	in DMSO-d ₆	+26 (NO ₂) +219.4 (N1) ? (N3) +25 (NO ₂)	(c) (c) (c) (c)
	in DMSO-d ₆	+205.8 (N1) +133.2 (N3) +17.0 (NO ₂)	(c) (c) (c)
	in DMSO-d ₆	+210.3 (N1) +130.2 (N3)	(c) (c)
	in DMSO-d ₆	+224.1 (N1) +121.0 (N3)	(c) (c)
	in CDCl ₃	+79.0 (N1, 3) +61.9 (N2)	(a) (a)
	in DMSO	+69.0 (N1, 3) +75.9 (N2)	(a) (a)
	0.5 M in DMSO	+68.8 (N1, 3) (broadened) +77.8 (N2) (broadened)	(c) (c)

TABLE 87—*cont.*

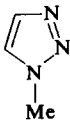
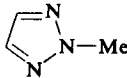
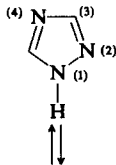
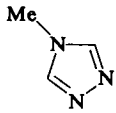
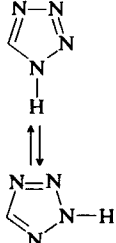
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	in CDCl ₃	+145.0 (N1) +16.3 (N2) +30.7 (N3)	(a) (a) (a)
	in DMSO	+143.0 (N1) +16.2 (N2) +29.2 (N3)	(a) (a) (a)
	0.25 M in DMSO	+143.3 (N1) +16.2 (N2) +28.4 (N3)	(b) (b) (b)
	in CDCl ₃	+51.1 (N1, 3) +132.8 (N2)	(a) (a)
	in DMSO	+50.1 (N1, 3) +134.4 (N2)	(a) (a)
	in DMSO	+44.0 (N1, 3) +135.0 (N2)	(b) (b)
	in DMSO	+127.4 (N1, 2) +134.7 (N4)	(a) (a)
	in DMSO	+171.3 (N1) +82.2 (N2) +129.1 (N4)	(a) (a) (a)
	0.5 M in DMSO	+171.3 (N1) +81.9 (N2) +127.4 (N4)	(b) (b) (b)
	in DMSO	+60.3 (N1, 2) +217.1 (N4)	(a) (a)
	0.25 M in DMSO	+59.8 (N1, 2) +217.8 (N4)	(b) (b)
	in DMSO	+98.7 (N1, 4) +5.8 (N2, 3)	(a) (a)
	0.5 M in DMSO	+98.3 (N1, 4) +5.8 (N2, 3)	(d) (d)
	0.5 M in DMSO	+98.6 (N1, 4)	(d)
	+2.5 M H ₂ O	+6.0 (N2, 3)	(d)
	0.5 M in DMSO	+67.0	(d)
	+2.5 M H ₂ O	(broadened)	
	+0.5 M NaOH	-3.0 (N2, 3)	(d)

TABLE 87—*cont.*

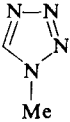
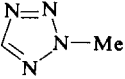
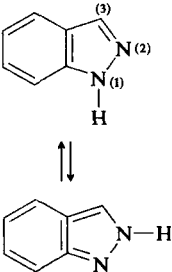
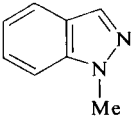
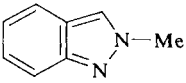
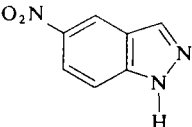
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	in DMSO	+151.4 (N1)	(a)
		+10.8 (N2)	(a)
		-12.3 (N3)	(a)
		+50.2 (N4)	(a)
	0.5 M in DMSO	+151.1 (N1)	(b)
		+10.8 (N2)	(b)
		-12.7 (N3)	(b)
	in DMSO	+73.2 (N1)	(a)
		+102.2 (N2)	(a)
		+0.9 (N3)	(a)
		+47.1 (N4)	(a)
	0.5 M in DMSO	+72.8 (N1)	(b)
		+101.8 (N2)	(b)
		+0.8 (N3)	(b)
	0.5 M in DMSO	+194.4 (N1)	(e)
		+65.6 (N2)	(e)
	0.5 M in DMSO	+196.3 (N1)	(f)
		+66.1 (N2)	(f)
	0.5 M in acetone	+200.6 (N1)	(f)
		+65.1 (N2)	(f)
	0.5 M in DMSO	+202.8 (N1)	(e)
		+56.6 (N2)	(e)
	0.4 M in DMSO	+203.8 (N1)	(b)
	0.5 M in DMSO	+91.2 (N1)	(e)
		+161.0 (N2)	(e)
	0.5 M in DMSO	+92.3 (N1)	(b)
		+162.1 (N2)	(b)
	satd. in DMSO	+56.1 (N2)	(e)

TABLE 87—*cont.*

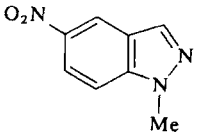
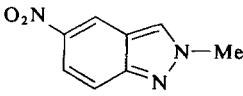
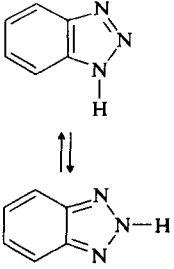
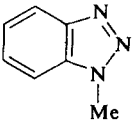
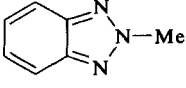
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	satd. in DMSO	+47.9 (N2)	(e)
	satd. in DMSO	+151.0 (N2)	(e)
	0.5 M in DMSO	+96.7 (N1, 3) +7.9 (N2)	(f) (f)
	0.5 M in MeOH	+108.7 (N1, 3) +14.5 (N2)	(f) (f)
	0.5 M in acetone	+102.0 (N1, 3) +10.3 (N2)	(f) (f)
	in DMSO	+96.7 (N1, 3) +7.5 (N2)	(a) (a)
	in CDCl ₃	+103.4 (N1, 3) +11.6 (N2)	(a) (a)
	in CDCl ₃	+164.1 (N1) +2.2 (N2)	(a) (a)
	in DMSO	+42.4 (N3) +161.8 (N1) +0.9 (N2) +40.8 (N3)	(a) (a) (a) (a)
	0.5 M in DMSO	+161.5 (N1) +1.1 (N2) +41.0 (N3)	(b) (b) (b)
	in CDCl ₃	+63.1 (N1, 3) +119.2 (N2)	(a) (a)
	in DMSO	+62.5 (N1, 3) +117.0 (N2)	(a) (a)
	0.5 M in DMSO	+62.6 (N1, 3) +116.8 (N2)	(b) (b)

TABLE 87—*cont.*

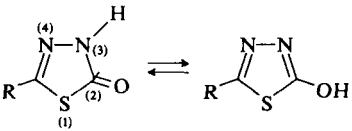
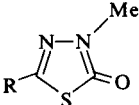
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
			
R			
H	in DMSO	+190.0 (N3) +65.0 (N4)	(g) (g)
CH ₃	in DMSO	+192.7 (N3) +75.9 (N4)	(g) (g)
CH ₃	in CDCl ₃	+196.4 (N3) +80.2 (N4)	(g) (g)
CN	in DMSO	+179.9 (N3) +40.8 (N4)	(g) (g)
NH ₂	in DMSO	+113.8 (CN) +209.3 (N3) +139.2 (N4)	(g) (g) (g)
OMe	in DMSO	+317.8 (NH ₂) +209.3 (N3) +128.0 (N4)	(g) (g) (g)
			
R			
H	in DMSO	+195.5 (N3) +56.8 (N4)	(g) (g)
Me	in DMSO	+199.0 (N3) +67.3 (N4)	(g) (g)
Me	in CDCl ₃	+199.8 (N3) +68.5 (N4)	(g) (g)
CN	in DMSO	+185.8 (N3) +35.2 (N4)	(g) (g)
NH ₂	in DMSO	+112.6 (CN) +216.0 (N3) +129.6 (N4)	(g) (g) (g)
OMe	in DMSO	+316.9 (NH ₂) +215.5 (N3) +118.2 (N4)	(g) (g) (g)

TABLE 87—*cont.*

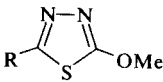
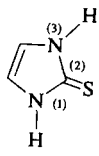
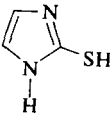
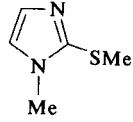
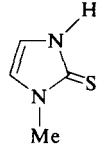
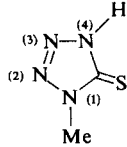
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
 R			
H	in DMSO	+69.8 (N3) +18.0 (N4)	(g) (g)
Me	in DMSO	+69.7 (N3) +27.5 (N4)	(g) (g)
Me	in CDCl_3	+72.8 (N3) +30.6 (N4)	(g) (g)
CN	in DMSO	+64.7 (N3) -8.2 (N4)? +110.7 (CN)	(g) (g) (g)
NH_2	in DMSO	+81.1 (N3) +96.2 (N4) +318.8 (NH_2)	(g) (g) (g)
 	0.544 M in DMSO	+213.1 (broadened)	(d)
	0.5 M in DMSO	+222.8 (N1) +121.3 (N3)	(d) (d)
	0.5 M in DMSO	+219.5 (N1) +214.3 (N3) (broadened)	(d) (d)
	0.5 M in DMSO	+151.9 (N1) +25.4 (N2) +17.4 (N3) +145.7 (N4) (broadened)	(d) (d) (d) (d)

TABLE 87—*cont.*

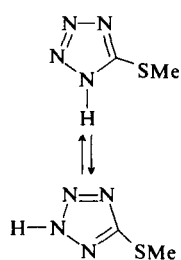
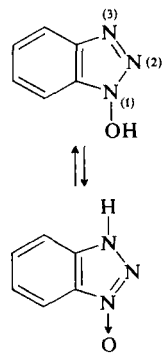
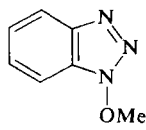
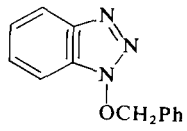
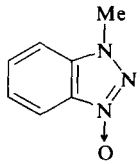
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	0.5 M in DMSO	+100.5 (N1, 4) (broadened)	(d)
		+4.5 (N2, 3) (broadened)	(d)
	0.5 M in MeOH	+120.3 (N1) +27.1 (N2) +100.9 (N3)	(f) (f) (f)
	0.5 M in HCONH ₂	+81.0 (N3)	(f)
	0.5 M in acetone	+127.0 (N1) +18.3 (N2) +70.5 (N3)	(f) (f) (f)
	0.5 M in DMSO	+123.7 (N1) +14.4 (N2) +60.3 (N3)	(f) (f) (f)
	0.5 M in MeOH	+116.7 (N1) +20.2 (N2) +63.2 (N3)	(f) (f) (f)
	0.5 M in HCONH ₂	+53.3 (N3)	(f)
	0.5 M acetone	+116.1 (N1) +16.8 (N2) +52.9 (N3)	(f) (f) (f)
	0.5 M in DMSO	+112.3 (N1) +14.7 (N2) +50.9 (N3)	(f) (f) (f)
	0.5 M in DMSO	+115.6 (N1) +13.2 (N2) +50.1 (N3)	(h) (h) (h)
	0.5 M in MeOH	+88.6 (N1) +47.5 (N2) +205.7 (N3)	(f) (f) (f)
	0.5 M in HCONH ₂	+204.4 (N3)	(f)
	0.5 M in acetone	+76.9 (N1) +48.0 (N2) +215.5 (N3)	(f) (f) (f)

TABLE 87—*cont.*

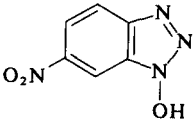
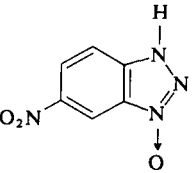
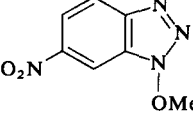
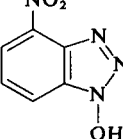
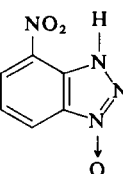
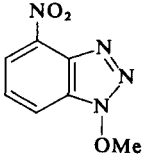
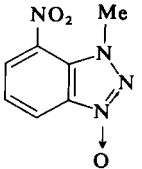
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	0.5 M in DMSO	+74.8 (N1) +44.7 (N2) +208.0 (N3)	(f) (f) (f)
 	0.5 M in DMSO	+118.4 (N1) +11.4 (N2) +58.7 (N3) +1.4 (NO ₂)	(f) (f) (f) (f)
	0.5 M in DMSO	+108.6 (N1) +11.8 (N2) +50.1 (N3) +1.9 (NO ₂)	(f) (f) (f) (f)
	0.5 M in DMSO	+71.1 (N1) +37.9 (N2) +205.2 (N3) +12.6 (NO ₂)	(f) (f) (f) (f)
 	0.5 M in DMSO	+116.0 (N1) +12.0 (N2) +78.2 (N3) +14.0 (NO ₂)	(f) (f) (f) (f)

TABLE 87—*cont.*

Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	0.5 M in DMSO	+108.2 (N1)	(f)
		+7.4 (N2)	(f)
		+53.1 (N3)	(f)
		+13.1 (NO ₂)	(f)
	0.5 M in DMSO	+74.8 (N1)	(f)
		+40.2 (N2)	(f)
		+208.1 (N3)	(f)
		+15.6 (NO ₂)	(f)

(a) Data from ref. 249; ¹⁵N natural abundance spectra, 8.059 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk susceptibility effects; using solutions of 750 mg of the azole dissolved in 2 ml of solvent.

(b) Data from ref. 26; ¹⁵N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO₃ in D₂O, +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4), Cr(acac)₃ added as relaxation reagent.

(c) Data from ref. 120; ¹⁵N natural abundance spectra, 10.1 and 20.3 MHz, field perpendicular and parallel respectively to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; since resonance frequencies were not specified for individual compounds, uncertainty in the shieldings can reach 1–2 ppm; Cr(acac)₃ added as relaxation reagent.

(d) Data from ref. 248; ¹⁵N natural abundance spectra, 18.28 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; Cr(acac)₃ added as relaxation reagent.

(e) Data from ref. 236; selectively ¹⁵N-labelled compounds, ¹⁵N spectra, 8.108 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(f) Data from ref. 253; details as in note (d).

(g) Data from ref. 255; ¹⁵N natural abundance spectra, 40.55 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; using solutions of 1 g material in 3 ml of solvent.

(g) Data from ref. 252; details as in note (d).

TABLE 88

Protonation equilibria of some substituted imidazoles

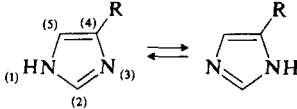
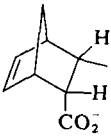
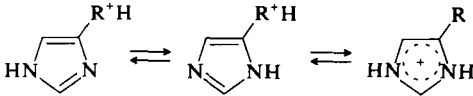
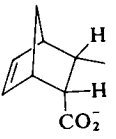
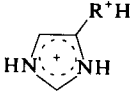
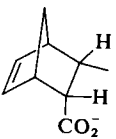
Compound	Solvent	Nitrogen shielding referred to neat nitromethane
		
R		
—CH ₂ CH ₂ NH ₂ (histamine)	H ₂ O	+187.2 (N1) +164.6 (N3)
—CH ₂ CH ₂ CO ₂ [−]	H ₂ O	+186.7 (N1) +166.7 (N3)
—CH ₂ CO ₂ [−]	H ₂ O	+189.6 (N1) +163.7 (N3)
—CH=CHCO ₂ [−] (cis)	H ₂ O	+148.6 (N1) +201.7 (N3)
—CH=CHCO ₂ [−] (trans)	H ₂ O	+195.6 (N1) +159.7 (N3)
	H ₂ O	+168.3 (N1) +186.2 (N3)
(endo-cis)		
		
R		
—CH ₂ CH ₂ NH ₂	H ₂ O	+200.9 (N1) +152.2 (N3)
—CH ₂ CH ₂ CO ₂ [−]	H ₂ O	+204.5 (N1) +208.2 (N3)
—CH ₂ CO ₂ [−]	H ₂ O	+209.8 (N1) +205.6 (N3)
—CH=CHCO ₂ [−] (cis)	H ₂ O	+208.2 (N1) +198.8 (N3)
—CH=CHCO ₂ [−] (trans)	H ₂ O	+205.8 (N1) +202.6 (N3)

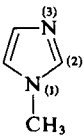
TABLE 88—*cont.*

Compound	Solvent	Nitrogen shielding referred to neat nitromethane
 (endo-cis)	H ₂ O	+209.9 (N1) +205.4 (N3)
 R		
—CH ₂ CH ₂ NH ₂	H ₂ O	+208.4 (N1) +187.2 (N3)
—CH ₂ CH ₂ CO ₂ [−]	H ₂ O	+209.4 (N1) +206.5 (N3)
—CH ₂ CO ₂ [−]	H ₂ O	+209.4 (N1) +206.2 (N3)
—CH=CHCO ₂ [−] (cis)	H ₂ O	+207.0 (N1) +206.7 (N3)
—CH=CHCO ₂ [−] (trans)	H ₂ O	+211.4 (N1) +195.6 (N3)
 (endo-cis)	H ₂ O	+210.3 (N1) +207.2 (N3)

Data from ref. 251; ¹⁵N natural abundance spectra, 18.25 MHz, field parallel to sample tube; originally referred to 1 M HNO₃ in D₂O, +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

TABLE 89

Nitrogen shieldings in some 1-methylimidazole complexes with zinc(II) and cadmium(II) in aqueous solution^a



N—Me imidazole

concentration (M)

Total HNO₃ concentration (M)

Total Zn(NO₃)₂ concentration (M)

pH ±0.05

Nitrogen shielding referred to neat nitromethane

N1

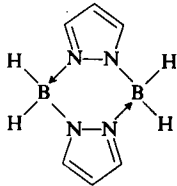
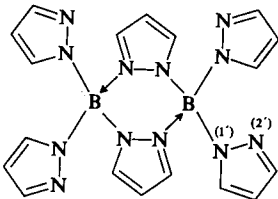
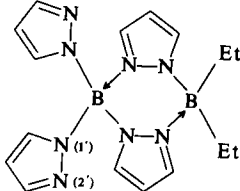
N3

0.0787	0.0501	0.0498	5.66	+211.6	+193.7
0.1121	0.0501	0.0495	5.90	+212.3	+186.8
0.1334	0.0500	0.0495	6.09	+212.4	+184.5
0.1649	0.0497	0.0494	6.22	+212.5	+182.6
0.2188	0.0496	0.0492	6.51	+212.5	+180.7
0.2489	0.0493	0.0492	6.70	+212.5	+179.3
0.3220	0.0491	0.0488	7.25	+213.3	+171.7
0.3544	0.0490	0.0488	7.34	+213.6	+168.5
Total Cd(NO ₃) ₂ concentration (M)					
0.0768	0.0503	0.0493	5.62	+211.6	+193.0
0.1299	0.0499	0.0492	6.29	+213.0	+179.1
0.1565	0.0499	0.0490	6.60	+213.6	+173.3
0.2391	0.0495	0.0486	7.14	+214.6	+163.4
0.3997	0.0487	0.0481	7.61	+215.6	+153.1

(a) Data from ref. 403, doubly ¹⁵N-labelled 1-methylimidazole, ¹⁵N labelled spectra, 10.158 MHz, field perpendicular to sample tube, referred originally to 1-methylimidazole (in H₂O, pH > 10) N1 + 217.7 ppm and N3 + 134.7 ppm from neat nitromethane.

TABLE 90

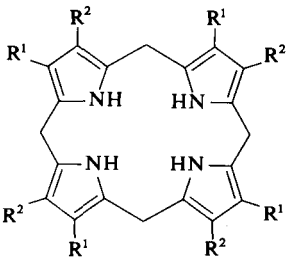
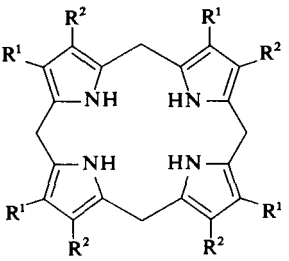
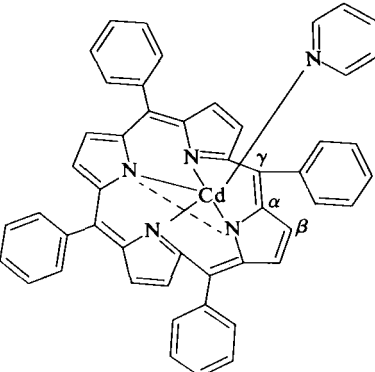
Nitrogen shieldings in some pyrazole derivatives of boron

Compound	Solvent	Nitrogen shielding referred to neat nitromethane
	CDCl ₃	+158.2
	CDCl ₃	+162.2 (bridging -N1') +77.8 (N2')
	CDCl ₃	+153.2 (bridging +N1') +77.5 (N2')

Data from ref. 653; ¹⁵N natural abundance spectra, 20.28 MHz, field parallel to sample tube, originally referred to liquid ammonia, +380.2 ppm from neat nitromethane (Table 6) conversion scheme IV (Table 4).

TABLE 91

Nitrogen shieldings in porphyrin ring systems

Structure	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	in H ₂ O	+225.9	(a)
 (uroporphyrinogen) $R^1 = \text{CH}_2\text{COOH}$ $R^2 = \text{CH}_2\text{CH}_2\text{COOH}$	in H ₂ O	+226.6 +226.8	(a) (a)
	in CDCl ₃	+170.9	(b)

(*meso*-tetraphenylporphyrin pyridine adduct 1:1)

(a) Data from ref. 654; ¹⁵N natural abundance spectra, 20.3 MHz, field parallel to sample tube, originally referred to liquid NH₃, +380.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(b) Data from ref. 401; ¹⁵N natural abundance spectra, 40.55 MHz, field parallel to sample tube, referred originally to neat nitromethane, uncorrected for bulk susceptibility effects.

TABLE 92

Nitrogen shieldings in some sydnones, sydnonimines and related structures

Structure	Solution	Nitrogen shielding referred to neat nitromethane	Notes
(sydnone) R			
Me	neat	+107.5 (N3)	(a)
	in acetone	+107.8 (N3)	(b)
		+34.7 (N2)	(b)
	in acetone	+112.5 (N3)	(c)
		+36.2 (N2)	(c)
Et	in acetone	+99.1 (N3)	(c)
		+36.9 (N2)	(c)
Pr ⁱ	in acetone	+85.7 (N3)	(c)
		+35.3 (N2)	(c)
Bu ^t	in acetone	80.0 (N3)	(c)
(protonated sydnone)	Cl ⁻ , in MeOH/D ₂ O (1:1 v/v)	+29.0 (N2)	(d)
(hypothetical sydnonimine) ↓ ↕	in MeOH/D ₂ O (1: v/v)	+154.9 (NMe) -156.4 (NO) +135.9 (CN)	(d) (d) (d)
		+149.7 (NMe) -161.3 (NO) +130.7 (CN)	(d) (d) (d)

TABLE 92—*cont.*

Structure	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	in MeOH/D ₂ O (1:1 v/v)	+150.6 (NMe) -158.0 (NO)	(d) (d)
		+147.1 (NMe) -151.5 (NO)	(d) (d)
	Cl ⁻ , in MeOH	+105.8 (N3) +16.0 (N2) +309.5 (exocyclic)	(c) (c) (c)
(protonated sydnimine)			
	Cl ⁻ , in MeOH/D ₂ O (1:1 v/v)	+104.9 (N3) +15.0 (N2) +309.2 (exocyclic)	(d) (d) (d)
(<i>N</i> -acetylsydnimine)			
R			
Me	in MeOH	+111.2 (N3) +33.6 (N2) +197.5 (exocyclic)	(c) (c) (c)
Et	in acetone	+97.1 (N3) +33.0 (N2) +197.2 (exocyclic)	(c) (c) (c)
Pr ⁱ	in acetone	+85.0 (N3) +31.7 (N2) +196.2 (exocyclic)	(c) (c) (c)
(protonated <i>N</i> -acetylsydnimine)			
Me	Cl ⁻ , in MeOH	+100.4 (N3) +6.5 (N2) +252.2 (exocyclic)	(c) (c) (c)

TABLE 92—*cont.*

Structure	Solution	Nitrogen shielding referred to neat nitromethane	Notes
Et	Cl^- , in MeOH	+88.1 (N3)	(c)
		+6.9 (N2)	(c)
		+252.2 (exocyclic)	(c)
Pr^i	Cl^- , in MeOH	+79.7 (N3)	(c)
		+9.6 (N2)	(c)
		+251.5 (exocyclic)	(c)

(a) Data from ref. 655; ^{14}N PFT spectrum, 6.42 MHz, field perpendicular to sample tube, originally referred to NH_4^+ ion from aqueous NH_4NO_3 , +359.6 ppm from neat nitromethane, corrected for bulk-susceptibility effects.

(b) Data from ref. 656; ^{14}N CW spectrum, 4.3342 MHz, originally referred to neat nitromethane, high-precision differential-saturation technique with full lineshape fitting, concentric spherical sample/standard containers in order to eliminate bulk-susceptibility effects.

(c) Data from ref. 656; ^{15}N natural abundance spectra, 18.24 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk susceptibility; $\text{Cr}(\text{acac})_3$ added as relaxation reagent.

(d) Data from ref. 337; selectively ^{15}N -labelled compounds, ^{15}N spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO_3 in D_2O , +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

TABLE 93

Nitrogen shieldings in some azoloazines with nitrogen atom at ring junction
(indolizine type)

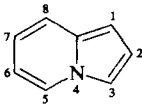
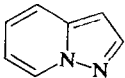
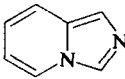
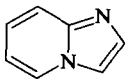
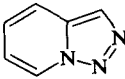
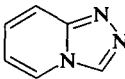
Compound	Solution	Nitrogen atom	Nitrogen shielding referred to neat nitromethane	Notes
	Et ₂ O satd.	4	+191.2	(a)
	acetone	4	+189.8	(b)
	DMSO, 0.5 M	4	+190.1	(b)
	Et ₂ O, 0.5 M	4	+145.5	(a)
	acetone	3	+93.9	(b)
		4	+144.8	(b)
	DMSO, 0.5 M	3	+92.8	(b)
		4	+143.2	(b)
	Et ₂ O, 0.5 M	4	+190.8	(a)
	acetone	2	+109.7	(b)
		4	+189.2	(b)
	DMSO, 0.5 M	2	+107.5	(b)
		4	+185.8	(b)
	Et ₂ O, 0.5 M	1	+135.5	(a)
		4	+181.6	(a)
	acetone	1	+140.0	(b)
		4	+179.4	(b)
	DMSO, 0.5 M	1	+139.6	(b)
		4	+178.6	(b)
	Et ₂ O, 0.5 M	3	+44.8	(a)
		4	+123.8	(a)
	acetone	2	+26.4	(b)
		4	+123.6	(b)
	DMSO, 0.2 M	2	+24.9	(b)
		3	+44.2	(b)
		4	+120.4	(b)
	Et ₂ O, 0.5 M	4	+189.4	(a)
	acetone	1	+89.3	(b)
		2	+55.8	(b)
		4	+187.5	(b)
	DMSO, 0.5 M	1	+80.9	(b)
		2	+49.5	(b)
		4	+183.8	(b)

TABLE 93---*cont.*

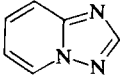
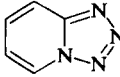
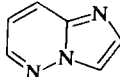
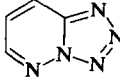
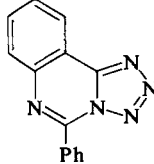
Compound	Solution	Nitrogen atom	Nitrogen shielding referred to neat nitromethane	Notes
	Et ₂ O, 0.5 M	1	+144.6	(a)
		3	+98.0	(a)
		4	+153.9	(a)
	acetone	1	+142.5	(b)
		3	+103.8	(b)
		4	+150.2	(b)
	DMSO, 0.5 M	1	+139.8	(b)
		3	+102.0	(b)
		4	+148.1	(b)
	Et ₂ O, 0.5 M	1	+65.7	(a)
		4	+133.1	(a)
	acetone	1	+70.0	(b)
		2	-17.1	(b)
		3	+34.4	(b)
		4	+131.9	(b)
	DMSO, 0.5 M	1	+67.8	(b)
		2	-18.3	(b)
		3	+31.8	(b)
		4	+128.3	(b)
	DMSO, 0.5 M without Cr(acac) ₃	1	+136.7	(b)
		4	+143.8	(b)
		5	+67.3	(b)
	DMSO, 0.5 M 0.01 M Cr(acac) ₃	1	+136.3	(b)
		4	+143.6	(b)
		5	+66.9	(b)
	DMSO, 0.5 M 0.03 M Cr(acac) ₃	1	+135.7	(b)
		4	+143.0	(b)
		5	+66.3	(b)
	DMSO, 0.2 M	1	+64.2	(b)
		2	-14.5	(b)
		3	+25.6	(b)
		4	+99.9	(b)
		5	+68.9	(b)
	TFA	1	+71.0	(a)
		3	+30.4	(a)

TABLE 93—*cont.*

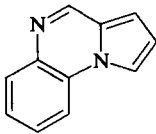
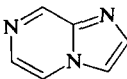
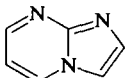
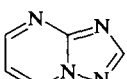
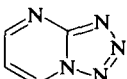
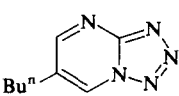
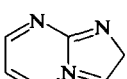
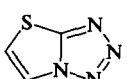
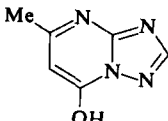
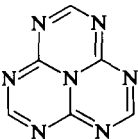
Compound	Solution	Nitrogen atom	Nitrogen shielding referred to neat nitromethane	Notes
	DMSO, 0.5 M	4	+203.8	(b)
		7	+97.4	(b)
	DMSO	1	+140.0	(c)
		4	+185.0	(c)
		7	+98.0	(c)
	DMSO	1	+151.0	(c)
		4	+200.0	(c)
		8	+109.0	(c)
	DMSO	1	+162.0	(c)
		3	+114.0	(c)
		4	+159.0	(c)
		8	+111.0	(c)
	DMSO, 0.25 M	1	+69.6	(b)
		2	-22.3	(b)
		3	+31.7	(b)
		4	+142.2	(b)
		8	+103.8	(b)
	neat	1	+69.0	(d)
		2	-23.3	(d)
		3	+32.0	(d)
		4	+142.4	(d)
		8	+103.4	(d)
	DMSO, 0.05 M	1	+131.0	(d)
		4	+62.0	(d)
		5	-34.0?	(d)
		8	+111.0?	(d)
	DMSO, 0.5 M	1	+73.4	(b)
		2	-29.3	(b)
		3	+28.4	(b)
		4	+114.4	(b)
	DMSO, 0.5 M	1	+109.8	(b)
		3	+164.7	(b)
		4	+251.8	(b)
		8	+154.3	(b)

TABLE 93—*cont.*

Compound	Solution	Nitrogen atom	Nitrogen shielding referred to neat nitromethane	Notes
	DMSO	N terminal	+143.2	(e)
		N central	+195.2	(e)

(a) See ref. 4, p. 192 and references therein.

(b) Data from ref. 24; ^{15}N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO_3 in D_2O , +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4); $\text{Cr}(\text{acac})_3$ added as relaxation reagent.

(c) Data from ref. 325; ^{15}N natural abundance spectra, 20.27 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; $\text{Cr}(\text{acac})_3$ added as relaxation reagent.

(d) Data from ref. 314; ^{15}N natural abundance spectra, 40.55 MHz, field parallel to sample tube, originally referred to NO_3^- in aqueous $^{15}\text{NH}_4^{15}\text{NO}_3$, +4.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

(e) Data from ref. 351; ^{15}N natural abundance spectra, frequency not reported, originally referred to internal HCONMe_2 , +277.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

TABLE 94

Nitrogen shieldings in some azoloazines without nitrogen atom at ring junction

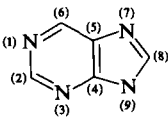
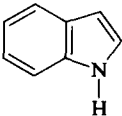
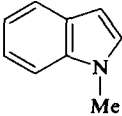
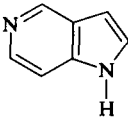
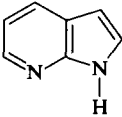
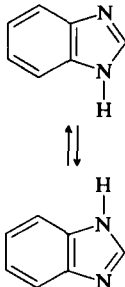
Structure	Solution (TFA = $\text{Cf}_3\text{CO}_2\text{H}$)	 Nitrogen shielding referred to neat nitromethane					Notes
		1-N	3-N	7-N	9-N	other nitrogens	
 (indole)	1.0 M in DMSO 1.0 M in CDCl_3				+249.0 +255.4		(a) (a)
	0.5 M in DMSO				+253.6		(b)
	0.5 M in DMSO	+90.9			+243.0		(c)
	0.5 M in DMSO		+110.2		+261.3		(c)
	0.5 M in DMSO			+190.3	+190.3		(d)

TABLE 94—*cont.*

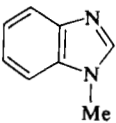
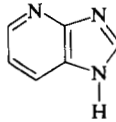
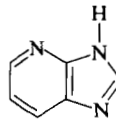
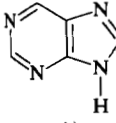
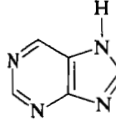
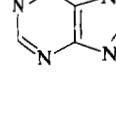
Structure	Solution (TFA = CF ₃ CO ₂ H)	Nitrogen shielding referred to neat nitromethane				other nitrogens	Notes
		1-N	3-N	7-N	9-N		
	0.5 M in DMSO			+136.3	+236.4		(c)
	0.5 M in DMSO			no signal (proton exchange)		+99.4 (N6)	(c)
							
	in 5% NaOH	+127.7	+131.8	+154.7	+157.0		(f)
	in H ₂ O	+115.9	+131.0	+187.8	+191.9		(e)
	in DMSO	+114.6	+130.8	+188.0	+190.8		(f)
		+104.6	+122.2	+173.0	+193.5		(e)
	in DMSO + 0.25 M equiv. of TFA	+103.1	+121.7	+169.4	+195.0		(f)
	in DMSO + 0.5 M equiv. of TFA	+121.1	+122.4	+173.3	+193.0		(e)
	in DMSO + 0.75 M equiv. of TFA	+133.7	+122.5	+173.0	+192.6		(e)
	in DMSO + 1.0 M equiv. of TFA	+141.5	+122.6	+172.9	+192.4		(e)
	in DMSO + 2.0 M equiv. of TFA	+148.8	+122.8	+173.3	+192.3		(e)
	in TFA	+165.1	+123.1	+171.7	+192.8		(e)
	in 20% D ₂ SO ₄	+182.2	+123.4	+194.2	+205.1		(f)
	in 90% D ₂ SO ₄	+192.7	+125.7	+186.2	+183.9		(f)
	in HSO ₃ F	+194.2	+120.2	+221.9	+216.8		(f)
		+195.6	+117.9	+223.6	+218.6		(f)
	in H ₂ O	+114.7	+122.9	+235.6	+149.2		(e)
	in D ₂ O	+114.9	+122.8	+235.7	+149.1		(f)
	in 20% D ₂ SO ₄	+189.7	+119.3	+227.7	+149.8		(f)
	in 90% D ₂ SO ₄	+195.0	+120.1	+220.1	+218.0		(f)
	in DMSO-d ₆	+102.3	+109.4	+237.6	+137.0		(f)
	in TFA	+185.4	+118.6	+226.0	+170.6		(f)

TABLE 94—*cont.*

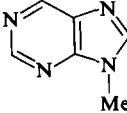
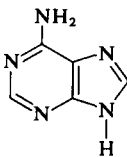
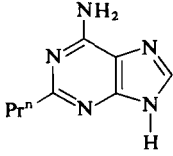
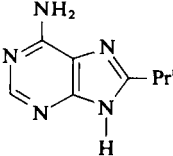
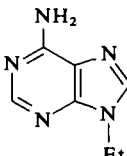
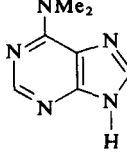
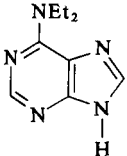
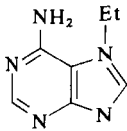
Structure	Solution (TFA = CF ₃ CO ₂ H)	Nitrogen shielding referred to neat nitromethane				other nitrogens	Notes
		1-N	3-N	7-N	9-N		
	in H ₂ O	+115.5	+138.9	+151.2	+230.3		(e)
	in D ₂ O	+117.9	+138.9	+151.5	+230.0		(f)
	in 20% D ₂ SO ₄	+193.4	+133.2	+150.2	+221.4		(f)
	in 90% D ₂ SO ₄	+193.5	+122.3	+223.5	+215.7		(f)
	in DMSO-d ₆	+103.4	+130.0	+140.8	+230.8		(f)
	in TFA	+196.5	+125.7	+166.8	+220.1		(f)
	in DMSO	+146.2	+151.2	+155.2	+212.2	+302.2	(g)
	in DMSO (¹⁵ N-labelled)		+151.1	+154.3	+212.5		(g)
	in H ₂ O						
	(¹⁵ N-labelled)	+157.3	+158.2	+166.8	+209.9	+304.0	(g)
(adenine)							
	in DMSO	+149.7	+156.0	+155.0	+214.4	+304.0	(g)
	in DMSO + 1.0 mM equiv. of TFA	+194.0	+170.5	+153.2	+199.4	+298.2	(g)
	in DMSO	+148.9	+153.1	+158.9	+213.5	+302.3	(g)
	in DMSO	+147.0	+156.4	+142.2	+216.2	+301.1	(g)
	in DMSO + 0.33 M equiv. of TFA	+186.2	+156.4	+141.2	+212.2	+297.2	(g)
	in DMSO + 0.66 M equiv. of TFA	+220.2	+156.5	+141.7	+209.2	+292.2	(g)
	in DMSO + 1.33 M equiv. of TFA	+224.2	+156.4	+139.7	+208.6	+291.7	(g)
	in DMSO	+147.7	+156.3	+138.6	+223.5	+306.5	(g)
	in DMSO + 3.0 M equiv. of TFA	+183.6	+195.8	+163.4	+197.3	+286.3	(g)

TABLE 94—*cont.*

Structure	Solution (TFA = CF ₃ CO ₂ H)	Nitrogen shielding referred to neat nitromethane					Notes
		1-N	3-N	7-N	9-N	other nitrogens	
	in DMSO	+148.8	+156.8	+136.5	+225.0	+277.7	(g)
	in DMSO + 3.0 M equiv. of TFA	+173.7	+196.9	+154.8	+204.9	+258.7	(g)
	in DMSO	+144.8	+138.5	+212.4	+137.6	+303.2	(g)
	in DMSO + 0.14 M equiv. of TFA	+154.1	+153.4	+220.2	+138.8	+300.3	(g)
	in DMSO + 0.27 M equiv. of TFA	+162.8	+155.7	+219.5	+141.9	+296.2	(g)
	in DMSO + 0.7 M equiv. of TFA	+186.2	+168.0	+214.6	+146.4	+284.3	(g)
	in DMSO + 1.52 M equiv. of TFA	+198.4	+168.4	+214.1	+147.5	+282.4	(g)
	in DMSO + 2.7 M equiv. of TFA	+199.7	+167.7	+214.1	+148.6	+282.8	(g)
	in DMSO + 3.1 M equiv. of TFA	+202.4	+167.4	+213.8	+148.8	+283.1	(g)

(a) See ref. 1, Table 112, p. 314.

(b) Data from ref. 26; ¹⁵N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO₃ in D₂O, +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4); Cr(acac)₃ added as relaxation reagent.

(c) Data from ref. 324; ¹⁵N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; Cr(acac)₃ added as relaxation reagent.

(d) Data from ref. 253; ¹⁵N natural abundance spectra, details as in note (c).

(e) Data from ref. 327; ¹⁵N natural abundance spectra, details as in note (b).

(f) Data from ref. 125; ¹⁵N natural abundance spectra, 40.53 MHz details as in note (c).

(g) Data from ref. 328; ¹⁵N natural abundance spectra, details as in note (b).

TABLE 95

Nitrogen shieldings in pyridine, its derivatives and some of its isomeric forms

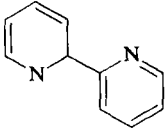
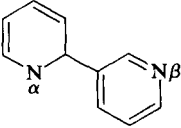
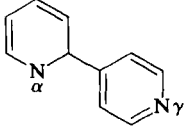
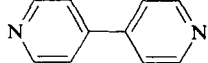
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
	neat, gaseous	+54.6	(a)
	neat liquid	+62.03 ± 0.11	(a)
		+63.5	(a)
		+62.2	(a)
	0.003 mol % in C ₂ Cl ₄	+60.9	(a)
	14.3 mol % in cyclohexane	+59.4	(a)
	14.3 mol % in CCl ₄	+62.1	(a)
	14.3 mol % in benzene	+62.3	(a)
	0.5 M in DMSO	+63.0	(a)
	2 M in DMSO	+63.8	(a)
	14.3 mol % in DMSO	+64.0	(a)
	14.3 mol % in CH ₂ Cl ₂	+66.2	(a)
	14.3 mol % in CHCl ₃	+69.2	(a)
	2 M in CHCl ₃	+70.0	(a)
	14.3 mol % in MeOH	+79.1	(a)
	14.3 mol % in H ₂ O	+82.1	(a)
	0.5 M in H ₂ O		
	(1 mol %)	+84.4	(a)
	2 M in CF ₃ CH ₂ OH	+90.2	(a)
	14.3 mol % in CF ₃ CH ₂ OH	+92.3	(a)
	DMSO	+72.6	(b)
	DMSO	+71.3 (N _α)	(b)
		+63.5 (N _β)	(b)
	DMSO	+70.0 (N _α)	(b)
		+63.2 (N _γ)	(b)
	DMSO	+63.2	(b)

TABLE 95—*cont.*

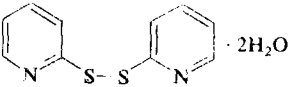
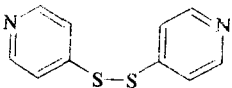
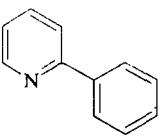
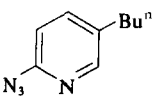
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
 · 2H ₂ O	DMSO	+75.1	(b)
	DMSO	+69.9	(b)
	DMSO	+71.4	(b)
	neat	+111.1	(i)
Substituted pyridines			
2-Me	DMSO	+64.4	(b)
2-F	acetone-d ₆	+105.1	(c)
2-Cl	acetone-d ₆	+71.6	(c)
2-Br	acetone-d ₆	+63.5	(c)
2-CN	acetone-d ₆	+61.8	(c)
2-OMe	acetone-d ₆	+112.0	(c)
2-OSiMe ₃	C ₆ D ₆ (25% v/v)	+101.3	(d)
2-NH ₂	acetone-d ₆	+115.7	(e)
		+311.8 (NH ₂)	(e)
2-NMe ₂	acetone-d ₆	+112.6	(e)
		+323.0 (NMe ₂)	(e)
3-Me	DMSO	+63.5	(b)
3-Cl	acetone-d ₆	+57.1	(c)
3-Br	acetone-d ₆	+56.4	(c)
3-NH ₂	acetone-d ₆	+64.5	(e)
		+328.3 (NH ₂)	(e)
3-NMe ₂	acetone-d ₆	+63.6	(e)
		+340.0 (NMe ₂)	(e)
4-Me	DMSO	+71.8	(b)
	acetone-d ₆	+71.2	(c)
4-COMe	acetone-d ₆	+50.2	(c)
4-NH ₂	acetone-d ₆	+101.5	(e)
		+317.2 (NH ₂)	(e)
4-NMe ₂	acetone-d ₆	+105.6	(e)
		+328.6 (NMe ₂)	(e)

TABLE 95—*cont.*

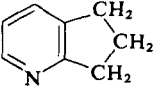
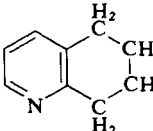
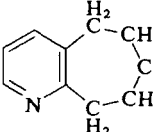
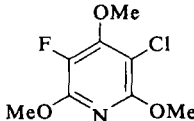
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
	DMSO	+73.9	(b)
	DMSO	+64.1	(b)
	DMSO	+65.7	(b)
2,4-Me ₂	DMSO	+72.5	(b)
2,6-Me ₂	DMSO	+64.9	(b)
2,6-Cl ₂	acetone-d ₆	+79.0	(c)
2,6-Br ₂	acetone-d ₆	+62.1	(c)
2,6-OMe ₂	acetone-d ₆	+145.7	(c)
3,4-Me ₂	DMSO	+70.7	(b)
3,5-Me ₂	DMSO	+63.7	(b)
3,5-Cl ₂	acetone-d ₆	+53.6	(c)
3,5-Br ₂	acetone-d ₆	+52.3	(c)
3,5-Me ₂	acetone-d ₆	+64.4	(c)
	acetone-d ₆	+160.5	(e)
	acetone-d ₆	+165.5	(e)
	acetone-d ₆	+158.3	(e)

TABLE 95—*cont.*

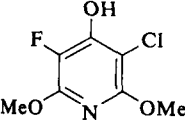
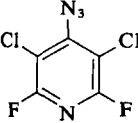
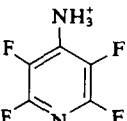
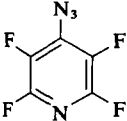
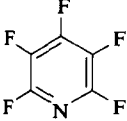
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
	acetone-d ₆	+164.7	(e)
	CDCl ₃	+147.8	(f)
	CDCl ₃	+146.4	(f)
	CDCl ₃	+170.9	(g)
	CDCl ₃	+168.4	(g)
	CDCl ₃	+167.4	(g)
	CDCl ₃	+147.8	(g)
	CDCl ₃	+146.5	(g)

TABLE 95—*cont.*

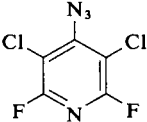
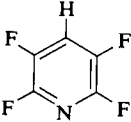
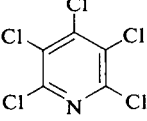
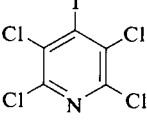
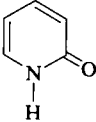
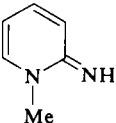
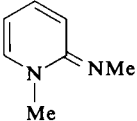
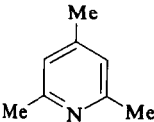
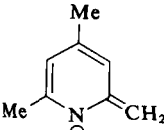
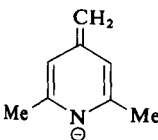
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
	CDCl ₃	+146.0	(g)
	CDCl ₃	+146.4	(g)
	CDCl ₃	+131.0	(g)
	CDCl ₃	+82.5	(g)
	CDCl ₃	+79.4	(g)
	DMSO, satd.	+208.7	(d)
	acetone-d ₆	+242.6 +194.2 (=NH)	(e) (e)
	acetone-d ₆	+239.3 +191.3 (=NMe)	(e) (e)

TABLE 95—*cont.*

Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
	Et ₂ O	+71.3	(h)
	Et ₂ O	+173.9	(h)
	Et ₂ O	+180.7	(h)

(a) See ref. 1, Table 120 and reference therein.

(b) Data from ref. 25; ¹⁵N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO₃ in D₂O, +6.2 ppm from neat nitromethane (Table 6), conversion scheme VI (Table 4); Cr(acac)₃ added as relaxation reagent.

(c) Data from ref. 117; ¹⁵N natural abundance spectra, 10.14 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(d) Data from ref. 350; ¹⁵N abundance spectra, 20.82 MHz, field parallel to sample tube, originally referred to neat HCONH₂, +267.8 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

(e) Data from ref. 348; ¹⁵N natural abundance spectra, 18.24 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(f) Data from ref. 316; ¹⁵N natural abundance spectra, details as in footnote (e).

(g) Data from ref. 657; details as in footnote (e).

(h) Data from ref. 142; ¹⁵N natural abundance, frequency not reported, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(i) Data from ref. 314; ¹⁵N natural abundance spectra, 40.55 MHz field parallel to sample tube, originally referred to NO₃⁻ in aqueous ¹⁵NH₄¹⁵NO₃, +4.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

Table 96

Nitrogen shieldings in pyridine adsorbed on various solid
phases

Sample	Nitrogen shielding (in ppm, referred to neat nitro- methane)	Notes
Pyridine on γ -alumina, physically adsorbed	+69	(a)
physically adsorbed and hydrated	+81	(a)
Lewis acid site I	+115	(a)
Lewis acid site II	+143	(a)
pyridinium ion	+179	(a)
Pyridine on mordenite, physically adsorbed in channels	+89	(a)
Lewis acid	+126	(a)
Bronsted acid (pyridinium ion)	+176	(a)
Pyridine on partially dehydroxylated silica gel, Coverage of statistical monolayers		
3.79	+68.2	(b)
1.30	+77.6	(b)
0.79	+83.8	(b)
0.62	+84.7	(b)
0.41	+86.9	(b)
0.16	+87.4	(b)
0.08	+87.4	(b)
0.04	+87.7	(b)
Pyridine on silica gel, Coverage of statistical monolayers		
0.08	+89.3	(c)
0.16	+89.9	(c)
0.79	+85.7	(c)
1.35	+78.9	(c)

Table 96 (continued)

Pyridine on NaY type zeolites,
Coverage of molecules per large
cavity (NaY) or multiples

2.4	+90.7	(c)
5.6	+89.2	(c)

Pyridine on silica alumina,

1.50 g on 10 g of	+87.7	(d)
0.5 g on 10 g of	+100.7	(d)
1.02 g on 10 g of + additional 0.31 g HCl	+115.2	(d)

Pyridine (protonated), on silica
alumina

	+182	(e)
+ addition of 0.4 - 0.8 equiv. of n-butylamine	109-119	(e)
+ more than 1 equiv. of n-butylamine	77-91	(e)

(a) Data from ref. 181, ^{15}N natural abundance, solid state CP-MASS spectra, 18.25 MHz, originally referred to the nitrate line of solid external NH_4NO_3 , +5 ppm from neat nitromethane (Table 6).

(b) Data from ref. 339, ^{15}N (95%) labelled pyridine, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to neat pyridine, +62 ppm from neat nitromethane.

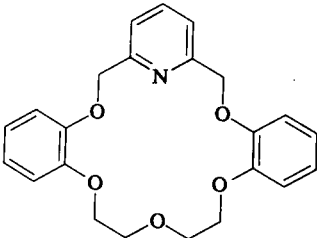
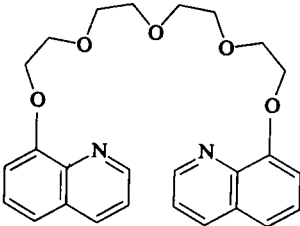
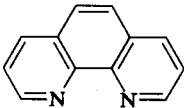
(c) Data from ref. 262, ^{15}N (95%) labelled pyridine, ^{15}N labelled spectra, 9.12 MHz, field perpendicular to sample tube, originally indirectly referred to liquid nitromethane (Table 6), uncorrected for bulk susceptibility effects.

(d) Data from ref. 340, ^{15}N natural abundance solid state CP-MASS spectra, 20.3 MHz, originally referred to liquid ammonia, +380.2 ppm from neat nitromethane.

(e) Data from ref. 341, details as in note (d).

TABLE 97

Nitrogen shieldings of pyridine-type nitrogen atoms in some cryptands and their complexes
(0.2–0.9 M solutions)

Ligand	Salt or acid added	Nitrogen shielding referred to neat nitromethane of pyridine-type nitrogen atoms in ligand		
		in CHCl_3	in DMSO	in MeOH
	none KSCN	+68.7	+71.6	
	none NaSCN $\text{Ba}(\text{SCN})_2$		+75.5	+89.0 +92.7 +93.5
	none LiSCN HClO_4		+69.3 +83.3 +134.5	

Data from ref. 267; results quoted are free from bulk-susceptibility effects; for details, see Table 17.

TABLE 98
Nitrogen shieldings in unsubstituted azine ring systems

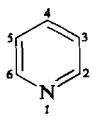
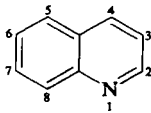
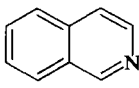
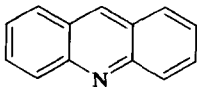
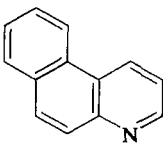
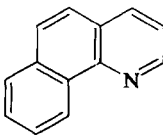
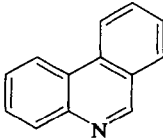
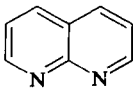
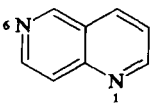
Compound	Solvent and concentration	Nitrogen shielding referred to neat nitromethane	Notes
	DMSO, 0.5 M acetone, 85% v/v	+63.5 +61.8	(a) (b)
	DMSO, 0.5 M acetone	+67.2 +66.9	(a) (c)
	DMSO, 0.5 M acetone	+69.3 +69.1	(a) (c)
	DMSO, 0.5 M	+74.4	(a)
	DMSO, 0.5 M	+67.5	(a)
	DMSO, 0.5 M	+76.8	(a)
	DMSO, 0.5 M	+70.8	(a)
	DMSO, 0.1 M acetone	+65.7 +65.8	(a) (c)
	DMSO, 0.5 M acetone	+65.3 (N1) +69.0 (N6) +67.9 (N1) +71.3 (N6)	(a) (a) (c) (c)

TABLE 98—*cont.*

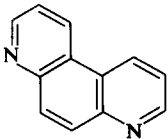
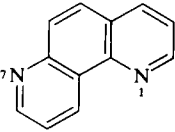
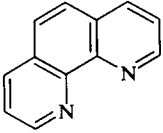
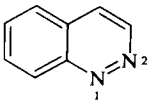
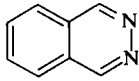
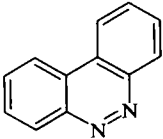
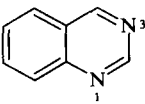
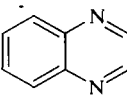
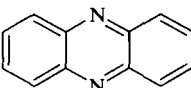
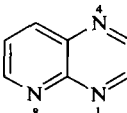
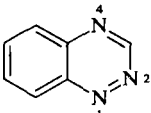
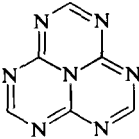
Compound	Solvent and concentration	Nitrogen shielding referred to neat nitromethane	Note
	DMSO, 0.5 M	+67.1	(a)
	DMSO, 0.5 M	+76.9 (N1) +68.2 (N7)	(a) (a)
	DMSO, 0.5 M DMSO, 0.9 M	+69.3 +69.3	(a) (d)
	DMSO, 0.5 M CHCl ₃	-20.2 -16.7	(a) (e)
	DMSO, 0.5 M CHCl ₃	+84.5 +89.1	(a) (e)
	DMSO, 0.5 M DMSO CHCl ₃	+46.1 +46.9 +48.9	(a) (f) (e)
	DMSO, 0.4 M	-44.0 (N1) -40.9 (N2)	(a) (a)
	DMSO, 0.5 M acetone	+10.3 +8.8	(a) (c)
	DMSO, 0.5 M	-59.9	(a)

TABLE 98—*cont.*

Compound	Solvent and concentration	Nitrogen shielding referred to neat nitromethane	Note
	DMSO, 0.5 M	+97.8 (N1)	(a)
		+86.5 (N3)	(a)
	DMSO	+96.7 (N1)	(g)
		+85.6 (N3)	(g)
	acetone	+97.4 (N1)	(c)
	DMSO, 0.5 M	+50.1	(a)
	acetone	+51.4	(c)
	DMSO, 0.1 M	+53.9	(a)
	acetone	+54.0	(c)
	DMSO, 0.5 M	+49.1 (N1)	(a)
		+45.0 (N4)	(a)
		+62.2 (N8)	(a)
	DMSO, 0.5 M	+98.5	(a)
	CHCl ₃	+100.3	(e)
	DMSO, 0.5 M	-68.3 (N1)	(a)
		-23.4 (N2)	(a)
		+98.1 (N4)	(a)
	acetone	-4.0	(h)
	DMSO	+143.2 (terminal)	(i)
		+195.2 (central)	(i)

(a) Data from ref. 25; ¹⁵N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO₃ in D₂O, +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4); Cr(acac)₃ added as relaxation reagent.

(b) Data from ref. 117; ¹⁵N natural abundance spectra, 10.14 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

TABLE 98—*cont.*

(c) Data from ref. 23; ^{14}N CW spectra, 4.3342 MHz, originally referred to neat nitromethane, high-precision differential-saturation technique with full lineshape fitting, concentric spherical sample/standard containers, in order to eliminate bulk-susceptibility effects.

(d) Data from ref. 267; ^{15}N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO_3 , corrected for bulk-susceptibility effects; therefore conversion constant +4.4 ppm relative to neat nitromethane was employed (see Table 6) in order to obtain shieldings referred to nitromethane that do not contain bulk-susceptibility effects.

(e) Data from ref. 657; ^{15}N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; $\text{Cr}(\text{acac})_3$ added as relaxation reagent.

(f) Data from ref. 338; ^{15}N natural abundance spectra, 40.53 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(g) Data from ref. 345; ^{15}N natural abundance spectra, 9.04 MHz, field perpendicular to sample tube, originally referred to what was considered as aqueous NH_4Cl , +352.9 ppm from neat nitromethane, (Table 6); however, using the latter value, one obtains shieldings referred to neat nitromethane that show systematic differences when compared with data for the same compounds and solvent in Table 121 in ref. 1; the differences suggest that NH_4NO_3 rather than NH_4Cl was actually employed as references, +359.6 ppm (NH_4^+) from neat nitromethane; the latter value was thus used for recalculation, scheme II (Table 4).

(h) See ref. 3, p. 221; since the data were originally referred to internal nitromethane standard, the value was recalculated here using +0.7 ppm shielding of MeNO_2 in acetone relative to neat MeNO_2 .

(i) Data from ref. 351; ^{15}N natural abundance spectra, frequency not reported, originally referred to internal HCONMe_2 , +227.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

TABLE 99
Nitrogen shielding in some derivatives of azines

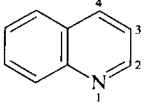
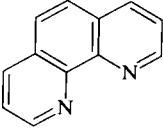
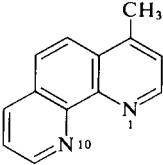
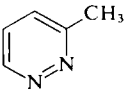
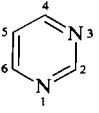
Compound	Solvent	Nitrogen shielding referred to neat nitromethane	Notes
	acetone	+66.9	(a)
	DMSO	+67.2	(b)
Substituted quinolines			
2-Me	DMSO	+73.1	(b)
3-Me	DMSO	+67.4	(b)
4-Me	DMSO	+72.8	(b)
	DMSO	+69.3	(b)
	DMSO	+75.4 (N1) +68.4 (N10)	(b) (b)
	DMSO	-20.2	(b)
	CHCl ₃	-16.7	(c)
	DMSO	-19.0 (N1) -15.1 (N2)	(b) (b)
	DMSO	+84.5	(b)
	CHCl ₃	+89.1	(c)
Substituted pyrimidines			
4-Me	DMSO	+92.9 (N1) +84.5 (N3)	(b) (b)
4,6-Me ₂	DMSO	+92.4	(b)
2-NH ₂	DMSO	+130.1 +296.8 (NH ₂)	(d) (d)

TABLE 99—*cont.*

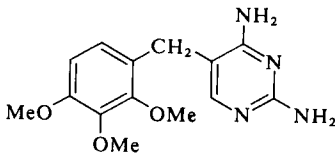
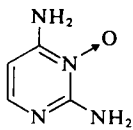
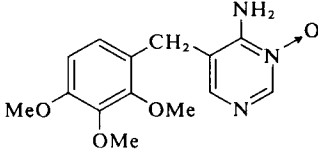
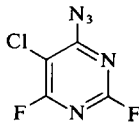
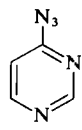
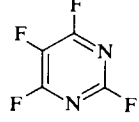
Compound	Solvent	Nitrogen shielding referred to neat nitromethane	Notes
2,4-(NH ₂) ₂	DMSO	+163.9 (N1) +173.0 (N3) +299.2 (2-NH ₂) +297.9 (4-NH ₂)	(d) (d) (d) (d)
	H ₂ O	+172.0 (N1) +179.2 (N3) +304.3 (2-NH ₂) +299.9 (4-NH ₂)	(d) (d) (d) (d)
	DMSO	+159.9 (N1) +172.2 (N3) +303.0 (2-NH ₂)	(d) (d) (d)
	DMSO	+166.2 (N1) +167.2 (N3) +305.2 (2-NH ₂) +303.9 (4-NH ₂)	(d) (d) (d) (d)
	DMSO	+164.3 (N1) +168.0 (N3) +308.4 (2 NH ₂) +307.7 (4NH ₂)	(d) (d) (d) (d)
	CHCl ₃	+160.7 (N1) +152.9 (N3)	(c) (c)
	CHCl ₃	+158.6 (N1) +150.1 (N3)	(c) (c)
	CHCl ₃	+154.0	(c)
	CHCl ₃	+152.5	(c)

TABLE 99—*cont.*

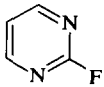
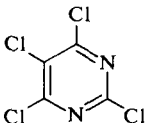
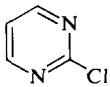
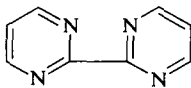
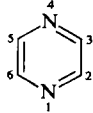
Compound	Solvent	Nitrogen shielding referred to neat nitromethane	Notes
	acetone	+132	(c)
	CHCl ₃	+95.9	(c)
	DMSO	+88.2	(c)
	DMSO	+85.1	(b)
	DMSO	+46.1	(b)
	DMSO	+46.9	(e)
	CHCl ₃	+48.9	(c)
Substituted pyrazines			
H	DMSO	+46.9 (N1)	(e)
		+46.9 (N4)	(e)
F	DMSO	+91.9 (N1)	(e)
		+29.2 (N4)	(e)
Cl	DMSO	+57.1 (N1)	(e)
		+37.3 (N4)	(e)
Br	DMSO	+54.3 (N1)	(e)
		+45.2 (N4)	(e)
I	DMSO	+32.0 (N1)	(e)
		+41.8 (N4)	(e)
Me	DMSO	+48.8 (N1)	(e)
		+46.8 (N4)	(e)
Me	DMSO	+47.9 (N1)	(b)
		+45.9 (N4)	(b)
OMe	DMSO	+101.6 (N1)	(e)
		+38.6 (N4)	(e)
SMe	DMSO	+63.7 (N1)	(e)
		+47.8 (N4)	(e)
CO ₂ H	DMSO	+47.3 (N1)	(e)
		+45.3 (N4)	(e)
CO ₂ Me	DMSO	+47.8 (N1)	(e)
		+45.0 (N4)	(e)

TABLE 99—*cont.*

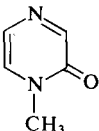
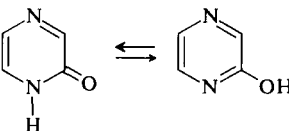
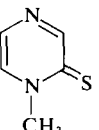
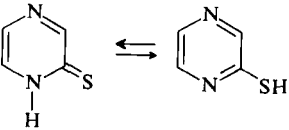
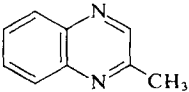
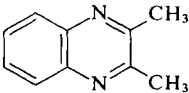
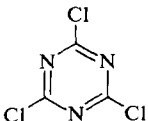
Compound	Solvent	Nitrogen shielding referred to neat nitromethane	Notes
CONH ₂	DMSO	+57.4 (N1) +279.1 (NH ₂)	(e) (e)
		+44.2 (N4)	(e)
CN	DMSO	+46.5 (N1) +119.5 (CN)	(e) (e)
		+44.5 (N4)	(e)
COMe	DMSO	+51.5 (N1) +44.8 (N4)	(e) (e)
NH ₂	DMSO	+106.6 (N1) +309.2 (NH ₂)	(e) (e)
		+45.9 (N4)	(e)
NMe ₂	DMSO	+104.3 (N1) +320.6 (NMe ₂)	(e) (e)
		+45.4 (N4)	(e)
2,6-Me ₂	DMSO	+48.9 (N1) +45.5 (N4)	(b) (b)
2,5-Me ₂	DMSO	+47.0	(b)
2,3-Me ₂	DMSO	+48.3	(b)
2-Me,3-Et	DMSO	+47.3 +50.6	(b) (b)
	DMSO	+211.8 (N1) +38.9 (N4)	(f) (f)
	DMSO	+198.3 (N1) +35.6 (N4)	(f) (f)
	DMSO	+180.1 (N1) +58.3 (N4)	(f) (f)
	DMSO	+179.7 (N1) +51.2 (N4)	(f) (f)

TABLE 99—*cont.*

Compound	Solvent	Nitrogen shielding referred to neat nitromethane	Notes
	DMSO	+57.8 (N1) +50.2 (N4)	(b) (b)
	DMSO	+57.8 (N1)	(b)
	DMSO CDCl ₃	+98.5 +100.3	(b) (c)
	CHCl ₃	+168.8	(c)
	CHCl ₃	+110.6	(c)

(a) Data from ref. 23; ¹⁴N CW spectra, 4.3342 MHz, originally referred to neat nitromethane, high-precision differential-saturation technique with full lineshape fitting, concentric spherical sample/standard containers in order to eliminate bulk-susceptibility effects.

(b) Data from ref. 25; ¹⁵N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO₃ in D₂O, +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4); Cr(acac)₃ added as relaxation reagent. (c) Data from ref. 657; ¹⁵N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; Cr(acac)₃ added as relaxation reagent.

(d) Data from ref. 345; ¹⁵N natural abundance spectra, 9.04 MHz, field perpendicular to sample tube, originally referred to what was considered as aqueous NH₄Cl, +352.9 ppm from neat nitromethane, (Table 6); however, using the latter value, one obtains shieldings referred to neat nitromethane that show systematic differences when compared with data for the same compounds and solvent in Table 121 in ref. 1; the differences suggest that NH₄NO₃ rather than NH₄Cl was actually employed as reference, +359.6 ppm (NH₄⁺) from neat nitromethane; the latter value was thus used for recalculation, scheme II (Table 4).

(e) Data from ref. 338; ¹⁵N natural abundance spectra, 40.53 MHz field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(f) Data from ref. 256; ¹⁵N natural abundance spectra, 40.53 MHz field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

TABLE 100

Nitrogen shieldings in some azinium ions

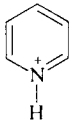
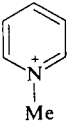
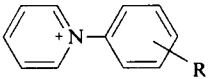
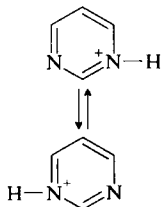
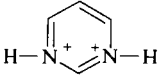
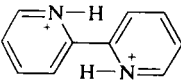
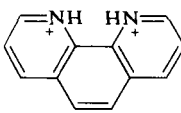
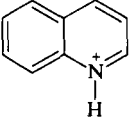
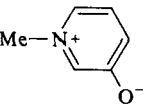
Cation	Anion	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	Cl ⁻	0.5 M in HCl (10 M)	+178.96 ± 0.09 (doublet)	(a)
	Cl ⁻	16.0 mol % in CHCl ₃	+167.8	(a)
	Cl ⁻	15.6 mol % in DMSO	+165.6	(a)
	Cl ⁻	4.0 mol % in MeOH	+176.6	(a)
	Cl ⁻	4.3 mol % in H ₂ O	+179.6	(a)
	CF ₃ COO ⁻	33 mol % in TFA	+172.1	(a)
	CF ₃ COO ⁻	20 mol % in TFA/CHCl ₃ (1:1)	+175.4	(a)
	CF ₃ COO ⁻	14.5 mol % in TFA	+184.8 (doublet)	(a)
	CF ₃ COO ⁻	2 M in TFA	+179.0	(a)
	CF ₃ COO ⁻	0.5 M in TFA	+182.5	(a)
	SO ₃ F ⁻	0.5 M in FSO ₃ H	+186.9	(a)
	Cl ⁻	3.7 mol % in H ₂ O	+180.2	(a)
	I ⁻	4.4 mol % in H ₂ O	+180.7	(a)
	I ⁻	1 M in DMSO	+179.9	(a)
	I ⁻	1 M in CF ₃ CH ₂ OH	+181.3	(a)
	I ⁻	1 M in TFA	+182.0	(a)
				
R				
H	Cl ⁻	1 M in D ₂ O	+162.6	(b)
<i>p</i> -Me	Cl ⁻	1 M in D ₂ O	+162.9	(b)
<i>p</i> -OMe	Cl ⁻	1 M in D ₂ O	+164.1	(b)
<i>p</i> -Cl	Cl ⁻	1 M in D ₂ O	+164.0	(b)
<i>p</i> -Br	Cl ⁻	1 M in D ₂ O	+166.1	(b)
<i>p</i> -I	Cl ⁻	1 M in D ₂ O	+164.5	(b)
<i>m</i> -NO ₂	Br ⁻	1 M in D ₂ O	+168.2	(b)
<i>p</i> -NO ₂	Br ⁻	1 M in D ₂ O	+166.3	(b)
	CF ₃ COO ⁻	0.5 M in TFA	+134.8 ((N ⇌ NH ⁺))	(a)

TABLE 100—*cont.*

Cation	Anion	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	SO_3F^-	0.5 M in FSO_3H	+182.6	(a)
	Cl^-	2 M in $\text{H}_2\text{O}/\text{HCl}$	+164.2	(a)
	Cl^-	2 M in $\text{H}_2\text{O}/\text{HCl}$	+148.2	(a)
	Cl^-	1:3 v/v in H_2SO_4	+193.1	(a)
	Cl^-	1:3 v/v in MeOH	+181 ± 1	(a)

(a) See ref. 1, Table 123 and references therein.

(b) Data from ref. 342; ^{14}N spectra, 7.196 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

TABLE 101

Nitrogen shieldings in some azine *N*-oxides and their isomeric forms

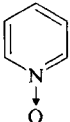
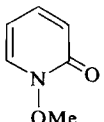
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	0.2 M in CS ₂	+82	(a)
	1.0 M in CDCl ₃	+84	(a)
	in acetone	+86	(a)
	in DMSO	+85.5	(a)
	2 M in DMSO	+86.8	(a)
	2 M in CF ₃ CH ₂ OH	+99.5	(a)
	in H ₂ O	+99	(a)
Substituted pyridine			
<i>N</i> -oxides			
2-OMe	acetone	+140 ± 3	(b)
3-OMe	acetone	+94	(b)
4-OMe	acetone	+102	(b)
3-OH	MeOH	+96	(b)
2-NMe ₂	MeOH	+123	(b)
		+343 ± 4 (NMe ₂)	(b)
2-NHMe	MeOH	+138 ± 3	(b)
		+311 ± 4 (NHMe)	(b)
3-NMe ₂	acetone	+85	(b)
		+340 ± 3 (NMe ₂)	(b)
3-NHMe	acetone	+86	(b)
		+336 ± 3 (NHMe)	(b)
4-NMe ₂	MeOH	+134 ± 2	(b)
		+350 ± 10 (NMe ₂)	(b)
4-NHMe	MeOH	+146 ± 3	(b)
		+335 ± 7 (NHMe)	(b)
2-SH	acetone	+136	(b)
		+131	(b)
4-SH	acetone/DMSO 1:1 v/v	+87 ± 2	(b)
	MeOH/DMSO 1:1 v/v	+91 ± 2	(b)
2,6-Me ₂	acetone 1:3 v/v	+91	(c)
2,4-Me ₂	acetone 1:3 v/v	+93	(c)
2-Me, 4-NO ₂	acetone, satd.	+74 ± 2	(c)
		+15 (NO ₂)	(c)
3-Me, 4-NO ₂	acetone, satd.	+73	(c)
		+13 (NO ₂)	(c)
3-Cl, 4-NO ₂	acetone, satd.	+72	(c)
		+19 (NO ₂)	(c)
	acetone	+143 ± 3	(b)

TABLE 101—*cont.*

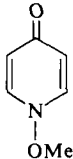
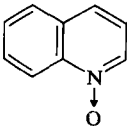
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	acetone	+104 ± 2	(b)
	acetone, satd.	+95	(c)
	chloroform, satd.	+99	(c)
	MeOH, satd.	+107	(c)
Substituted quinoline			
<i>N</i> -oxides			
2-OMe	acetone, satd.	+125 ± 2	(c)
4-OMe	acetone, satd.	+118 ± 4	(c)
	MeOH	+124 ± 5	(c)
2-Me	acetone, satd.	+103 ± 4	(c)
3-Me	acetone, satd.	+98 ± 2	(c)
4-Me	acetone, satd.	+101 ± 4	(c)
2-Cl	acetone, satd.	+102	(c)
3-Cl	acetone, satd.	+91 ± 2	(c)
4-Cl	acetone, satd.	+97	(c)
	MeOH, satd.	+108 ± 2	(c)
2-Br	acetone, satd.	+102	(c)
3-Br	acetone, satd.	+94	(c)
	MeOH, satd.	+104	(c)
4-Br	acetone, satd.	+92 ± 4	(c)
	MeOH, satd.	+104 ± 2	(c)
2-CN	acetone, satd.	+87 ± 2	(c)
4-CN	DMSO: acetone	+77 ± 4	(c)
	1:3 v/v		
2-CHO	acetone, satd.	+90	(c)
4-CHO	acetone, satd.	+86 ± 2	(c)
2-COOH	DMSO	+129 ± 8	(c)
	CH ₂ Br ₂	+120 ± 5	(c)
3-NO ₂	acetone, satd.	+91	(c)
		+11 ± 2 (NO ₂)	(c)
4-NO ₂	acetone, satd.	+83	(c)
		+12 (NO ₂)	(c)
	MeOH, satd.	+93 ± 5	(c)

TABLE 101—*cont.*

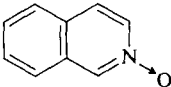
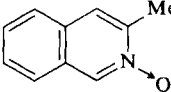
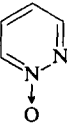
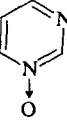
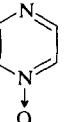
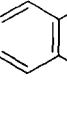
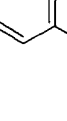
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	acetone, satd.	+90	(c)
	CHCl ₃ , satd.	+97	(c)
	MeOH, satd.	+112 ± 2	(c)
	dioxane, satd.	+100 ± 3	(c)
	dioxane/H ₂ O (2:1 v/v), satd.	+85 ± 3	(c)
	acetone, satd.	+91	(c)
	MeOH, satd.	+105 ± 2	(c)
	acetone	+55.8	(d)
	DMSO	+34.4 (N2)	(d)
		+55.1	(a)
		+33.6 (N2)	(a)
	CHCl ₃	+54.7	(a)
		+32.8 (N2)	(a)
	MeOH	+59	(e)
		+36 ± 2 (N2)	(e)
	acetone	+91	(e)
	DMSO	+90	(a)
		+80.3 (N3)	(a)
	CHCl ₃	+89.9	(a)
		+79.5 (N3)	(a)
	acetone	+68	(a)
		+78 ± 5 (N4)	(a)
	acetone	+70.2	(d)
		+78.7 (N4)	(d)
	DMSO	+70.4	(a)
		+75.7 (N4)	(a)
	CHCl ₃	+69.1	(a)
		+75.2 (N4)	(a)
	acetone	+59	(a)
	acetone	+53	(a)

TABLE 101—*cont.*

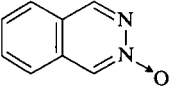
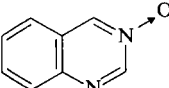
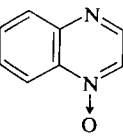
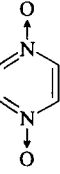
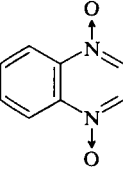
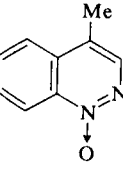
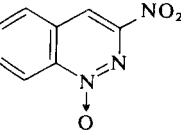
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	acetone	+67	(a)
	DMSO	+68.9	(a)
		+53.2 (N3)	(a)
	acetone	+92 ± 2	(a)
	acetone	+92.2	(d)
		+74.3 (N1)	(d)
	DMSO	+89.5	(a)
		+89.5 (N1)	(a)
	acetone	+77	(a)
		+83 ± 3	(a)
	DMSO	+76.8	(a)
		+80.7 (N4)	(a)
	CHCl ₃	+80	(a)
		+84 ± 4 (N4)	(a)
			
	DMSO	+98.6	(d)
			
	DMSO	+108.7	(d)
			
	acetone, satd.	+62	(c)
	MeOH, satd.	+68	(c)
			
	acetone, satd.	+61 ± 2	(c)
		+17 ± 2 (NO ₂)	(c)
	acetone : DMSO, satd. (3 : 1 v/v)	+61 ± 2	(c)
		+15 ± 2 (NO ₂)	(c)

TABLE 101—*cont.*

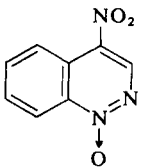
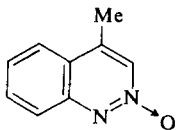
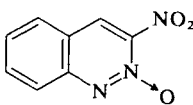
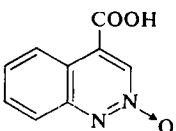
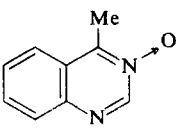
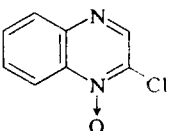
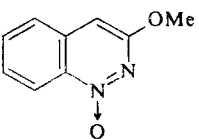
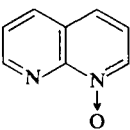
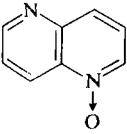
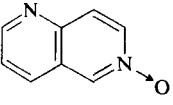
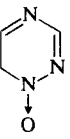
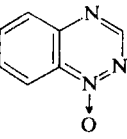
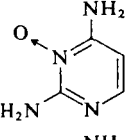
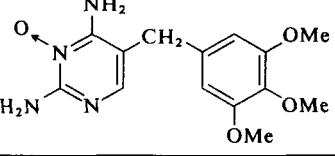
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	acetone, satd. acetone:DMSO, satd. (3:1 v/v)	+52 +16 (NO ₂) +51 +15 (NO ₂)	(c) (c) (c) (c)
	MeOH, satd.	+60	(c)
	acetone:DMSO, satd. (3:1 v/v)	+51 ± 2	(c)
	acetone:DMSO, satd. (3:1 v/v) DMSO, satd.	+55 +57	(c) (c)
	MeOH, satd.	+107	(c)
	MeOH, satd.	+94 ± 2	(c)
	acetone, 1:3 v/v MeOH, satd.	+41 +43	(c) (c)
	acetone, satd.	+90	(c)

TABLE 101—*cont.*

Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	acetone, satd.	+93	(c)
	acetone, satd.	+89 ± 2	(c)
	acetone	+43	(f)
	acetone	+46	(f)
	DMSO	+167.2	(g)
	DMSO	+168	(g)

(a) See ref. 1, Table 124 and references therein.

(b) Data from ref. 258; ^{14}N CW spectra, 4.3342 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(c) Data from ref. 347; details as in note (b).

(d) Data from ref. 346; ^{15}N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to neat nitromethane uncorrected for bulk-susceptibility effects.

(e) Data from ref. 346; ^{14}N CW spectra, see note (b).

(f) Data from ref. 658; details as in note (b).

(g) Data from ref. 345; ^{15}N natural abundance spectra, 9.04 MHz, field perpendicular to sample tube, originally referred to what was considered as aqueous NH_4Cl (+352.9 ppm from neat nitromethane) (Table 6); however, using the latter value, one obtains shieldings referred to neat nitromethane that show systematic differences when compared with data for the same compounds and solvent in Table 121 in ref. 1; the differences suggest that NH_4NO_3 rather than NH_4Cl was actually employed as reference, +359.6 ppm (NH_4^+) from neat nitromethane; the latter value was thus used for recalculation, scheme II (Table 4).

TABLE 102
Nitrogen shieldings in some 1,4-benzodiazepines

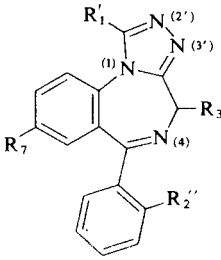
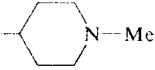
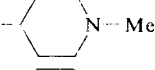
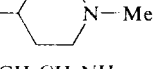
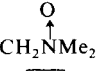
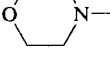
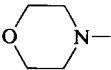
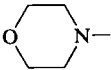
Structure			Nitrogen shielding referred to neat nitromethane							Notes
										
R ₃	R ₇	R ₁ '	R ₂ ''	1-N	4-N	2'-N	3'-N	other nitrogens		
H	Cl	H	H	+200.5	+49.0	+61.2	+70.7			(a)
H	Cl	Me	H	+203.2	+47.7	+67.6	+77.0			(a)
H	Cl	Me	Cl	+203.3	+38.1	+67.5	+76.8			(a)
H	H	Me	H	+201.9	+50.8	+68.3	+77.8			(a)
H	H	Me	Cl	+201.9	+40.7	+67.4	+76.9			(a)
H	Cl		H	+206.8	+46.4	+67.3	+77.4	+341.8		(a)
H	H		Cl	+204.2	+39.7	67+1	+77.5	+341.0		(a)
H	Cl		Cl	+205.7	+37.0	+67.1	+77.3	+340.8		(a)
H	Br	CH ₂ CH ₂ NH ₂	H	+203.4	+47.6	+68.9	+77.7	+356.6		(a)
H	Br	CH ₂ NMe ₂	H	+202.2	+47.6	+60.9	+76.3	+354.1		(a)
H	H	CH ₂ CH ₂ NMe ₂	H	+202.5	+49.4	+67.1	+77.1	+355.4		(a)
H	H	CH ₂ CH ₂ NH ₂	Cl	+202.0	+41.2	+68.5	+77.8	+357.6		(a)
H	NO ₂	CH ₂ NMe ₂	H	+202.1	+45.9	+59.9	+75.4	+15.4 (R ₇)		(a)
								+354.6 (R ₁ ')		(a)
CH ₂ NMe ₂	Cl	CH ₂ NMe ₂	H	+203.6	+35.8	+61.2	+78.1	+357.5 (R ₃)		(a)
								+354.7 (R ₁ ')		(a)
H	Cl		H	+197.9	+49.3	+55.1	+74.9	+266.8		(a)
H	H		H	+214.8	+47.0	+95.9	+80.2	+323.1		(a)

TABLE 102—*cont.*

Structure			Nitrogen shielding referred to neat nitromethane						Notes
R ₃	R ₇	R' ₁	R'' ₂	1-N	4-N	2'-N	3'-N	other nitrogens	
Me	Cl		H	+222.0	+33.7	+101.0	+85.7	+328.6	(a)
H	Cl		Cl	+220.9	+38.6	+99.1	+80.8	+325.6	(a)
H	Cl	CH ₂ OMe	H	+202.6	+47.0	+57.2	+74.2		(a)
Me	Cl	Br	H	+203.0	+32.2	+61.3	+70.1		(a)
H	Cl	OMe	H	+223.7	+49.7	+118.3	+89.6		(a)

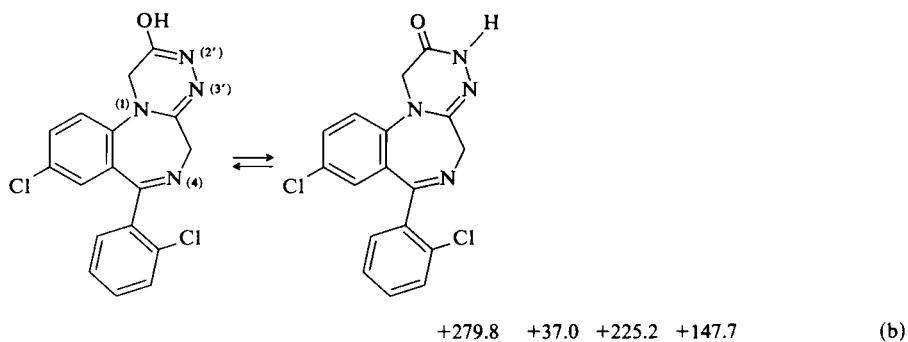
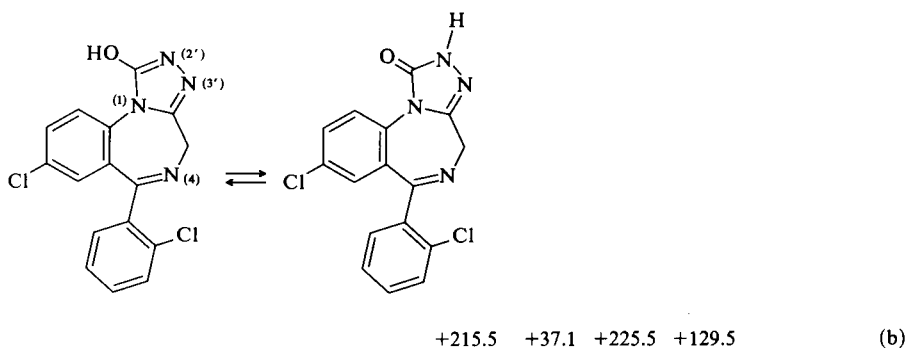


TABLE 102—*cont.*

Structure				Nitrogen shielding referred to neat nitromethane				Notes
R ₃	R ₇	R' ₁		R'' ₂	1-N	4-N	2'-N	3'-N
R ₃	R ₇	R' ₁	R' ₂	R'' ₂	1-N	4-N		3'-N
H	Cl	H	H	H	+202.3	+45.5		+125.8
H	Cl	H	Me	H	+203.1	+36.9		+120.9
H	Cl	H	H	Cl	+202.0	+36.8		+125.7
R ₁		R ₃	R ₇	R' ₂	1-N	4-N	other nitrogens	
Me		H	Cl	H	+253.0	+54.4		(b)
H		OH	Cl	H	+246.0	+37.9		(b)
H		H	NO ₂	Cl	+233.9	+45.1	+12.2 (NO ₂)	(b)
CH ₂ CH ₂ NEt ₂		H	Cl	F	+243.0	+45.1	+337.0 (NEt ₂)	(b)
					+257.0	+105.4	+363.0 (NHMe)	(b)

(a) Data from ref. 335; ¹⁵N natural abundance spectra, 20.28 MHz, field parallel to sample tube; originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; *ca.* 1 M solutions in CDCl₃ or DMSO.

(b) Data from ref. 363; details as in note (a).

Table 103

Nitrogen shieldings in some DNA and tRNA structures

Sample and nucleoside moiety	Nitrogen shielding (in ppm) referred to neat nitromethane for nitrogen atoms specified (numbering system in Table 104)						Notes
	1-N	3-N	7-N	9-N	NH ₂	other	
A = adenosine G = guanosine U = uridine T = thymidine C = cytidine							
Single-stranded circular B-form DNA of fd bacteriophage (solid sample)							
A	+158.1	+167.6	+149.9	+210.9	+299.1		(a)
G	+234.0	+221.5	+147.3	+210.9	+305.7		(a)
T	+237.8	+222.3	-	-	-		(a)
C	+229.5	+184.3	-	-	+282.7		(a)
Native DNA from <u>Escherichia coli</u> (in H ₂ O, pH = 7.5)							
A	+154.2	+164.3	+145.0	+207.9	+297.7		(b)
G	+230.7	+212.5	+140.5	+207.9	+303.0		(b)

Table 103 (continued)

T	+228.2	+227.8	-	-	-	(b)
C	+217.8	+181.6	-	-	+280.6	(b)
<u>tRNA_f^{Met} from</u> <u>Escherichia coli</u> (in H ₂ O, pH = 7.0, only NH moieties detected)						
U-8	?	+220.4	-	-	-	(c)
U-24	?	+221.2	-	-	-	(c)
U-27	?	+222.2	-	-	-	(c)
U-50	?	+225.7	-	-	-	(c)
T	?	+224.6	-	-	-	(c)
?		+225.2				(c)
Yeast tRNA (0.033 M in H ₂ O) 30°C, ¹ H-decoupled, pH = 4						
A	+155.0	+162.0	+147.9 to +149.8	+213.8	+301.9 to +303.3	(d)
G	+233.8	+214.5	+143.2 to +145.6	+213.8	+308.0	(d)

U	+233.8	+223.5	-	-	-	(d)
C	+229.7	+183.7	-	-	+287.6	(d)
30°C, ¹ H-coupled, renatured						
A	+156.2	+164.5	+150.7 to +151.0	+213.2	+303.2 to +303.7	(d)
G	+234.6	+215.8	+146.0 to +146.5	+213.2	+308.2	(d)
U	+234.6	+223.2	-	-	-	(d)
C	+229.2	+180.1 +171.9	-	-	+288.0 +248.8	(d)
amino acids					+360.7	(d)
					+349.3	(d)
					+349.0	(d)
					+343.9	(d)
					+341.5	(d)
					+336.3	(d)
65°C, ¹ H-coupled						
A	+153.8	+163.4	+148.8	+213.7	+305.3	(d)
G	+234.1	+214.5	+144.7	+213.7	+309.5	(d)

Table 103 (continued)

U	+234.1	+223.0	-	-	-	(d)
C	?	+178.7	-	-	+294.7	(d)
amino					+360.7	(d)
acids					+349.0	(d)
					+343.9	(d)
					+341.5	(d)
					+336.3	(d)
65°C, ^1H -decoupled						
A	+152.7	?	+147.9	?	+303.5	(d)
G	+233.5	?	+143.8	?	+308.6	(d)
U	+233.5	+222.6	-	-	-	(d)
C	+229.6	+177.3	-	-	+288.5	(d)
					+244.5	

(a) Data from ref. 178, ^{15}N labelled sample by growing *E. coli* on $^{15}\text{NH}_4\text{Cl}$ and infecting with fd bacteriophage; ^{15}N CP-MASS spectra, 15.24 MHz, originally referred to NH_4^+ in solid NH_4NO_3 , +358.4 ppm from neat liquid nitromethane (Table 30), uncorrected for bulk susceptibility effects.

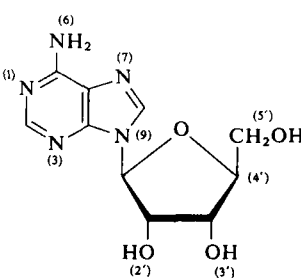
(b) Data from ref. 357, ^{15}N enriched *E. coli*, grown on $^{15}\text{NH}_4\text{Cl}$; ^{15}N spectrum, 30.4 MHz, field parallel to sample tube, originally referred to 2 M NH_4Cl in 2 M HCl , +352.5 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

(c) Data from ref. 143, ^1H - ^{15}N double-resonance spectra, 360/36 MHz, field parallel to sample tube, referred originally to liquid NH_3 , +380.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(d) Data from ref. 358, biologically ^{15}N enriched samples, ^{15}N spectra, 50.65 MHz, field parallel to sample tube, originally referred to 1 M HNO_3 , +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

TABLE 104

Nitrogen shieldings in some nucleosides, nucleotides and related structures

Compound and solution	Nitrogen shielding referred to neat nitromethane for nitrogen atoms specified						Note
	1-N	3-N	7-N	9-N	NH ₂	other	
							
(adenosine)							
0.50 M in DMSO	+145.7	+158.8	+140.8	+211.8	+300.0		(a)
0.50 M in DMSO	+155.2	+158.0	+142.0	+209.3	+297.8		(a)
+HgCl ₂ , 1 eq.							
0.50 M in DMSO	+147.3	+158.8	+148.3	+211.6	+298.6		(a)
+Zn(NO ₃) ₂ , 1 eq.							
in DMSO	+144.8	+158.0	+140.0	+211.2	+298.7		(b)
in DMSO + CF ₃ COOH,							
0.25 eq.	+168.9	+158.9	+139.9	+209.5	+296.8		(b)
0.50 eq.	+188.1	+157.8	+139.1	+207.4	+294.7		(b)
0.75 eq.	+204.6	+157.8	+138.4	+205.6	+292.7		(b)
0.90 eq.	+213.1	+157.0	+137.0	+204.3	+291.5		(b)
1.0 eq.	+216.1	+157.0	+135.8	+204.2	+290.5		(b)
6-NH—CH ₂ Ph derivative of adenosine							
in DMSO	+150.8	+159.4	+142.1	+211.8	+292.5		(b)
in DMSO + CF ₃ COOH,	+228.0	+163.6	+145.4	+205.4	+281.7		(b)
3.0 eq.							
2',3',5'-tri-OMe-adenosine							
0.5 M in CDCl ₃	+143.1	+150.0	+140.0	+205.7	+300.0		(c)
as above, 1:1 base pair with	+143.7	+151.0	+139.9	+206.1	+299.5		(c)
pair with							

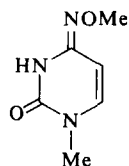


TABLE 104—*cont.*

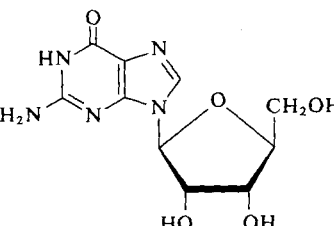
Compound and solution	Nitrogen shielding referred to neat nitromethane for nitrogen atoms specified						Notes
	1-N	3-N	7-N	9-N	NH ₂	other	
2',3',5'-tri- <i>O</i> -Ocetyl-adenosine							
0.05 M in CDCl ₃	+144.5	+154.0	+141.5	not obs.	+307.9		(d)
as above, dimer	+147.1	+157.4	+140.8	not obs.	+300.0		(d)
as above, 1:1 base pair with 1-cyclohexyluracil	+147.8	+156.9	+143.9	not obs.	+303.6		(d)
as above, 1:2 complex with 1-cyclohexyluracil	+152.7	+158.4	+144.7	not obs.	+299.8		(d)
2',3',5'-tri- <i>O</i> -acetyl-8-Br-adenosine							
0.05 M in CDCl ₃	+143.0	+151.9	+136.3	not obs.	+308.0		(d)
as above, dimer	+145.2	+155.0	+135.3	not obs.	+298.3		(d)
as above, 1:1 base pair with 1-cyclohexyluracil	+150.8	+155.1	+136.3	not obs.	+303.3		(d)
							
(guanosine)							
0.50 M in DMSO	+234.0	+215.0	+134.2	+211.2	+307.9		(a)
0.50 M in DMSO	+233.8	+215.5	+164.3	+206.8	+305.7		(a)
+HgCl ₂ , 1 eq.							
0.50 M in DMSO	+234.0	+215.6	+164.4	+203.8	+306.0		(a)
+Zn(NO ₃) ₂ , 1 eq.							
guanosine-3'-monophosphate (GMP)							
0.0225 M in H ₂ O	+232.9	+214.2	+146.1	+212.4	+307.6		(e)
as above + 0.0082 M ribonuclease T ₁	+232.5	+214.9	+145.2	+211.9	+305.7		(e)
guanosine (G) in <i>cis</i> [Pt(NH ₃) ₂ (G) ₂] ²⁺ in H ₂ O	+234.3	+217.6	+239.7	+208.9	+306.5		(f)
guanosine moiety (G*) in G*-G-C-U-phosphate 0.044 M in 0.1 M NaCl _{aq} .	+236	+214	+148	+210	+306		(i)
2',3'- <i>O</i> -isopropylidene-5'-(OSiMe ₂ Bu ¹)-guanosine							
0.125 M in CDCl ₃	+230.8	?	?	?	+284.8		(g)
+0.125 M analogous cytidine derivative							

TABLE 104—*cont.*

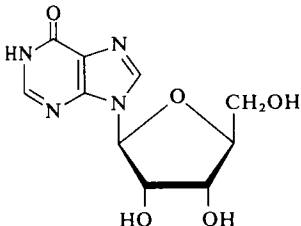
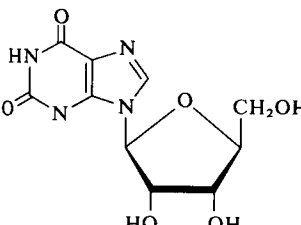
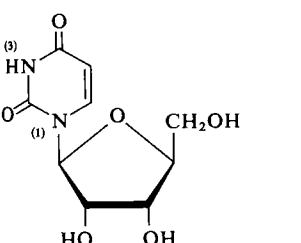
Compound and solution	Nitrogen shielding referred to neat nitromethane for nitrogen atoms specified						Notes
	1-N	3-N	7-N	9-N	NH ₂	other	
 (inosine)							
1.15 M in DMSO	+203.4	+163.9	+129.7	+203.4	—		(h)
1.15 M in DMSO	+202	+165	+137	+200	—		(h)
+CF ₃ COOH, 1 eq.							
1.15 M in DMSO	+203	+164	+135	+201	—		(h)
+HgCl ₂ , 1 eq.							
1.15 M in DMSO	+203	+164	+146	+202	—		(h)
+Zn(NO ₃) ₂ , 1 eq.							
 (xanthosine)							
in DMSO	ca. +226	ca. +266	ca. +131	ca. +213	—		(j)
 (uridine)							
in DMSO	ca. +236	ca. +222	—	—	—		(j)

TABLE 104—*cont.*

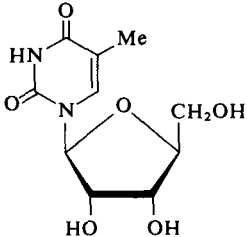
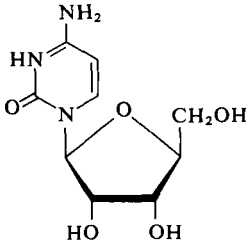
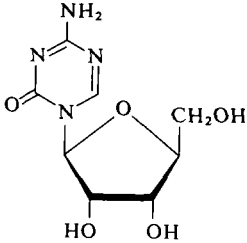
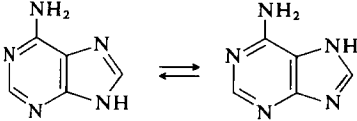
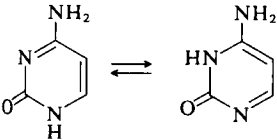
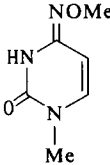
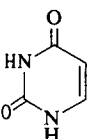
Compound and solution	Nitrogen shielding referred to neat nitromethane for nitrogen atoms specified						Notes
	1-N	3-N	7-N	9-N	NH ₂	other	
 (thymidine) in DMSO	<i>ca.</i> +236	<i>ca.</i> +224	—	—	—		(j)
 (cytidine) 0.75 M in DMSO	+228.1	+173.5	—	—	+287.2		(a)
0.75 M in DMSO	+229.0	+191.5	—	—	+279.7		(a)
+HgCl ₂ , 1 eq.							
0.75 M in DMSO	+229.2	+195.3	—	—	+277.5		(a)
+Zn(NO ₃) ₂ , 1 eq.							
cytidine (C) in <i>cis</i> [Pt(NH ₃) ₂ (C) ₂] ²⁺ in H ₂ O	+229.8	+257.2	—	—	+278.6		(f)
 (5-azacytidine) 1.1 M in DMSO	+214.1	+190.6	—	—	+284.6	+164.5 (5-N)	(k)

TABLE 104—*cont.*

Compound and solution	Nitrogen shielding referred to neat nitromethane for nitrogen atoms specified						Notes
	1-N	3-N	7-N	9-N	NH ₂	other	
 (adenine)							see Table 94
 (cytosine)							see Table 50
 (1-Me-N ⁴ (OMe)-cytosine)							
0.5 M in CDCl ₃	+265.1	+257.6	—	—	—	+77.7 (=NOMe)	(c)
as above, 1:1 base pair with tri(OMe)adenosine	+264.9	+256.2	—	—	—	+77.2 (=NOMe)	(c)
 (uracil)							see Table 50

For additional data see footnote (j)

(a) Data from ref. 352; ¹⁵N natural abundance spectra, 40.54 MHz, field parallel to sample tube, originally referred to aqueous NH₄Cl, +352.9 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); originally reported to liquid NH₃ standard taken at +380.2 ppm from nitromethane; this is erroneous, since the latter value refers to field perpendicular to sample tube; inverse-gated decoupling of ¹H; also, 20.27 MHz refocused INEPT spectra of ¹⁵N.

(b) Data from ref. 328; ¹⁵N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO₃, +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

TABLE 104—*cont.*

(c) Data from ref. 121; ^{15}N natural abundance INEPT spectra, set to various values of NH couplings, 20.28 MHz, field parallel to sample tube, originally referred to 0.1 M HNO_3 , +3.5 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

(d) Data from ref. 243; ^{15}N -labelled (1-N, 3-N, 7-N, NH_2) compounds, ^{15}N spectra, 10.05 MHz, field perpendicular to sample tube, originally referred to NH_4^+ in NH_4NO_3 in DMSO, +358.1 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

(e) Data from ref. 354; fully ^{15}N -labelled guanosine, details as in note (d).

(f) Data from ref. 276; ^{15}N natural abundance spectra, 50.56 MHz, field parallel to sample tube, other details as in note (b).

(g) Data from ref. 147; ^{15}N natural abundance spectra, frequency not reported, two-dimensional technique with multiquantum correlation procedure, originally referred to liquid NH_3 , +380.2 ppm from neat nitromethane.

(h) Data from ref. 353; ^{15}N natural abundance spectra, 20.27 MHz, field parallel to sample tube, other details and comments as in note (a).

(i) Data from refs. 355, 659; ^{15}N -labelled guanosine moiety, ^{15}N (proton-coupled) spectrum, 36.4 MHz, field parallel to sample tube, other details in note (d).

(j) See ref. 1, Table 126 and references therein.

(k) Data from ref. 349; details as in note (b).

TABLE 105

Nitrogen shieldings in some cyclophosphazenes (solutions in CDCl_3)

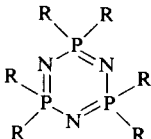
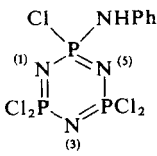
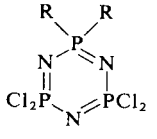
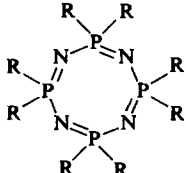
Compound	Nitrogen shielding referred to neat nitromethane	Notes
		
R		
OMe	+317.8	(a, b)
OEt	+314.3	(a, c)
OPh	+305.9	(b, c)
NHMe	+315.1 (ring)	(c)
NHEt	+312.4 (ring)	(b, c)
NMe ₂	+320.8 (ring)	(b, c)
NEt ₂	+316.3 (ring)	(c)
Me	+319.5	(b, c)
SEt	+284.2	(b, c)
SPh	+285.0	(c)
F	+314.5	(b, c)
Cl	+258.8	(b, c, d)
		
	+256.3 (3-N); +268.1 (1,5-N)	(d)
		
R		
NHPH	+255.1 (3-N); +279.1 (1,5-N)	(d)
NH ₂	+255.5 (3-N); +272.9 (1,5-N)	(e)
F	+259.8 (3-N); +286.9 (1,5-N)	(e)
SEt	+270.9 (1,5-N)	(e)

TABLE 105—*cont.*

Compound	Nitrogen shielding referred to neat nitromethane	Notes
 R		
OMe	+313.7	(b, f)
OPh	+302.5	(b, g)
NHEt	+306.7 (ring)	(b, g)
NMe ₂	+314.8 (ring)	(b, g)
Me	+300.0	(b)
SEt	+270.0	(b)
F	+314.4	(b, g)
Cl	+248.0	(b, g)
Br	+230.8	(b)
cyclo[NPF ₂] ₅	+322.8	(h)
cyclo[NP(OMe) ₂] ₅	+318.9	(h)
cyclo[NP(NMe ₂) ₂] ₅	+317.0 (ring)	(h)
cyclo[NPCl ₂] ₅	+253.1	(h)
cyclo[NP(OMe) ₂] ₆	+320.0	(h)
cyclo[NP(OMe ₂) ₂] ₆	+317.6 (ring)	(h)
cyclo[NPCl ₂] ₆	+253.3	(h)

For additional data see ref. 1, Table 127 therein

(a) Data from ref. 473; ¹⁵N-labelled compounds, ¹⁵N spectra, 20.282 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(b) Data from ref. 105; details as in note (a), but 9.12 MHz spectra, field perpendicular to sample tube.

(c) Data from ref. 660; details as in note (b).

(d) Data from ref. 622; details as in note (b).

(e) Data from ref. 474; details as in note (b).

(f) Data from ref. 473; details as in note (b).

(g) Data from ref. 49; details as in note (b).

(h) Data from ref. 475; details as in note (b).

TABLE 106

Nitrogen shieldings in imino moieties of isoamide and isothioamide structures and in related immonium ions

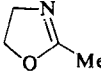
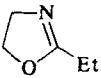
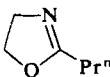
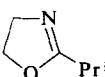
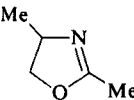
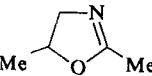
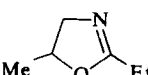
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane		Notes
		imino moiety =N-R	immonium moiety =NR ₂ ⁺	
Isoamide structures, $R-C=N-R$, $R-C=NR_2^+$ $\begin{array}{c} OR \\ \\ R-C=N-R \end{array}$ $\begin{array}{c} OR \\ \\ R-C=NR_2^+ \end{array}$ and their vinylogues $Me-C=NMe$ $\begin{array}{c} OMe \\ \\ Me-C=NMe \end{array}$				
	1:1 v/v in acetone	+155.5		(a)
	inf. dil. in acetone	+155.2		(b)
	neat liquid	+155.8		(a)
	in DMSO-d ₆	+154.5		(c)
	neat liquid	+162.6		(c)
	in DMSO-d ₆	+161.9		(c)
	in CDCl ₃	+166.6		(c)
	neat liquid	+164.5		(c)
	in DMSO-d ₆	+163.3		(c)
	in CDCl ₃	+168.9		(c)
	neat liquid	+164.5		(c)
	in DMSO-d ₆	+163.3		(c)
	in CDCl ₃	+168.9		(c)
	neat liquid	+166.4		(c)
	in DMSO-d ₆	+164.9		(c)
	in CDCl ₃	+171.4		(c)
	in DMSO-d ₆	+134.8		(c)
	in CDCl ₃	+139.3		(c)
	neat liquid	+163.2		(c)
	in DMSO-d ₆	+162.3		(c)
	in CDCl ₃	+167.7		(c)
	neat liquid	+161.8		(c)
	in DMSO-d ₆	+161.0		(c)
	in CDCl ₃	+167.4		(c)

TABLE 106—*cont.*

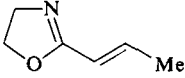
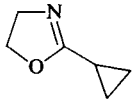
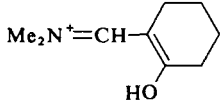
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane		Notes
		imino moiety $=N-R$	immonium moiety $=NR_2^+$	
	in DMSO- d_6	+157.6		(c)
	neat liquid	+172.6		(c)
	in DMSO- d_6	+170.7		(c)
	in $CDCl_3$	+176.5		(c)
$Me_2N^+=CHOMe$ ($MeSO_4^-$)	2.5 M in CH_2Cl_2		+239.4	(d)
(FSO_3^-)	2 M in $CDCl_3$		+236.0	(d, e)
$Me_2N^+=CH-CH=CH-OMe$ (FSO_3^-)	2 M in $CDCl_3$		+224.0	(e)
$Me_2N^+=CH-CH=CH-OEt$ (Cl^-)	2 M in $CDCl_3$		+220.1	(e)
$Et_2N^+=CH-CH=C(Me)-OH$ (CF_3COO^-)	in TFA-d		+203.0	(d)
			(<i>trans-s-cis</i>)	
			+205.2	(d)
$Me_2N^+=CH-CH=C(Pr^i)-OH$ (CF_3COO^-)	in TFA-d		(<i>trans-s-skew</i>)	
			+230.9	(d)
			(<i>trans-s-cis</i>)	
$Et_2N^+=CH-CH=C(Pr^i)-OH$ (CF_3COO^-)	in TFA-d		+233.7	(d)
			(<i>trans-s-skew</i>)	
			+202.1	(d)
$Me_2N^+=CH-CH=C(Bu^t)-OH$ (CF_3COO^-)	in TFA-d		(<i>trans-s-cis</i>)	
			+206.6	(d)
			(<i>trans-s-skew</i>)	
$Me_2N^+=CH-CH=C(Bu^t)-OH$ (CF_3COO^-)	in TFA-d		+227.7	(d)
$Me_2N^+=CH-CH=C(Me)-OMe$ (CF_3COO^-)	in TFA-d		+225.0	(d)
$Me_2N^+=CH-CH=C(Ph)-OH$ (CF_3COO^-)	in TFA-d		+228.3	(d)
 (CF_3COO^-)	in TFA-d		+227.0	(d)
$Me_2N^+=C(Me)-OMe$ (FSO_3^-)	2 M in CH_2Cl_2		+239.0	(f)
$PhCH_2NH^+=CH-OMe$ (FSO_3^-)	4 M in CD_3CN		+217.5	(g)

TABLE 106—*cont.*

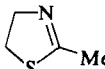
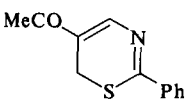
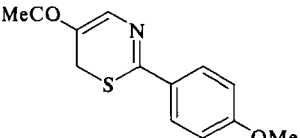
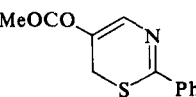
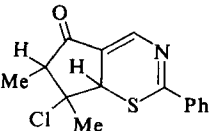
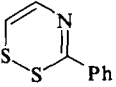
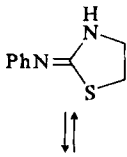
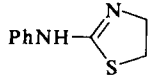
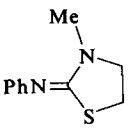
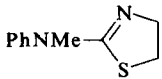
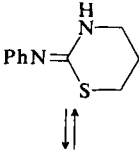
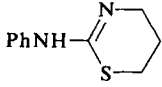
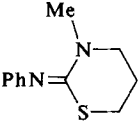
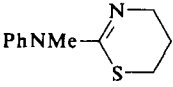
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane		Notes
		imino moiety =N-R	immonium moiety =NR ₂ ⁺	
Isothioamide structures, R-C=N-R, R-C=NR ₂ ⁺ SR SR				
	in DMSO-d ₆ in CDCl ₃	+79.3 +87.9		(c) (c)
	1 M in CDCl ₃	+87.6		(h)
	1 M in CDCl ₃	+88.2		(h)
	1 M in CDCl ₃	+90.8		(h)
	1 M in CDCl ₃	+94.4		(h)
	1 M in CDCl ₃	+90.0		(h)
Me ₂ N ⁺ =CH-SMe				
(FSO ₃ ⁻)	3 M in MeCN		+205.7	(f)
(MeSO ₄ ⁻)	4 M in MeCN		+204.5	(f)
(Br ⁻)	4 M in MeCN		+205.9	(f)
Me ₂ N ⁺ =CCl-SMe				
(CF ₃ COO ⁻)	2 M in CH ₂ Cl ₂		+260.5	(f)
(Cl ⁻)	2 M in CH ₂ Cl ₂		+258.0	(f)

TABLE 106—*cont.*

Compound	Solution or state	Nitrogen shielding referred to neat nitromethane		Notes
		imino moiety =N—R	immonium moiety =NR ₂ ⁺	
	0.5 M in CDCl ₃	+206.0 (<i>exo</i>)		(i)
		+242.5 (<i>endo</i>)		(i)
	0.5 M in CDCl ₃	+156.2 (<i>exo</i>)		(i)
		+296.7 (<i>endo</i> , NMe)		(i)
	0.5 M in CDCl ₃	+292.4 (<i>exo</i> , NMe)		(i)
		+155.2 (<i>endo</i>)		(i)
	0.5 M in CDCl ₃	+182.6 (<i>exo</i>)		(i)
		+253.9 (<i>endo</i>)		(i)
	0.5 M in CDCl ₃	+143.9 (<i>exo</i>)		(i)
		+298.6 (<i>endo</i> , NMe)		(i)
	0.5 M in CDCl ₃	+286.6 (<i>exo</i> , NMe)		(i)
		+161.5 (<i>endo</i>)		(i)

(a) Data from ref. 230; high-precision ¹⁴N CW spectra, 4.3342 MHz, concentric spherical sample/standard containers in order to eliminate bulk-susceptibility effects, differential-saturation technique with full lineshape fitting, referred to neat nitromethane.

TABLE 106—*cont.*

(b) Data from ref. 230; ^{15}N natural abundance spectrum, 18.25 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(c) Data from ref. 120; ^{15}N natural abundance spectra, 10.1 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; $\text{Cr}(\text{acac})_3$ added as relaxation reagent.

(d) Data from ref. 122; ^{15}N natural abundance INEPT spectra, 20.28 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(e) Data from ref. 619; ^{15}N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NO_3^- standard calibrated (+1.5 ppm) against neat nitromethane, conversion scheme IV (Table 4); $\text{Cr}(\text{acac})_3$ added as relaxation reagent.

(f) Data from ref. 282; details as in note (e).

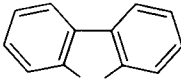
(g) Data from ref. 118; ^{15}N -enriched (30%) compounds, ^{15}N spectra (selective population-transfer technique), 25.32 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(h) Data from ref. 661; details as in note (e), but calibration +3.1 ppm against neat nitromethane.

(i) Data from ref. 460; ^{15}N natural abundance spectra, 10.04 MHz, field perpendicular to sample tube, originally referred to aqueous KNO_3 , and originally converted to neat nitromethane standard, uncorrected for bulk-susceptibility effects.

TABLE 107

Nitrogen shieldings in some ketenimines

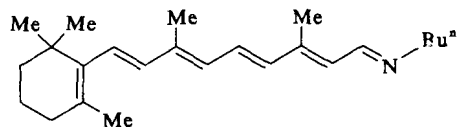
$\begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{C}=\text{N}-\text{R}^3 \\ \diagup \\ \text{R}^2 \end{array}$			
(1–2 M solutions in CH_2Cl_2 , 10 °C)			
Substituents			Nitrogen shielding referred to neat nitromethane
R^1	R^2	R^3	
H	Me	Ph	+174.7
H	Ph	Ph	+166.7
Me	Ph	Ph	+165.7
Me	Me	Ph	+270.9
Ph	Ph	Ph	+168.3
Ph	Ph	Bu^n	+173.4
Me	Me	Bu^n	+185.7
Me	Me	<i>p</i> -Me.C ₆ H ₄	+172.6
Me	Me	<i>p</i> -Cl.C ₆ H ₅	+173.2
Me	Me	<i>p</i> -MeO.C ₆ H ₄	+174.0
			Ph
			+160.6

Data from ref. 360; ^{15}N -labelled and unlabelled compounds, ^{15}N spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO_3 , +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

TABLE 108

Nitrogen shieldings in some imines, immonium cations and related structures

Imine or immonium ion	Solution	Nitrogen shielding referred to neat nitromethane		Notes
		imino moiety $=N-R$	immonium moiety $=N^+H-R$ or $=N^+R_2$	
$(E)-Pr^n-CH=N-Bu^n$	0.5 M in CH_2Cl_2	+52.6		(a)
its hydrochloride	0.5 M in CH_2Cl_2		+163.1	(a)
$(E-E)-Me-CH=CH-CH=N-Bu^n$	0.5 M in CH_2Cl_2	+52.1		(a)
its hydrochloride	0.5 M in CH_2Cl_2		+181.7	(a)
$(E-E-E)-Me-CH=CH-CH=CH-CH=N-Bu^n$ its hydrochloride	in cyclohexane	+37		(a)
	in acetone	+41		(a)
	in MeCN	+44		(a)
	0.5 M in CH_2Cl_2	+44.6		(a)
	in $CDCl_3$	+52		(a)
	in MeOH	+66		(a)
	in CF_3CH_2OH	+81		(a)
	in $(CF_3)_2CHOH$	+83		(a)
	in acetone		+184	(a)
	in MeCN		+183	(a)
	0.5 M in CH_2Cl_2		+183.6	(a)
	in $CDCl_3$		+186	(a)
	in MeOH		+192	(a)
	in CF_3CH_2OH		+194	(a)
	in $(CF_3)_2CHOH$		+196	(a)



0.5 M in CH_2Cl_2

+43.1

(a)

its hydrochloride
 $Me_2C=N-CH_2CH_2OH$

0.5 M in CH_2Cl_2

+190.0

(a)

neat liquid

+74.5

(b)

in $DMSO-d_6$

+69.3

(b)

in $CDCl_3$

+76.4

(b)

neat liquid

+73.5

(b)

in $DMSO-d_6$

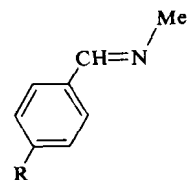
+70.8

(b)

in $CDCl_3$

+74.0

(b)



R

2 M in $CDCl_3$

NMe_2

+76.5

(c)

OMe

+67.7

(c)

Me

+63.3

(c)

H

+59.8

(c)

Br

+57.2

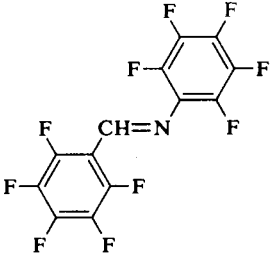
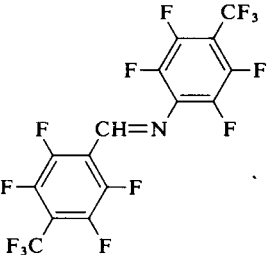
(c)

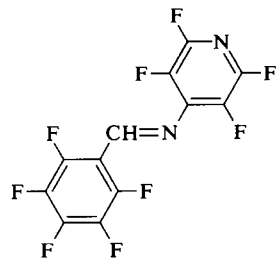
NO_2

+44.0

(c)

TABLE 108—*cont.*

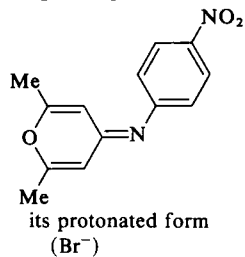
Imine or immonium ion	Solution	Nitrogen shielding referred to neat nitromethane		Notes
		imino moiety $=N-R$	immonium moiety $=N^+H-R$ or $=N^+R_2$	
	satd. in CH_2Cl_2	+64.4		(d)
its protonated form	in FSO_3H		+214.5	(d)
	satd. in CH_2Cl_2	+57.5		(d)
its protonated form	in FSO_3H		+214.5	(d)



satd. in CH_2Cl_2

+58.6
(CH=N)

(d)



in CDBr_3
in CD_3CN
in CD_3NO_2

+117.8
+115.1
+118.0

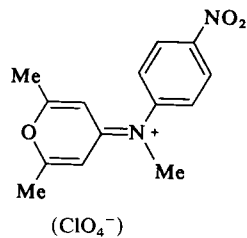
(e)
(e)
(e)

(ClO_4^-)

in CDBr_3
in CD_3CN
in CD_3NO_2
in CD_3CN
in CD_3NO_2

+235.1
+240.6
+240.4
+248.1
+252.6

(e)
(e)
(e)
(e)
(e)

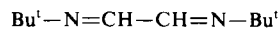


in CD_3CN
in CD_3NO_2
in CD_3CN

+254.2
+255.3
+254.0

(e)
(e)
(e)

(I^-)

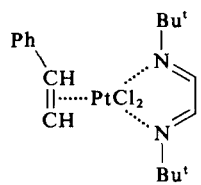
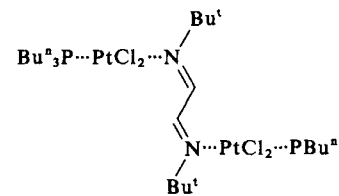
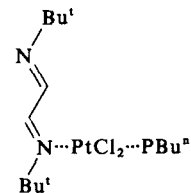


in CD_2Cl_2

-2.4

(f)

TABLE 108—*cont.*

Imine or immonium ion	Solution	Nitrogen shielding referred to neat nitromethane		Notes
		imino moiety $=N-R$	immonium moiety $=N^+H-R$ or $=N^+R_2$	
	in acetone- d_6 ($-80^\circ C$)	$\left\{ \begin{array}{l} +35.2 \\ +49.9 \end{array} \right.$		(f) (f)
	in acetone- d_6 ($-80^\circ C$)	+56.9		(f)
	acetone- d_6 ($-80^\circ C$)	$\left\{ \begin{array}{l} -17.1 \\ +69.4 \end{array} \right.$		(f) (f)

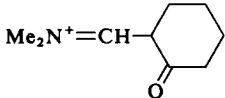
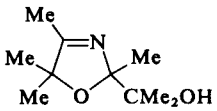
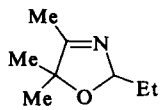
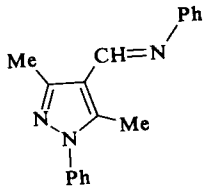
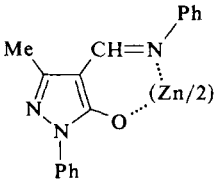
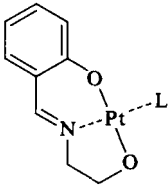
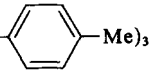
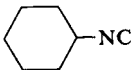
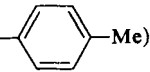
$\text{Me}_2\text{N}^+=\text{CH}_2$ (CF_3COO^-)	2 M in CDCl_3	+156.5	(g)
$\text{Me}_2\text{N}^+=\text{CH}-\text{CH}(\text{Me})-\text{C}(=\text{O})\text{Me}$ (CF_3COO^-)	in TFA-d	+175.5	(h)
$\text{Me}^2\text{N}^+=\text{CH}-\text{CH}(\text{Me})-\text{C}(=\text{O})\text{Et}$ (CF_3COO^-)	in TFA-d	+176.0	(h)
$\text{Me}_2\text{N}^+=\text{CHCl}$ (OPOCl_2^-)	2 M in CDCl_3	+174.4	(h, i)
(Cl^-)	2 M in CDCl_3	+171.4	(h, i)
$\text{Me}_2\text{N}^+=\text{CH}-\text{CH}=\text{CHCl}$ (OPOCl_2^-)	2 M in CDCl_3	+197.7	(i)
 (CF_3COO^-)	in TFA-d	+173.0	(h)
	in DMSO-d ₆	+66.6	(j)
	in CDCl_3	+75.0	(j)
	in DMSO-d ₆	+73.3	(j)
	in CDCl_3	+75.2	(j)
	in CDCl_3	+69.0 ($\text{CH}=\text{N}$)	(k)

TABLE 108—cont.

Imine or immonium ion	Solution	Nitrogen shielding referred to neat nitromethane		Notes
		imino moiety $=N-R$	immonium moiety $=N^+H-R$ or $=N^+R_2$	
	in $CDCl_3$		185.1 (N—Zn)	(k)
$Me_2N^+=CH-NMe_2$ $\updownarrow$ (ClO_4^-) $Me_2N-CH=NMe_2^+$ $Me_2N^+=CH-CH=CH-NMe_2$ $\updownarrow$ (ClO_4^-) $Me_2N-CH=CH-CH=NMe_2^+$ $Me_2N^+=CH-CH=CH-CH=CH-NMe_2$ $\updownarrow$ $Me_2N-CH=CH-CH=CH-CH=NMe_2^+$ $\updownarrow$ (ClO_4^-) $Me_2N^+=CH-(CH=CH)_3-NMe_2$ $\updownarrow$ (Cl^-) $Me_2N-(CH=CH)_3-CH=NMe_2^+$ $Me_2N^+=C(Cl)-NMe_2$ $\updownarrow$ ($OPOCl_2^-$) $Me_2N-C(Cl)=NMe_2^+$	in DMSO- d_6		+282.5	(l)
	in DMSO- d_6		+264.5	(l)
	in DMSO- d_6		+264.6	(l)
	in DMSO- d_6		+264.4	(l)
	in CH_2Cl_2		+269.0	(m)

$\text{Bu}^n_2\text{N}^+=\text{C}(\text{Cl})-\text{NBu}^n_2$ $\updownarrow$ $\text{Bu}^n_2\text{N}-\text{C}(\text{Cl})=\text{NBu}^n_2^+$	in CH_2Cl_2	+243.8	(m)
$\text{Me}_2\text{N}^+=\text{CH}-\text{CH}=\text{C}(\text{Cl})-\text{NMe}_2$ $\updownarrow$ $\text{Me}_2\text{N}-\text{CH}=\text{CH}-\text{C}(\text{Cl})=\text{NMe}_2^+$	2 M in CDCl_3	+248.1 (CH=N) +258.3 (CCl=N)	(g, i) (g, i)
$\text{Me}_2\text{N}^+=\text{C}(\text{Et})-\text{C}(\text{Me})=\text{C}(\text{Cl})-\text{NMe}_2$ (OPOCl_2^-) (steric hindrance forces non-coplanarity)	2 M in CDCl_3	+191.4 ($\text{Me}_2\text{N}^+=$) +322.8 ($-\text{NMe}_2$)	(g, i) (g, i)
$\text{Me}_2\text{N}^+=\text{CH}-\text{C}(\text{Me})=\text{C}(\text{Cl})-\text{NMe}_2$ $\updownarrow$ $\text{Me}_2\text{N}-\text{CH}=\text{C}(\text{Me})-\text{C}(\text{Cl})=\text{NMe}_2^+$	1 M in CDCl_3	+244.2 (CH=N) +262.5 (CCl=N)	(g) (g)
$\text{Me}_2\text{N}^+=\text{C}(\text{Me})-\text{CH}=\text{C}(\text{Cl})-\text{NMe}_2$ $\updownarrow$ $\text{Me}_2\text{N}-\text{C}(\text{Me})=\text{CH}-\text{C}(\text{Cl})-\text{NMe}_2^+$	1 M in CDCl_3	+239.7 (CMe=N) +264.1 (CCl=N)	(g) (g)
$\text{Me}_2\text{N}^+=\text{C}(\text{CH}_2\text{Ph})-\text{C}(\text{Ph})=\text{C}(\text{Cl})-\text{NMe}_2$ (OPOCl_2^-)	1 M in CDCl_3	+210.0 ($\text{Me}_2\text{N}^+=$) +273.5 ($-\text{NMe}_2$)	(g) (g)
$\begin{array}{c} \text{R} \\ \\ \text{Me}_2\text{N}^+=\text{C} \\ / \quad \backslash \\ \text{CH} \quad \text{C}-\text{NMe}_2 \\ \\ \text{R} \end{array}$ $\longleftrightarrow$ $\begin{array}{c} \text{R} \\ \\ \text{Me}_2\text{N}-\text{C} \\ / \quad \backslash \\ \text{CH} \quad \text{C}=\text{NMe}_2^+ \\ \\ \text{R} \end{array}$ (OPOCl₂[−])			
R			
Me	1 M in CDCl_3	+272.8	(g)
Et	1 M in CDCl_3	+271.6	(g)
Ph	1 M in CDCl_3	+269.8	(g)

TABLE 108—*cont.*

Imine or immonium ion	Solution	Nitrogen shielding referred to neat nitromethane		Notes
		imino moiety =N—R	immonium moiety =N ⁺ H—R or =N ⁺ R ₂	
				
PBu ⁿ ₃	in CDCl ₃		+142.7	(o)
P(OEt) ₃	in CDCl ₃		+145.9	(o)
P() ₃	in CDCl ₃		+146.1	(o)
AsBu ⁿ ₃	in CDCl ₃		+152.4	(o)
 -NC	in CDCl ₃		+161.5	(o)
As() ₃	in CDCl ₃		+156.4	(o)
	in DMSO		+157.5	(o)
Me ₂ SO	in CDCl ₃		+166.9	(o)
	in DMSO		+167.3	(o)
SbPh ₃	in CDCl ₃		+157.4	(o)
piperidine	in CDCl ₃		+179.3	(o)

$\text{H}_2\text{N}(\text{CH}_2)_5\text{Me}$	in CDCl_3	+178.7	(o)
		+386.4 (NH_2)	(o)
pyridine	in CDCl_3	+182.4	(o)
$\text{R}_2\text{N}^+=\text{CR}_2$ (?) moieties in polymer obtained from methyl α -isocyano-propionate	in CDCl_3	ca. +154	(n)

For additional data see ref. 1, Table 128 therein

(a) Data from ref. 362; ^{15}N natural abundance spectra, 10.14 MHz, field perpendicular to sample tube, originally referred to NO_3^- in 2 M NH_4NO_3 in 1.5 M HNO_3 , +5.6 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); measurements at 0 °C, $\text{Cr}(\text{acac})_3$ added as relaxation reagent.

(b) Data from ref. 120; ^{15}N natural abundance spectra, 10.1 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; $\text{Cr}(\text{acac})_3$ added as relaxation reagent.

(c) Data from ref. 610; ^{15}N natural abundance spectra, 10.13 MHz, field perpendicular to sample tube, originally referred to internal CD_3CN standard taken at +137.2 ppm from nitromethane; the latter value, however, represents acetonitrile dissolved in nitromethane (see ref. 1, Table 108 therein); the data were recalculated using neat acetonitrile shielding, +135.8 ppm from neat nitromethane, to yield values that do not contain bulk-susceptibility effects (Table 6).

(d) Data from refs 435, 624; ^{15}N -labelled compounds, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to liquid NH_3 , +380.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(e) Data from ref. 461; ^{15}N -labelled amino moiety, ^{15}N spectra, 9.06 MHz, other details as in note (d).

(f) Data from ref. 410; ^{15}N -labelled compound, ^{15}N spectra, 25.34 MHz, field parallel to sample tube, originally referred to aqueous NH_4Cl , +352.9 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

(g) Data from ref. 282; ^{15}N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NO_3^- standard calibrated (+1.5 ppm) against neat nitromethane, conversion scheme IV (Table 4); $\text{Cr}(\text{acac})_3$ added as relaxation reagent.

(h) Data from ref. 122; ^{15}N natural abundance spectra, 20.28 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(i) Data from ref. 619; ^{15}N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, details as in note (g).

(j) See note (b).

(k) Data from ref. 452; ^{15}N -labelled imino moiety, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to aqueous KNO_2 , -228.9 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); originally reported relative to what was considered as NH_4Cl standard taken at +590.7 ppm from KNO_2 , but this corresponds to NH_4NO_3 rather than NH_4Cl (Table 6).

(l) Data from ref. 449; ^{15}N -labelled compounds, ^{15}N spectra, details as in note (k).

(m) Data from ref. 637; details as in note (g), but referred originally to neat nitromethane, uncorrected for bulk-susceptibility effects.

(n) Data from ref. 308; ^{15}N -labelled substrate, ^{15}N spectrum, 20.2 MHz, field parallel to sample tube, originally referred to NO_3^- in aqueous NH_4NO_3 , +4.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

(o) Data from ref. 409; ^{15}N -labelled imino moiety, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to aqueous $\text{NH}_4\text{Cl}/\text{HCl}$, +352 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

Table 109

Nitrogen shieldings in imino and immonium moieties in bacteriorhodopsin and imino-derivatives of retinal

Sample (solid state)	Moiety	Isotropic nitrogen shielding from CP-MASS spectra (in ppm, referred to neat liquid nitromethane)	Nitrogen shielding tensor from powder spectra (in ppm, referred to neat liquid nitromethane)			
			$\text{Tr}(\sigma)/3$	σ_{11}	σ_{22}	σ_{33}
Retinal reacted with Bu^nNH_2	$-\text{C}=\text{NBu}^n$	+37.6	+38.0	+341.4	+43.3	-270.2
its hydrochloride	$-\text{C}=\text{NH}^+\text{Bu}^n$ (Cl^-)	+181.2	+180.4	+325.6	+158.3	+56.6
its hydrobromide	$-\text{C}=\text{NH}^+\text{Bu}^n$ (Br^-)	+186.8	+187.4	+326.2	+169.6	+66.3
its hydroiodide	$-\text{C}=\text{NH}^+\text{Bu}^n$ (I^-)	+198.5	+198.3	+326.6	+189.1	+79.1

Bacteriorhodopsin
 of purple membrane
 of Halobacterium
 halobium grown on
 ϵ - ^{15}N labelled
 lysine

$-\text{C}=\text{NH}^+\text{R}$	+208.0
	+201.3
amide backbone	+259.3
terminal NH_3^+ of lysine	+344.5

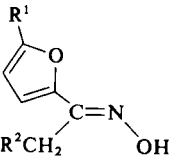
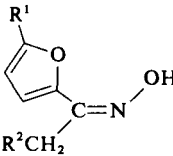
Data from ref. 187, ^{15}N labelled substances, solid state ^{15}N spectra at 29,8 MHz, originally referred to satd. aqueous NH_4Cl , +352.9 ppm from neat nitromethane, uncorrected for bulk susceptibility effects; see also ref. 361.

TABLE 110

Nitrogen shieldings in some oximes, their ethers and protonated forms

Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
$\begin{array}{c} \text{Me} \\ \diagdown \\ \text{C}=\text{N} \\ \diagup \quad \diagdown \\ \text{Me} \quad \text{OH} \end{array}$	melt, 70–140 °C in 1-octanol, 80 to 150 °C in MeOH, –80 °C	+44.0 (mean value) +40.1 (mean value) +44.7 (mean value)	(a) (a) (a)
its protonated form ($pK_a = 1.65$)	in H ₂ O, 13–60 °C 0.4 M in 1 M aqueous NaCl	+53.3 (mean value) +55.8	(a) (b)
$\begin{array}{c} \text{Cyclopentyl} \\ \diagdown \\ \text{C}=\text{N} \\ \diagup \quad \diagdown \\ \text{OH} \end{array}$	0.4 M in 1 M aqueous NaCl	+58.7	(b)
its protonated form ($pK_a = 1.6$)	in aqueous HCl/NaCl	+128 ± 11	(b)
$\begin{array}{c} \text{Me} \\ \diagdown \\ \text{C}=\text{N} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{OH} \end{array} \quad (E\text{-isomer})$	in H ₂ O/KCl, 0–95 °C	+38.1 (mean value)	(a)
$\begin{array}{c} \text{H} \\ \diagdown \\ \text{C}=\text{N} \\ \diagup \quad \diagdown \\ \text{Me} \quad \text{OH} \end{array} \quad (Z\text{-isomer})$	in H ₂ O/KCl, 0–95 °C	+34.1 (mean value)	(a)
$\begin{array}{c} \text{Ph} \\ \diagdown \\ \text{C}=\text{N} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{OH} \end{array} \quad (E\text{-isomer})$	neat liquid, 30–150 °C in MeOH, –80–20 °C in 1-octanol, 30–150 °C	+26.6 (mean value) +17.2 (mean value) +12.8 (mean value)	(a) (a) (a)
$\begin{array}{c} \text{Ph} \\ \diagdown \\ \text{C}=\text{N} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{OMe} \end{array} \quad (E\text{-isomer})$	in MeOH, 0–60 °C in 1-octanol, 30–115 °C	–2.9 (mean value) –5.8 (mean value)	(a) (a)
$\begin{array}{c} \text{Me}_3\text{N}^+\text{CH}_2 \\ \diagdown \\ \text{C}=\text{N} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{OH} \end{array}$	in H ₂ O	–3.1 (N=OH)	(a)

TABLE 110—*cont.*

Compound		Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
 (<i>E</i> -isomer)				
 (<i>Z</i> -isomer)				
R ¹	R ²			
Me	H	in acetone	+27.9 (100% <i>E</i>)	(c)
its protonated form		in acetone	+129.9 (<i>E</i>)	(c)
		+CF ₃ COOH	+153.9 (<i>Z</i>)	(c)
		(2:1)		
H	H	in acetone	+21.8 (100% <i>E</i>)	(c)
its protonated form		in acetone	+104.7 (<i>E</i>)	(c)
		+CF ₃ COOH	+134.6 (<i>Z</i>)	(c)
		(2:1)		
Br	H	in acetone	+8.5 (<i>E</i> , 85%)	(c)
NO ₂	H	in acetone	+5.7 (<i>E</i> , 85%)	(c)
NO ₂	Cl	in acetone	+0.2 (<i>E</i> , 80%)	(c)
			+0.8 (<i>Z</i> , 20%)	(c)
NO ₂	Br	in acetone	-1.6 (<i>E</i> , 75%)	(c)
			-1.3 (<i>Z</i> , 25%)	(c)

For additional data see ref. 1, Table 129 therein

(a) Data from ref. 247; ¹⁵N-labelled oxime moiety, ¹⁵N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to 2 M PhNO₂ in DMSO, +9.3 ppm from neat nitromethane (as can be inferred from 0.3 M aqueous KNO₃ shielding reported there, -5.8 ppm from the standard used, +3.5 ppm from neat nitromethane, Table 6), conversion scheme II (Table 4).

(b) Data from ref. 278; ¹⁵N-labelled compounds, ¹⁵N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to 2 M HNO₃, +5.1 ppm from neat nitromethane (as can be inferred from Table 6), conversion scheme II (Table 4); reported shieldings were calculated from ¹⁵N NMR titration curves.

(c) Data from ref. 365; ¹⁵N-labelled oxime moiety, ¹⁵N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

Table 111
Nitrogen shieldings in some nitrones

Compound	Solution	Nitrogen shielding referred to neat nitromethane
PhCH=N(O)Me	satd. in acetone	+104
PhCH=N(O)Bu^t	satd. in acetone	+72
PhCH=N(O)Ph	satd. in acetone	+95
PhC(Me)=N(O)Me	satd. in acetone	+109
$\text{Ph}_2\text{C=N(O)Ph}$	satd. in acetone	+111
$\text{PhCH=N(O)CH}_2\text{Ph}$	satd. in acetone	+95

See ref. 1, p. 382, Table 130 and references therein.

TABLE 112

Nitrogen shieldings in various sulphur-nitrogen compounds and ions containing sulphur-nitrogen multiple bonds

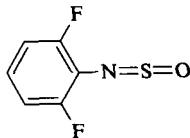
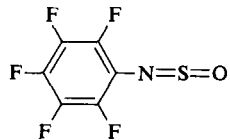
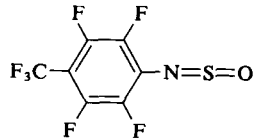
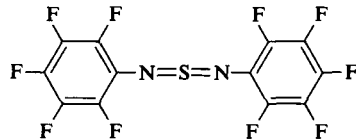
Compound or ion	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
Sulphonylamines, $\text{RN}=\text{S}=\text{O}$			
Me-N=S=O	in Et ₂ O	+54.8	(a)
Et-N=S=O	in Et ₂ O	+37.4	(a)
Pr ⁱ -N=S=O	in Et ₂ O	+26.6	(a)
Bu ⁱ -N=S=O	in Et ₂ O	+27.4	(a)
Ph-N=S=O	in Et ₂ O	+62.1	(a)
various alkyl and aryl sulphonylamines	various	+25 to +79	(a)
	satd. in CH ₂ Cl ₂	+86.4	(b)
	satd. in CH ₂ Cl ₂	+87.9	(b)
	satd. in CH ₂ Cl ₂	+88.2	(b)
Sulphodiimides, $\text{RN}=\text{S}=\text{NR}$			
PhN=S=NPh	various	+83 to +120	(a)
	satd. in CH ₂ Cl ₂	+107.2	(b)
Me ₃ Si-N=S=N-SiMe ₃	neat liquid	+58.9	(c)

TABLE 112—*cont.*

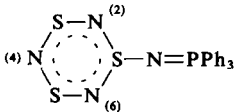
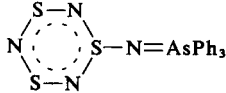
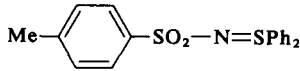
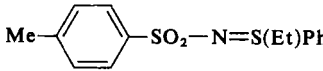
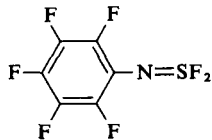
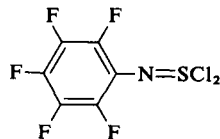
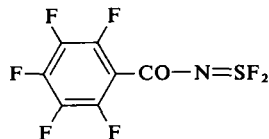
Compound or ion	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
	in CHCl ₃	+113.9	(c)
	in CHCl ₃	+97.7 (4-N) +176.7 (2,6-N) +268.2 (N=P)	(c) (c) (c)
	in CHCl ₃	+97.6 (4-N) +170.6 (2,6-N) +275.3 (N=As)	(c) (c) (c)
Sulphilimines and related structures, R—N=SR ₂			
HN=SPh ₂	in CDCl ₃	+309.5	(d)
HN=SPh ₂ ·H ₂ O	in CDCl ₃	+335.5	(d)
	in CDCl ₃	+266.0	(d)
	in CDCl ₃	+272.7	(d)
	satd. in CH ₂ Cl ₂	+247.3	(b)
	satd. in CH ₂ Cl ₂	+112.0	(b)
	satd. in CH ₂ Cl ₂	+199.0	(b)

TABLE 112—*cont.*

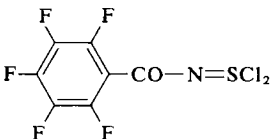
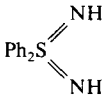
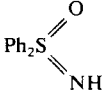
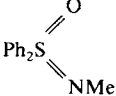
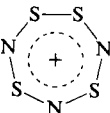
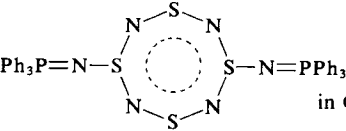
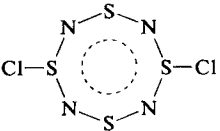
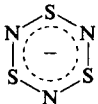
Compound or ion	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
	satd. in CH_2Cl_2	+66.2	(b)
Sulphone imines,			
			
	in CDCl_2	+295.1	(d)
	in CDCl_3	+293.6	(d)
	in CDCl_3	+301.6	(d)
Some miscellaneous structures			
 (S_4N_3^+)	in aqueous HNO_3	+4.1 (N—S—S—N) +11.8 (S—N—S)	(c) (c)
	in CHCl_3	+220.4 +226.4 +294.0 (P=N) +299.1 (P=N) (axial-equatorial inequivalence)	(c) (c) (c) (c)
	in CHCl_3	+148.7	(c)

TABLE 112—*cont.*

Compound or ion	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
S_4N_4	in $CHCl_3$	+257.0	(c)
$Cl_3S_3N_3$	in $CHCl_3$	+261.7	(c)
S_4N_5Cl	in $HCONMe_2$	$\begin{cases} +155.1 \text{ (four Ns)} \\ +340.9 \text{ (single N)} \end{cases}$	(c)
$Ph_3P=N-S \begin{array}{c} \diagup \quad \diagdown \\ N=S=S \end{array}$	in $CHCl_3$	+293.3 (P=N)	(c)
		-91.8 (S-N=S)	(c)
$S_4N_5^-$	in CH_2Cl_2	+240.5 (four Ns)	(e)
		+325.9 (single N)	(e)
	in $CHCl_3$	+241.5 (four Ns)	(c)
		+326.9 (single N)	(c)
	in $CHCl_3$	+231.8	(c)
$(S_3N_3^-)$			
S_4N^-	in $CHCl_3$	+167.4	(c)
$S_4N_5O^-$	in CH_2Cl_2	+232.3 (two Ns)	(e)
		+251.2 (two Ns)	(e)
		+276.2 (single N)	(e)
$S_3N_3O^-$	in CH_2Cl_2	+91.3 (single N)	(e)
		+154.8 (two Ns)	(e)
$S_3N_3O_2^-$	in CH_2Cl_2	+26.9 (single N)	(e)
		+165.0 (two Ns)	(e)

For additional data see footnote (a)

(a) See ref. 1, Table 131 and references therein.

(b) Data from ref. 624; ^{15}N -labelled compounds, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to liquid NH_3 , +380.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(c) Data from ref. 367; ^{15}N -labelled compounds, ^{15}N spectra, 20.27 MHz, field perpendicular to sample tube, originally referred to 2 M NH_4NO_3 standard which was originally calibrated against neat nitromethane, but results were reported relative to NH_3 standard taken at +380.2 ppm from neat nitromethane, conversion scheme IV (Table 4).

(d) Data from ref. 368; ^{15}N natural abundance spectra, 20.27 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(e) Data from ref. 366; details as in note (c); $Cr(acac)_3$ added as relaxation reagent.

TABLE 113

Nitrogen shieldings in some nitramines, nitroguanidines and related structures

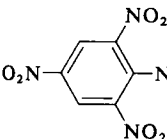
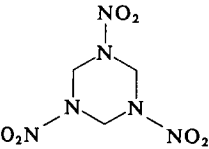
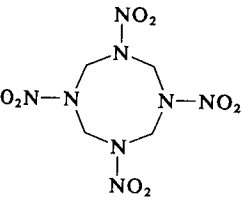
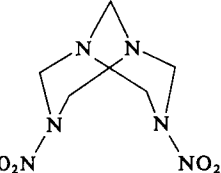
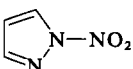
Compound	Solution	Nitrogen shielding referred to neat nitromethane			Notes
		nitramine moiety			
		R ₂ N or R=N	N-nitro group	other moieties	
Me ₂ N—NO ₂	in acetone	+215.6	+23.6		(a)
 N—NO ₂	in acetone	+196.0	+22.0		(a)
Et ₂ N—NO ₂	in CDCl ₃	+192.6	+27.6		(b)
 N(Me)—NO ₂	in acetone	+208.8	+23.1		(a)
	in acetone	+198.1	+32.9		(a)
	in acetone	+199.1	+34.7		(a)
	in acetone	+203.7	+25.3	+328.7	(a)
 N—NO ₂	in DMSO +Cr(acac) ₃	+108.5	+59.6	+84.6	(c)
	in CDCl ₃ +Cr(acac) ₃	+109.1	+59.0	+86.1	(c)

TABLE 113—*cont.*

Compound	Solution	Nitrogen shielding referred to neat nitromethane			Notes
		nitramine moiety			
		R ₂ N or R=N	N-nitro group	other moieties	
$\begin{array}{c} \text{NNO}_2 \\ \\ \text{H}_2\text{N}-\text{C}-\text{NHMe} \end{array}$	2.5 M in DMSO	+140.5	+11.0	+297.2 (NH ₂ , NHMe)	(d)
$\begin{array}{c} \text{NNO}_2 \\ \\ \text{H}_2\text{N}-\text{C}-\text{NMe}_2 \end{array}$	1 M in DMSO	+138.9	+12.3	$\begin{cases} +295.7 \text{ (NMe}_2\text{)} \\ +303.4 \text{ (NH}_2\text{)} \end{cases}$	(d)
$\begin{array}{c} \text{NNO}_2 \\ \\ \text{H}_2\text{N}-\text{C}-\text{N(NO)Me} \end{array}$	3 M in DMSO	+128.6	+14.8	$\begin{cases} +286.1 \text{ (NH}_2\text{)} \\ +121.6 \text{ (NMe)} \\ -186.6 \text{ (NO)} \end{cases}$	(d)

For additional data see ref. 1, Table 132 therein

(a) Data from ref. 462; ¹⁵N natural abundance spectra, 20.27 MHz, field parallel to sample tube, originally referred to neat PhNO₂, +9.9 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

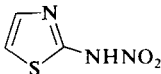
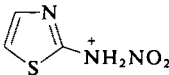
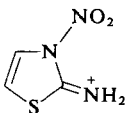
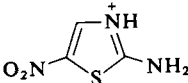
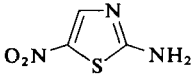
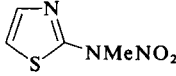
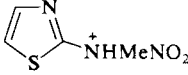
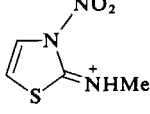
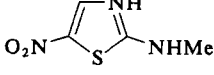
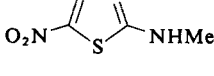
(b) ¹⁵N natural abundance spectrum, 9.12 MHz, field perpendicular to sample tube, originally referred to NO₃⁻ standard calibrated (+1.5 ppm) against neat nitromethane, conversion scheme IV (Table 4); Cr(acac)₃ added as relaxation reagent.

(c) Data from ref. 120; ¹⁵N natural abundance spectra, 10.1 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(d) Data from ref. 284; ¹⁵N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; Cr(acac)₃ added as relaxation reagent.

TABLE 113A

Nitrogen shieldings in two nitroamine rearrangement processes

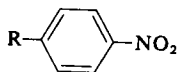
Substance		Solvent	Nitrogen shielding referred to neat nitromethane
Starting material		DMSO-d ₆	+15.6 (NO ₂) +219.9 (NH)
Intermediate		D ₂ SO ₄ (92%)	+49.8 (NO ₂)
		D ₂ SO ₄ (92%)	+3.7 (NO ₂)
		D ₂ SO ₄ (92%)	+24.2 (NO ₂)
Final product		DMSO-d ₆	+17.6 (NO ₂) +281.3 (NH ₂)
Starting material		DMSO-d ₆	+17.2 (NO ₂)
Intermediate		D ₂ SO ₄	+51.6 (NO ₂)
		D ₂ SO ₄	+4.5 (NO ₂)
		D ₂ SO ₄	+25.9 (NO ₂)
Final product		DMSO-d ₆	not specified

Data from ref. 332; ¹⁵N natural abundance spectra, 10.04 MHz, field perpendicular to sample tube, originally referred to saturated aqueous K¹⁵NO₃, +3.55 ppm from neat nitromethane, uncorrected for bulk-susceptibility effects.

TABLE 114

Nitrogen shieldings in some nitro compounds, nitrates and related structures

Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
MeNO ₂ (nitromethane)	neat liquid (18.42 M)	0.0000 (arbitrary)	(a)
	various solvents	-2.0 to +7.1	(a)
EtNO ₂	various	-11.4 to -4.1	(a)
Pr ⁿ NO ₂	various	-10.1 to -3.8	(a)
Pr ⁱ NO ₂	various	-19.5 to -14.7	(a)
Bu ⁱ NO ₂	various	-28.2 to -21.6	(a)
C(NO ₂) ₄ (tetranitromethane)	neat liquid	+46.6	(a)
PhNO ₂ (nitrobenzene)	neat liquid	+9.6	(a)
	0.7 M in CHCl ₃	+9.5	(a)
	0.3 M in CCl ₄	+12.2	(a)
	10% in DMSO	+9.8	(b)



R

NMe ₂	in 72% H ₂ SO ₄	+12.4 (NO ₂)	(c)
	4 M in CDCl ₃	+10.1 (NO ₂)	(d)
NH ₂	in DMSO	+10.2 (NO ₂)	(b)
OMe	in DMSO	+10.8	(b)
F	in DMSO	+12.4	(b)
Cl	in DMSO	+12.3	(b)
Br	in DMSO	+11.9	(b)
Me	in DMSO	+9.9	(b)
CHO	in DMSO	+11.7	(b)
CF ₃	in DMSO	+12.9	(b)
CN	in DMSO	+13.3 (NO ₂)	(b)
NO ₂	in DMSO	+13.8	(b)
	in DMSO	+10.3	(g)

TABLE 114—*cont.*

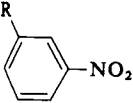
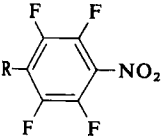
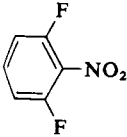
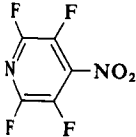
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
			
R			
NMe ₂	in 72% H ₂ SO ₄	+12.9 (NO ₂)	(c)
NH ₂	in DMSO	+9.0 (NO ₂)	(b)
OH	in DMSO	+9.7	(b)
F	in DMSO	+12.8	(b)
Br	in DMSO	+13.1	(b)
Me	in DMSO	+9.5	(b)
CHO	in DMSO	+12.1	(b)
CF ₃	in DMSO	+13.6	(b)
CN	in DMSO	+14.0 (NO ₂)	(b)
NO ₂	in DMSO	+14.8	(b)
			
R			
H	in CH ₂ Cl ₂	+29.8	(e)
F	in CH ₂ Cl ₂	+29.8	(e)
CF ₃	in CH ₂ Cl ₂	+30.0	(e)
OMe	in CH ₂ Cl ₂	+25.4	(e)
NO ₂	in CH ₂ Cl ₂	+31.0	(e)
			
	in CH ₂ Cl ₂	+25.9	(e)
			
	in CH ₂ Cl ₂	+31.0 (NO ₂)	(e)

TABLE 114—*cont.*

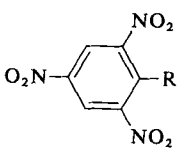
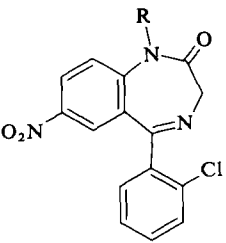
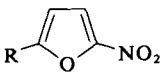
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
			
R			
Me	0.001 M in 0.15 M aqueous NaCl	{ +12.7 (2-NO ₂) +18.5 (4-NO ₂)	(f) (f)
	in H ₂ O + myeloma protein M 315	{ +16.0 (2-NO ₂) +20.0 (4-NO ₂)	(f) (f)
NH ₂	0.001 M in 0.15 M aqueous NaCl	{ +14.5 (2-NO ₂) +16.8 (4-NO ₂)	(f) (f)
	in H ₂ O + myeloma protein M 315	{ +16.6 (2-NO ₂) +18.4 (4-NO ₂)	(f) (f)
OH	0.001 M in 0.15 M aqueous NaCl	{ +11.4 (2-NO ₂) +14.5 (4-NO ₂)	(f) (f)
	in H ₂ O + myeloma protein M 315	{ +14.4 (2-NO ₂) +16.3 (4-NO ₂)	(f) (f)
			
R			
H	in DMSO-d ₆	+15.1 (NO ₂)	(h)
	in CDCl ₃	+12.2 (NO ₂)	(i)
Me	in DMSO-d ₆ , 120 °C	+14.9 (NO ₂)	(h)
			
H	in DMSO-d ₆	+27.7 +28.3	(j) (k)
Me	in DMSO-d ₆	+29.6	(k)
CN	in DMSO-d ₆	+31.1 (NO ₂)	(k)
CHO	in DMSO-d ₆	+28.8	(k)

TABLE 114—*cont.*

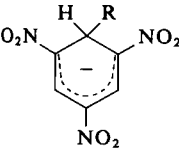
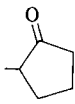
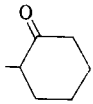
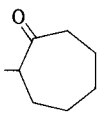
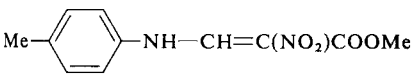
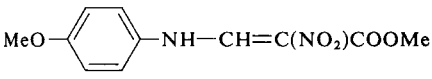
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
COMe	in DMSO-d ₆	+29.7	(k)
CF ₃	in DMSO-d ₆	+31.0	(k)
COOMe	in DMSO-d ₆	+28.6	(k)
I	in DMSO-d ₆	+27.3	(k)
CH(OCOMe) ₂	in DMSO-d ₆	+28.7	(k)
CH=NNHCONH ₂	in DMSO-d ₆	+28.3 (NO ₂)	(k)
 (Na ⁺)			
R			
OMe	in DMSO-d ₆ + Cr(acac) ₃	+7.0 (2,6-NO ₂) +13.6 (4-NO ₂)	(l) (l)
	in DMSO/MeOH (3:1) in DMSO-d ₆ + Cr(acac) ₃	+6.8 (2,6-NO ₂) +13.3 (4-NO ₂) +7.3; +8.7 (2,6-NO ₂) +16.1 (4-NO ₂)	(l) (l) (l) (l)
	in DMSO-d ₆ + Cr(acac) ₃	+6.1; +7.9 (2, 6-NO ₂) +15.7 (4-NO ₂)	(l) (l)
	in DMSO-d ₆ + Cr(acac) ₃	+7.2; +8.5 (2,6-NO ₂) +15.6 (4-NO ₂)	(l) (l)
CH ₂ COMe	in DMSO-d ₆ + Cr(acac) ₃	+8.9 (2,6-NO ₂) +16.2 (4-NO ₂)	(l) (l)
CH(COOMe) ₂	in DMSO-d ₆ + Cr(acac) ₃	+8.8 (2,6-NO ₂) +15.6 (4-NO ₂)	(l) (l)
	in CH ₂ Cl ₂	+8 ± 2 (NO ₂)	(m)
	in CH ₂ Cl ₂	+10 ± 2 (NO ₂)	(m)

TABLE 114—*cont.*

Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
$\text{H}_2\text{N}-\text{CH}=\text{C}(\text{NO}_2)\text{COOMe}$	in CH_2Cl_2	$+10 \pm 2$ (NO_2)	(m)
$\text{MeNH}-\text{CH}=\text{C}(\text{NO}_2)\text{COOMe}$	in CH_2Cl_2	$+10 \pm 2$ (NO_2)	(m)
$\text{MeCH}(\text{OH})\text{C}(\text{Me})\text{NO}_2$	in MeNO_2	-15; -16 (diastereomers)	(n) (n)
$\text{CF}_3\text{CH}(\text{OH})\text{C}(\text{Me})\text{NO}_2$	in MeNO_2	ca. -17	(n)
$\text{CCl}_3\text{CH}(\text{OH})\text{C}(\text{Me})\text{NO}_2$	in MeNO_2	-10; -11 (diastereomers)	(n) (n)
Ionic nitrates, M^+NO_3^-			
KNO_3	0.3 M in H_2O	+3.5	(a)
NaNO_3	0.3 M in H_2O	+3.5	(a)
	satd. in H_2O (7.93 M)	+3.7	(a)
NH_4NO_3	satd. in H_2O (12.30 M)	+4.0 (NO_3^-)	(a)
	solid state	+5.0 (NO_3^-)	(r)
	acidified aqueous solutions	see Table 6	
TlNO_3	1 M in liquid NH_3	+3.0	(o)
	7 M in liquid NH_3	+4.5	(o)
	9.6 M in liquid NH_3	+5.7	(o)
Covalent nitrates, $\text{R}-\text{ONO}_2$ (R = alkyl)			
Nitric acid, HNO_3	neat liquids	ca. +40	(a)
	0.5 M in H_2SO_4	+43 (HONO_2)	(p)
	with various content of H_2O	+133 (nitronium ion, NO_2^+)	(p)
	neat liquid	+42.5	(a)
	15.71 M in H_2O (70.0% w/w)	+31.3	(a)
	10.00 M in H_2O	+18.2	(a)
	7.00 M in H_2O	+12.6	(a)
	1.00 M in H_2O	+4.4	(a)
	$\text{HNO}_3/\text{Bu}^n_3\text{PO}_4$ mol ratio 0.1	+31.7	(q)
	0.6	+25.7	(q)
	1.0	+28.3	(q)
	2.2	+34.7	(q)

For additional data see footnote (a)

(a) See ref. 1, Tables 6 and 133 and references therein; see also Table 6.

(b) Data from ref. 369; ^{15}N natural abundance spectra, 36.5 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

TABLE 114—*cont.*

(c) Data from ref. 210; ^{15}N -labelled NO_2 group, ^{15}N spectra, frequency not reported, originally referred to NO_3^- in aqueous NH_4NO_3 , +4.0 ppm from neat nitromethane (see the present table and Table 6), conversion scheme II (Table 4) without information about magnetic-field direction relative to sample tube.

(d) Data from ref. 44; ^{15}N natural abundance spectra, 10.09 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; originally reported relative to liquid NH_3 standard taken at +380.2 ppm from neat nitromethane.

(e) Data from refs. 435, 624; ^{15}N -labelled compounds, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to liquid NH_3 , +380.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(f) Data from ref. 371; fully and selectively ^{15}N -labelled compounds, ^{15}N spectra, 18.24 MHz, field parallel to sample tube, originally referred to neat nitromethane, *corrected* for bulk-susceptibility effects; MnCl_2 added as relaxation reagent.

(g) Data from ref. 379; ^{15}N natural abundance spectra, 10.095 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(h) Data from ref. 364; ^{15}N natural abundance spectra, 10.1 MHz, field perpendicular to sample tube, originally referred to liquid NH_3 , +380.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(i) Data from ref. 363; ^{15}N natural abundance spectra, 20.28 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(j) Data from ref. 370; ^{15}N -labelled NO_2 group, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(k) Data from ref. 370; ^{14}N PFT spectra, 6.5 MHz, field perpendicular to sample tube, other details as in note (j).

(l) Data from ref. 372; ^{15}N natural abundance spectra, details as in note (g).

(m) Data from ref. 620; low-precision ^{14}N spectra, 6.4 MHz, originally referred to neat nitromethane.

(n) Data from ref. 662; ^{15}N natural abundance spectra, 10.1 MHz, originally referred to internal nitromethane used as solvent; reported relative to liquid NH_3 standard taken at +380 ppm from nitromethane; this was incorrect since the latter value includes bulk-susceptibility effects of external standard for field perpendicular to sample tube.

(o) Data from ref. 263; ^{14}N spectra, 6.49 MHz, field perpendicular to sample tube, originally referred to NO_3^- in satd. aqueous NH_4NO_3 , +4.0 ppm from neat nitromethane (see the present table and Table 6), conversion scheme II (Table 4).

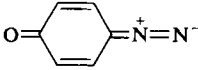
(p) Data from ref. 374; ^{14}N spectra, 8.06 MHz, field perpendicular to sample tube, originally referred to NH_4^+ in NH_4NO_3 in H_2SO_4 , *ca.* +359 ppm from neat nitromethane (Table 6).

(q) Data from ref. 375; ^{15}N natural abundance spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to NO_3^- , probably +3.5 ppm from neat nitromethane (Table 6).

(r) Data from ref. 264; ^{15}N natural abundance CP-MASS spectra, 18.25 MHz, originally referred to solid NH_4Cl , +341.0.0 ppm from neat nitromethane (Table 30), uncorrected for bulk-susceptibility effects.

TABLE 115

Nitrogen shieldings in some diazo compounds

Compound	Solution	Nitrogen shielding referred to neat nitromethane		Notes
		$=N^+=$	$=N^-$	
$\text{Ph}_2\text{C}=\text{N}^+=\text{N}^-$	in various solvents	+75 to +78	-60 to -58	(a)
$\begin{array}{c} \text{R}' \\ \diagdown \\ \text{C}=\text{N}^+=\text{N}^- \\ \diagup \\ \text{R} \end{array}$	in various solvents	+75 to +112	-67 to -3	(a)
(R, R' = various unsaturated systems or aryl groups) as above, but containing C=O or CN groups conjugated with diazo moiety	in various solvents	+99 to +153	-8 to +66	(a)
$\text{EtOOC}-\text{CH}=\text{N}^+=\text{N}^-$	in CH_2Cl_2 , 25 °C	+112.1	-3.5	(b)
	-30 °C	+112.1	+2.4 -6.6	(E,Z-isomers) (b)
	in MeOH, -30 °C	+124.0	+18.2	(b)

(a) For details see ref. 1, Table 134 and references therein.

(b) Data from ref. 376; ^{15}N -labelled compounds, ^{15}N spectra, 8.927 MHz, field perpendicular to sample tube, originally referred to satd. aqueous NaNO_3 , +3.7 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

TABLE 116

Nitrogen shieldings in some diazonium salts and diazotates

Ion	Counter-ion	Solution (in MeOH, -30 °C, if not indicated otherwise	Nitrogen shielding referred to neat nitromethane		Notes
Diazonium ions, R—N ⁺ ≡N					
R			—N ⁺ ≡	≡N	
Ph	Cl ⁻	(1.1 M in MeCN)	+146.0	+64.3	(a)
	BF ₄ ⁻		+149.8	+66.3	(b)
<i>p</i> -(Me ₂ N)C ₆ H ₄	Cl ⁻		+130.7	+31.9	(a)
<i>p</i> -HOC ₆ H ₄	Cl ⁻	(in MeCN)	+142.6	+54.7	(a)
<i>p</i> -MeOC ₆ H ₄	Cl ⁻		+143.4	+56.2	(a)
	BF ₄ ⁻		+146.7	+58.1	(b)
<i>p</i> -MeC ₆ H ₄	Cl ⁻	(0.5 M in MeCN)	+144.2	+62.3	(a)
<i>p</i> -Bu ⁿ C ₆ H ₄	BF ₄ ⁻		+148.6	+63.8	(b)
<i>m</i> -MeC ₆ H ₄	Cl ⁻		+145.8	+64.0	(a)
<i>p</i> -(⁻ O ₃ S)C ₆ H ₄	none	(in H ₂ O)	+146.7	+63.5	(a)
<i>m</i> -(⁻ O ₃ S)C ₆ H ₄	none		+146.4	+62.8	(a)
<i>p</i> -ClC ₆ H ₄	Cl ⁻		+146.9	+62.1	(a)
	BF ₄ ⁻	(0.3 M in MeCN)	+148.9	+63.6	(c)
<i>m</i> -Cl(C ₆ H ₄	Cl ⁻		+148.5	+64.9	(a)
<i>p</i> -O ₂ NC ₆ H ₄	Cl ⁻		+148.9	+64.2	(a)
	BF ₄ ⁻	(0.5 M in MeCN)	+152.3	+65.6	(b)
<i>m</i> -O ₂ NC ₆ H ₄	Cl ⁻		+149.1	+65.1	(a)
<i>o</i> -O ₂ NC ₆ H ₄	Cl ⁻		+151.7	61.1	(a)
<i>p</i> -HOCC ₆ H ₄	BF ₄ ⁻	(in CH ₂ Cl ₂)	+150.8	+65.8	(b)
C ₆ F ₅	Cl ⁻		+167.0	+44.7	(d)
F	AsF ₆ ⁻	(in HF, -50 °C)	+191.2	+166.1	(e)
(Me ₂ PhP) ₄ Re	Cl ⁻	(in CH ₂ Cl ₂ , 25 °C)	+85.4	+62.7	(a)
		(in CH ₂ Cl ₂ , -100 °C)	{+84.8 +81.9}	{+62.5 +67.0}	{ (a)
For additional data see ref. 1, Table 135 therein					
Diazotate ions, R N=N O ⁻					
			R—N=	=N—O ⁻	
R = Ph	Na ⁺	(in H ₂ O)	+10.6	-148.9	(f)
R = <i>p</i> -ClC ₆ H ₄	Na ⁺	(in H ₂ O)	-6.4	-147.7	(f)

(a) Data from ref. 376; ¹⁵N-labelled -N⁺≡N moiety; ¹⁵N spectra, 8.927 MHz, field perpendicular to sample tube, originally referred to satd. aqueous NaNO₃, +3.7 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

TABLE 116—*cont.*

(b) Data from ref. 320; ^{15}N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO_3 , +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(c) Data from ref. 488; ^{15}N -labelled ion, ^{15}N spectrum, 9.12 MHz, field perpendicular to sample tube, originally referred to NO_3^- in aqueous NH_4NO_3 , +4.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

(d) Data from refs. 435, 624; ^{15}N -labelled ion, ^{15}N spectrum, 9.12 MHz, field perpendicular to sample tube, originally referred to liquid NH_3 , +380.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(e) Data from ref. 99; ^{14}N spectrum, 28.9 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(f) As in note (c), but CINDP spectra of decomposition products of diazonium salts.

TABLE 117

Nitrogen shieldings in some azo, azoxy and azodioxy compounds

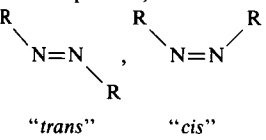
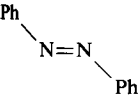
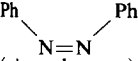
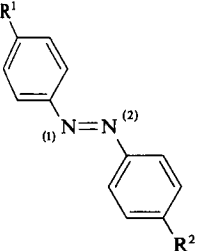
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
Azo compounds,			
 “trans” “cis”			
 (<i>trans</i>-azobenzene)	in CDCl ₃	-129.0	(a)
	in CDCl ₃	-127.6	(a)
	+ Cr(acac) ₃	-127.5	(b)
	1 M in DMSO	-129.0	(c)
	in DMSO	-130.1	(a)
	in DMSO	-128.7	(a)
	+ Cr(acac) ₃	-128.4	(b)
	in n-hexane	-129.1	(a)
 (<i>cis</i>-azobenzene)	in CDCl ₃	-146.5	(a)
	in DMSO	-150.6	(a)
			
R ¹	R ²		
NH ₂	H	1 M in DMSO	-118.2 (1-N) (c)
			-91.2 (2-N) (c)
		in DMSO + Cr(acac) ₃	-118.2 (1-N) (b)
			-91.4 (2-N) (b)
		in DMSO	-118.9 (1-N) (d)
			-91.4 (2-N) (d)

TABLE 117—*cont.*

Compound		Solution	Nitrogen shielding referred to neat nitromethane	Notes
NMe ₂	H	in DMSO + 20% HCl	-114.9 (1-N)	(d)
			-103.5 (2-N)	(d)
		in 95% H ₂ SO ₄	+315.6 (NH ₂)	(d)
			+69.8 (1-N)	(d)
			-24.6 (2-N)	(d)
			+332.2 (NH ₃ ⁺)	(d)
		in CDCl ₃ + Cr(acac) ₃	-118.2 (1-N)	(b)
			-101.7 (2-N)	(b)
		in CDCl ₃	-119.2 (1-N)	(a)
			? (2-N)	(a)
OH	H	in CDCl ₃ + Cr(acac) ₃	-116.5 (1-N)	(a)
			-117.7 (1-N)	(b)
		1 M in DMSO	-96.2 (2-N)	(b)
			-122.3 (1-N)	(c)
OMe	H	in DMSO	-108.3 (2-N)	(c)
			-124.2 (1-N)	(a)
			-110.2 (2-N)	(a)
Me	H	in CDCl ₃ + Cr(acac) ₃	-121.8 (1-N)	(b)
			-113.7 (2-N)	(b)
			-123.6 (2-N)	(a)
Br	H	in CDCl ₃	-126.1 (1-N)	(b)
			-122.2 (2-N)	(b)
			-122.1 (1-N)	(b)
NO ₂	H	in CDCl ₃ + Cr(acac) ₃	-128.6 (2-N)	(b)
			-130.7 (2-N)	(a)
			-120.9 (1-N)	(b)
OH	NO ₂	in CDCl ₃	-144.0 (2-N)	(b)
			-138.7 (1-N)	(a)
			-137.2 (1-N)	(a)
NH ₂	OH	in DMSO + Cr(acac) ₃	-138.0 (1-N)	(b)
			-101.2 (2-N)	(b)
			-91.8 (2-N)	(a)
NMe ₂	Me	in DMSO	-103.6 (1-N)	(b)
			-91.1 (2-N)	(b)
			-113.1 (1-N)	(b)
NMe ₂	NO ₂	in CDCl ₃ + Cr(acac) ₃	-96.2 (2-N)	(b)
			-132.1 (1-N)	(a)
			-132.1 (1-N)	(a)
NEt ₂	NMe ₂	in CDCl ₃	-95.0 (1-N)	(e)
			-92.2 (2-N)	(e)
			-92.2 (2-N)	(e)
NEt ₂	OMe	in CDCl ₃	-107.6 (1-N)	(e)
			-92.2 (2-N)	(e)
			-92.2 (2-N)	(e)
NEt ₂	Me	in CDCl ₃	-104.1 (1-N)	(e)
			-104.1 (1-N)	(e)
			-118.3 (1-N)	(e)
NEt ₂	H	in CDCl ₃	-94.2 (2-N)	(e)
			-94.2 (2-N)	(e)

TABLE 117—*cont.*

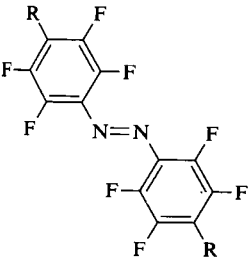
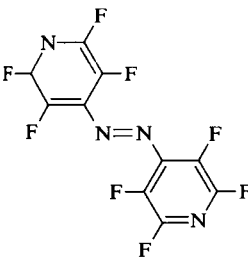
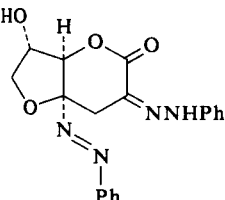
Compound		Solution	Nitrogen shielding referred to neat nitromethane	Notes
NEt ₂	Cl	in CDCl ₃	−118.3 (1-N) −87.3 (2-N)	(e) (e)
NEt ₂	Br	in CDCl ₃	−118.8 (1-N)	(e)
NEt ₂	SCN	in CDCl ₃	−122.2 (1-N) −83.8 (2-N)	(e) (e)
NEt ₂	CN	in CDCl ₃	−126.8 (1-N)	(e)
NEt ₂	NO ₂	in CDCl ₃	−128.6 (1-N) −79.9 (2-N)	(e) (e)
				
R = F		in CH ₂ Cl ₂ in FSO ₃ H (protonated form)	−147.5 −6.3	(f) (f)
R = CF ₃		in CH ₂ Cl ₂ in FSO ₃ H (protonated form)	−149.7 −76.3	(f) (f)
				
		in CH ₂ Cl ₂	−162.0 (N=N)	(f)
				
		in CDCl ₃	−135.8 } (N=N) −143.5 }	(g)

TABLE 117—*cont.*

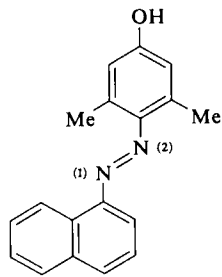
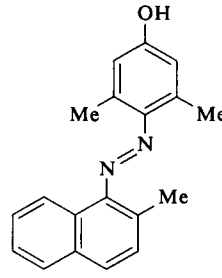
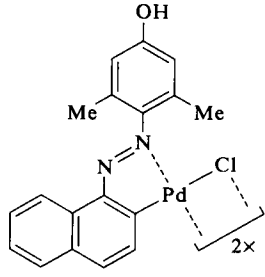
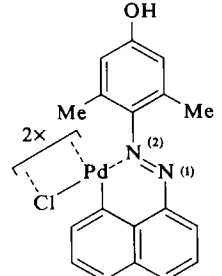
Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	in DMSO	-144.6 (2-N)	(h)
	in DMSO	-135.3 (1-N) -164.8 (2-N)	(h) (h)
	in DMSO	+6.4 (2-N)	(h)
	in DMSO	-85.4 (1-N) +31.0 (2-N)	(h) (h)

TABLE 117—*cont.*

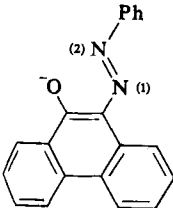
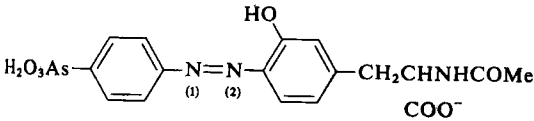
Compound	Solution	Nitrogen shielding referred to neat nitromethane	
	in DMSO	−27.6 (1-N)	(i)
		−93.6 (2-N)	(i)
 (arsanilazo- <i>N</i> -acetyltyrosine)	in H ₂ O, pH = 7.0	−75.9 (1-N)	(i)
		−121.6 (2-N)	(i)
	pH = 8.8	−76.3 (1-N)	(i)
		−119.8 (2-N)	(i)
	pH = 9.6	−76.2 (1-N)	(i)
		−126.6 (2-N)	(i)
	pH = 10.3	−76.4 (1-N)	(i)
		−121.1 (2-N)	(i)
	in DMSO	−97.7 (1-N)	(i)
		? (2-N)	(i)
	in DMSO/H ₂ O (3:1 v/v),		
	pH = 8.8	−95.2 (1-N)	(i)
		−130.8 (2-N)	(i)
	pH = 10.3	−71.9 (1-N)	(i)
	(phenolate ion)	−123.9 (2-N)	(i)
Arsanilazo derivative of tyrosine-248 moiety in carboxypeptidase its Zn complex via 1-N in aqueous 1 M NaCl,	pH = 7.0	−71.8 (1-N)	(i)
		−123.6 (2-N)	(i)
	pH = 8.8	−49.4 (1-N)	(i)
		−111.7 (2-N)	(i)
	pH = 9.6	−72.3 (1-N)	(i)
		−116.1 (2-N)	(i)
	pH = 10.3	−74.6 (1-N)	(i)
		−117.6 (2-N)	(i)

TABLE 117—*cont.*

Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
its complex with Gly-Tyr in aqueous 1 M NaCl,			
	pH = 8.8	-81.6 (1-N)	(i)
		-118.9 (2-N)	(i)
	pH = 9.6	-78.2 (1-N)	(i)
		-118.3 (2-N)	(i)
	pH = 10.3	-74.3 (1-N)	(i)
		-118.7 (2-N)	(i)
its complex with sodium β -phenylpropionate in aqueous 1 M NaCl,			
	pH = 8.8	-101.2 (1-N)	(i)
		-119.7 (2-N)	(i)
	pH = 10.3	-70.7 (1-N)	(i)
		-119.9 (2-N)	(i)
PhNHNH-CO-N=N-Ph	1 M in DMSO	-138.0 (=NPh)	(c)
		-162.6 (CO-N=)	(c)
EtOOC-N=N-COOEt (diethyl azodicarboxylate)	neat liquid	-167.4	(c)
$F_2N^+=NF$ (AsF_6^-)	in HF, -50 °C	+75.9 ($F_2N^+=$)	(j)
		-26.0 (=NF)	(j)
$\begin{array}{c} Bu^t \\ \diagdown \\ N=N \\ \diagup \\ Bu^t \end{array}$	neat liquid	-152.6	(k)
	0.2 M in n-hexane	-152.1	(k)
	0.3 M in MeOH	-151.6	(k)
Azoxy compounds,			
$\begin{array}{c} R \\ \diagdown \\ N=N \\ \diagup \\ R \end{array} \begin{array}{c} O \\ \nearrow \end{array}$			
R = Ph	1 M in DMSO	+52.2 (-N=)	(c)
(azoxybenzene)		+57.2 (=NO-)	(c)
	1 M in CF_3CH_2OH	+46.2 (-N=)	(c)
		+59.7 (=NO-)	(c)
	1 M in TFA	+34.4 (-N=)	(c)
		+64.6 (=NO-)	(c)
R = C_6F_5	in CH_2Cl_2	+52.2 (-N=)	(f)
		+64.3 (=NO-)	(f)
Azodioxy compounds (dimers of corresponding nitroso compounds),			
$\begin{array}{c} R \\ \diagdown \\ N=N \\ \diagup \\ R \end{array} \begin{array}{c} O \\ \nearrow \\ O \\ \searrow \end{array}$			

TABLE 117—*cont.*

Compound	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	in n-hexane (in equilibrium with Bu ^t NO)	+64.7	(k)
	in MeOH (in equilibrium with Bu ^t NO)	+62.0	(k)

For additional data see ref. 1, Table 136 therein

(a) Data from ref. 379; ¹⁵N-labelled compounds, ¹⁵N spectra, 10.095 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(b) As in note (a), but ¹⁵N natural abundance spectra.

(c) Data from ref. 378; ¹⁵N natural abundance spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO₃, +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(d) Data from ref. 382; ¹⁵N-labelled compounds, ¹⁵N spectra, 10.09 MHz, field perpendicular to sample tube, originally referred to NO₃⁻ in aqueous NH₄NO₃, +4.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

(e) Data from ref. 380; ¹⁵N-labelled compounds, ¹⁵N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(f) Data from refs. 435, 624; ¹⁵N-labelled compounds, ¹⁵N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to liquid NH₃, +380.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(g) Data from ref. 279; ¹⁵N natural abundance spectra, 40.5 MHz, field parallel to sample tube, originally referred to NO₃⁻ in aqueous NH₄NO₃, +4.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

(h) Data from ref. 408; singly ¹⁵N-labelled molecules, ¹⁵N spectra, 25.33 MHz, field parallel to sample tube, originally referred to neat HCONH₂, +268.6 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(i) Data from ref. 384; ¹⁵N-labelled azo moiety, ¹⁵N spectra, 18.25 MHz, details as in note (c).

(j) Data from ref. 99; ¹⁴N spectra, 28.9 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(k) Data from ref. 605, high-precision ¹⁴N spectra, 4.3342 MHz; differential-saturation technique with full lineshape fitting; referred to external neat nitromethane, concentric spherical sample/standard containers in order to eliminate bulk-susceptibility effects; spectra run at 35.0 ± 0.2 °C.

TABLE 118

Nitrogen shieldings in some diazenes (aminonitrenes), triazenes and tetrazenes

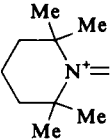
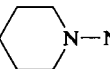
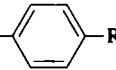
Compound	Solution	Nitrogen shielding referred to neat nitromethane			Notes
Diazene structure, $R_2N^+=N^-$		$R_2N^+=$	$=N^-$		
	in Et ₂ O, -90 °C	+62.5	-533.1	(a)	
Triazene structure, aminoazo type, $R_2N^{(3)}-N^{(2)}=N^{(1)}-R$		1-N	2-N	3-N	
Me ₂ N-N=N-Ph	in CDCl ₃	+20.4	-71.6	+225.2	(b)
	40% in CDCl ₃ + Cr(acac) ₃				
R					
OMe		+17.5	-67.7	+213.4	(c)
OEt		+17.9	-67.8	+214.3	(c)
Me		+18.4	-68.7	+212.1	(c)
H		+21.6	-68.9	+210.8	(c)
F		+23.1	-69.0	+211.1	(c)
Cl		+26.3	-69.4	+208.9	(c)
Br		+25.9	-69.8	+208.5	(c)
COMe		+31.1	-70.7	+204.6	(c)
CN		+34.7	-71.6	+201.8	(c)
NO ₂		+37.5	-72.0	+199.2	(c)
Me-CO-N(Me)-N=N-					
	2 M in CDCl ₃				
R					
NMe ₂		-29.4	-31.2	+174.9	(d)
OMe		-27.2	-56.8	+173.3	(d)
OPh		-26.5	-62.2	+172.1	(d)
Me		-28.9	-63.0	+172.4	(d)
Et		-28.4	-63.0	+172.3	(d)
H		-27.9	-65.8	+171.4	(d)

TABLE 118—*cont.*

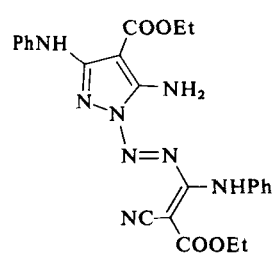
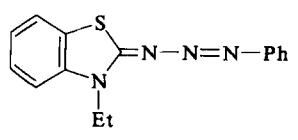
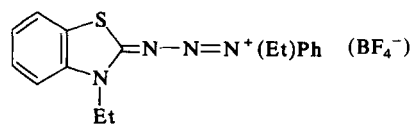
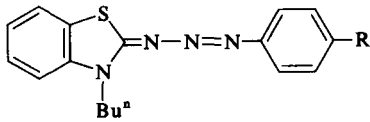
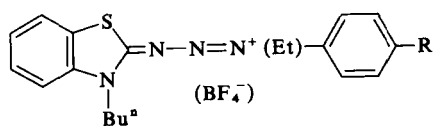
Compound	Solution	Nitrogen shielding referred to neat nitromethane			Notes
F		-24.7	-64.3	+171.8	(d)
Ph		-26.5	-64.9	+171.0	(d)
Br		-23.6	-66.5	+170.6	(d)
I		-24.1	-66.7	+170.4	(d)
COMe		-23.5	-71.2	+168.8	(d)
Bu ^t		-29.3	-63.6	+171.9	(d)
COOMe		-23.6	-70.8	+169.1	(d)
Cl		-23.1	-66.1	+171.0	(d)
COPh		-24.0	-70.9	+168.8	(d)
	in CDCl ₃	+20.0	-42.9	+144.0	(e)
Triazene structure, iminoazo type, $R_2C=N^{(3)}-N^{(1)}=N^{(2)}-R$, $R_2C=N-N=N-R$					
(<i>E</i> -isomer)	(<i>Z</i> -isomer)	1-N	2-N	3-N	
	in pyridine-d ₅				
<i>Z</i> -isomer		-26.4	-76.4	+91.7	(f)
<i>E</i> -isomer		-42.7	-105.2	+91.9	(f)
					
<i>Z</i> -isomer	in CDCl ₃	+154.8	-73.5	+78.0	(f)
<i>Z</i> -isomer	in DMSO-d ₆	+151.2	?	?	(f)
<i>E</i> -isomer	in DMSO-d ₆	+151.4	-66.4	+69.6	(f)

TABLE 118—*cont.*

Compound		Solution	Nitrogen shielding referred to neat nitromethane			Notes
		in pyridine-d ₅				
R						
OMe	<i>Z</i> -isomer		-29.0	-76.3	+86.9	(e)
	<i>E</i> -isomer		-49.4	-103.5	+86.4	(e)
Me	<i>Z</i> -isomer		?	-80.7	?	(e)
	<i>E</i> -isomer		?	-107.3	?	(e)
H	<i>Z</i> -isomer		-33.2	-82.3	+86.0	(e)
	<i>E</i> -isomer		-48.4	-111.7	+85.4	(e)
Cl	<i>Z</i> -isomer		?	-83.6	?	(e)
	<i>E</i> -isomer		?	-112.0	?	(e)
SCN	<i>Z</i> -isomer		-25.2	-40.2	?	(e)
	<i>E</i> -isomer		-87.4	-116.9	?	(e)
NO ₂	<i>Z</i> -isomer		-21.5	-88.8	+84.8	(e)
	<i>E</i> -isomer		-34.8	-122.2	+80.9	(e)

in DMSO- d_6

R						
OMe	<i>Z</i> -isomer		+150.3	-74.5	+71.5	(e)
	<i>E</i> -isomer		+145.1	-66.2	+69.6	(e)
H	<i>Z</i> -isomer		+150.6	-75.6	+74.0	(e)
	<i>E</i> -isomer		+147.1	-70.2	+65.4	(e)
NO ₂	<i>E</i> -isomer		+153.9	-73.2	+55.0	(e)

Tetrazene structure,

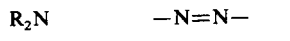
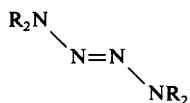
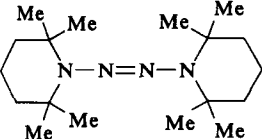


TABLE 118—*cont.*

Compound	Solution	Nitrogen shielding referred to neat nitromethane		Notes
	In Et ₂ O, -90 °C	+219.6	-35.6	(c)

For additional data see ref. 1, Table 136 therein

(a) Data from ref. 663; ¹⁵N-labelled compounds (selectively and fully), ¹⁵N spectra, 9.06 MHz, field perpendicular to sample tube, originally referred to nitromethane in CH₂Cl₂, +3.2 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); originally reported relative to liquid NH₃ standard taken at +380.7 ppm from the standard employed.

(b) Data from ref. 330; fully ¹⁵N-labelled compounds, ¹⁵N spectra, 20.3 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(c) Data from ref. 385; ¹⁵N-labelled and unlabelled compounds, ¹⁵N spectra, 9.04 MHz, field perpendicular to sample tube, originally referred to NO₃⁻ in 17% NH₄NO₃ in 10% HNO₃, +4.6 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

(d) Data from ref. 386; ¹⁵N natural abundance spectra, 25.4 MHz, field parallel to sample tube, originally referred to NH₄⁺ in aqueous NH₄NO₃, +359.6 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); originally reported relative to liquid NH₃ standard taken at +20.7 ppm from the standard employed.

(e) Data from ref. 380; ¹⁵N-labelled triazene moiety, ¹⁵N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; originally reported relative to liquid NH₃ standard, taken at +380.2 ppm from neat nitromethane.

(f) Data from ref. 664; ¹⁵N-labelled triazene moiety, ¹⁵N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to aqueous KNO₂, -228.9 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); originally reported to what was considered as NH₄Cl standard, taken at +590.7 ppm from the standard employed; recalculation and comparison with data in Table 6 indicates that the latter was probably NH₄NO₃ rather than NH₄Cl.

TABLE 119

Nitrogen shieldings in some *N*-nitrosamines

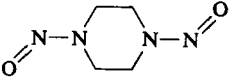
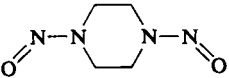
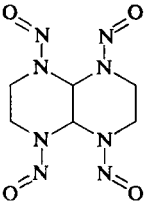
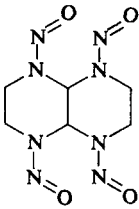
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane		Notes
		R_2N-	$-N=O$	
$Me_2N-N=O$	neat liquid	+148.8	-155.4	(a)
$Et_2N-N=O$	neat liquid	+122.8	-160.7	(a)
$R_2N-N=O$, R = alkyl, aryl	various	+107 to +156	-173 to -151	(a)
	0.5 M in DMSO	+139.5	-157.8	(b)
(<i>anti</i> isomer)				
	0.5 M in DMSO	+139.3	-158.0	(b)
(<i>syn</i> isomer)				
	in DMSO- d_6	?	-162.4	(c)
(<i>anti, anti, anti, anti</i> isomer)				
	in DMSO- d_6	?	-167.3 -162.0	(c) (c)
(<i>anti, anti, syn, syn</i> isomer)				

TABLE 119—*cont.*

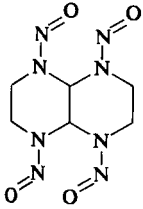
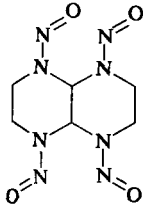
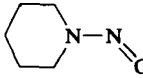
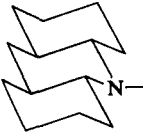
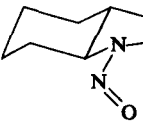
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane		Notes
		R ₂ N—	—N=O	
 (<i>anti, syn, syn, anti</i> isomer)	in DMSO-d ₆	?	-166.5 -151.8	(c)
 (<i>anti, anti, anti, syn</i> isomer)	in DMSO-d ₆	?	-177.1 -166.6 -156.1 -152.2	(c) (c) (c) (c)
	in benzene-d ₆	+131.7	-156.1	(d)
	in benzene-d ₆	+122.1	-184.8	(d)
 (<i>syn</i> and <i>anti</i>)	in benzene-d ₆	+114.0 +114.6	-165.0 -164.5	(d) (d)

TABLE 119—*cont.*

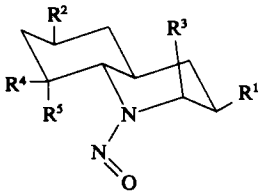
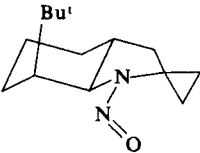
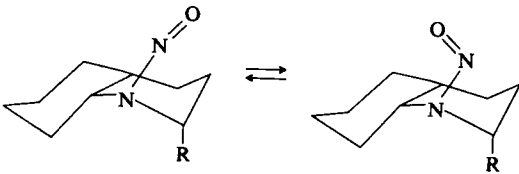
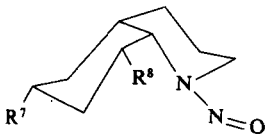
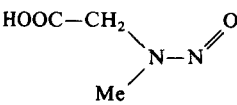
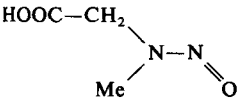
Compound	Solution or state	Nitrogen shielding referred to neat nitromethane		Notes
		R_2N-	$-N=O$	
	in benzene- d_6			
R (other than H)				
$R^1 = \text{Me}$		+124.1	-157.6	(d)
$R^2 = \text{Me}$		+123.5	-158.8	(d)
$R^3 = \text{Me}$		+112.0	-150.6	(d)
$R^4 = \text{Me}$		+127.0	-169.0	(d)
$R^5 = \text{Me}$ (major conformer)		+127.9	-169.6	(d)
$R^4 = \text{Bu}^t$		+123.8	-178.3	(d)
	in benzene- d_6	+122.4	-164.6	(d)
	in benzene- d_6			
R = H (anti isomer)		+122.5	-156.7	(d)
(syn isomer)		+121.6	-155.9	(d)
R = Me (anti isomer)		+112.4	-160.7	(d)
(syn isomer)		+113.5	-160.3	(d)

TABLE 119—*cont.*

Compound	Solution or state	Nitrogen shielding referred to neat nitromethane		Notes
		R ₂ N—	—N=O	
				
R (other than H)				
R ⁷ = Me		+131.5	−162.8	(d)
R ⁸ = Me		+130.0	−163.6	(d)
R ⁸ = Bu ^t		+129.9	−169.7	(d)
	melt	+136	−158	(e)
	melt	+138	−165	(e)
Cations derived from <i>N</i> -nitrosamines, R ₂ N ⁺ =N—OH, R ₂ N ⁺ =N—OR	various	+114 to +134	−99 to −93	(a)
For additional data see footnote (a)				

(a) See ref. 1, Tables 138 and 139 and references therein.

(b) Data from ref. 378; ¹⁵N-enriched compounds, ¹⁵N spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO₃, +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(c) Data from ref. 388; ¹⁵N-labelled nitroso group, ¹⁵N spectra, 36.6 MHz, field parallel to sample tube, originally referred to neat dimethylformamide, +277.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); originally reported relative to liquid NH₃ standard taken at +103.8 ppm from the standard employed.

(d) Data from ref. 389; ¹⁵N natural abundance spectra, 20.28 MHz, field parallel to sample tube, originally referred to neat formamide, +286.6 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4); originally reported relative to liquid NH₃ standard taken at +112.4 ppm from the standard employed.

(e) Data from ref. 665; ¹⁵N-labelled compounds, ¹⁵N spectra, 10.14 MHz, field perpendicular to sample tube, originally referred to 1 M NH₄Cl in 2 M HCl, and originally recalibrated to neat nitromethane standard, uncorrected for bulk-susceptibility effects.

Table 120

Nitrogen shieldings in some N-nitrosooureas, N-nitrosothioureas, N-nitrosocarbamates and N-nitrosoguanidines

Structure		Solution	Nitrogen shielding referred to neat nitromethane			Notes
$R^1NH-C(=O)-N(NO)R^2$ N-nitrosoourea structure			NR ¹	NR ₂	NO	
<u>R¹</u>	<u>R²</u>					
H	CH ₂ CH ₂ Cl	1M in CHCl ₃	+303.3	+112.5	+183.7	(a)
		0.01 M in dioxane	+304.3	?	-185.2	(b)
		0.01 M in CF ₃ CH ₂ OH	+303.5	?	-186.1	(b)
		0.01 M in MeCN	+301.7	?	-184.6	(b)
		0.01 M in DMSO	+296.1	?	-187.5	(b)
		0.01 M in pyridine	+297.5	?	-187.1	(b)
CH ₂ CH ₂ OH	CH ₂ CH ₂ Cl	1 M in CHCl ₃	+294.7	+112.5	-181.8	(a)
CH ₂ CH ₂ Cl	CH ₂ CH ₂ Cl	1 M in CHCl ₃	+296.5	+112.7	-181.3	(a,c)
		0.01 M in CHCl ₃	+296.4	+112.7	-181.3	(b,d)
		0.01 M in dioxane	+295.9	+112.4	-182.8	(b,d)

		0.01 M in $\text{CF}_3\text{CH}_2\text{OH}$	+292.8	+113.6	-182.8	(b,d)
		1 M in DMSO	+290.8	+111.3	-184.8	(a,c)
		0.01 M in DMSO	+290.8	+111.3	-184.7	(b,d)
		0.01 M in pyridine	+291.8	+111.2	-184.4	(b,d)
		0.01 M in dioxane + phosphate buffer,				
		pH = 5.0	+291.7	+112.0	-184.3	(b)
		7.2	+291.7	+111.9	-184.4	(b)
		9.2	+291.7	+112.0	-184.5	(b)
cyclohexyl	$\text{CH}_2\text{CH}_2\text{Cl}$	1 M in CHCl_3	+277.1	+112.4	-179.4	(a,c)
		0.01 M in CHCl_3	+277.2	?	-179.1	(b,d)
		0.01 M in $\text{CF}_3\text{CH}_2\text{OH}$	+274.3	?	-181.1	(b,d)
		0.01 M in DMSO	+273.3	?	-183.8	(b,d)
		1 M in DMSO	+273.1	+111.3	-183.5	(a,c)
		0.01 M in CHCl_3	?	+112.3	-179.1	(f)
		0.01 M in dioxane + phosphate buffer,				
		pH = 5.0	?	+111.6	-183.3	(f)
		7.2	?	+111.5	-183.4	(f)
trans-4-Me- cyclohexyl	$\text{CH}_2\text{CH}_2\text{Cl}$	1 M in dioxane + phosphate buffer, pH = 7.2	+277.1	+112.6	-179.4	(a,c)

Table 120 (continued)

gluco- pyranosyl (anomeric mixture)	$\text{CH}_2\text{CH}_2\text{Cl}$	1 M in DMSO	+283.7	+110.8	-184.1	(a)
			+285.8	+111.4	-183.5	
H	$\text{CH}_2\text{CH}_2\text{F}$	1 M in CHCl_3	+303.3	+114.3	-184.4	(a)
		0.01 M in CHCl_3	?	+114.3	-184.4	(b)
		0.01 M in DMSO	?	+111.9	-187.0	(b)
		0.01 M in pyridine	?	+112.1	-186.8	(b)
$\text{CH}_2\text{CH}_2\text{F}$	$\text{CH}_2\text{CH}_2\text{F}$	1 M in CHCl_3	+296.5	+114.7	-182.3	(a)
cyclohexyl	$\text{CH}_2\text{CH}_2\text{D}$	1 M in CHCl_3	+276.9	+114.5	-179.8	(a)
$\text{R}^1\text{NH}-\text{C}(=\text{S})-\text{N}(\text{NO})\text{R}^2$						
N-nitrosothiourea structure						
R^1	R^2					
Me	Me	1 M in CHCl_3	+282.3	+107.1	-175.2	(e,f)
		0.01 M in HCl	?	?	-180.0	(g)
		0.01 M in MeCN	?	?	-178.2	(g)
		0.01 M in EtOH	?	?	-180.1	(g)
		1 M in EtOH	+259.7	+106.9	-180.0	(e)

cyclohexyl	Me	1 M in CHCl_3	+238.9	+107.2	-174.7	(e,f)
		0.01 M in EtOH	?	?	-180.0	(e)
		1 M in EtOH	+233.3	+106.7	-179.3	(e)
Et	Et	1 M in CHCl_3	+250.3	+95.5	-175.3	(e,f)
		0.01 M in acetone	+246.6	+94.6	-179.5	(h)
		0.01 M in CHCl_3	+251.2	+95.8	-175.3	(h)
cyclohexyl	Et	1 M in CHCl_3	+239.7	+95.6	-171.4	(e,f)
		0.01 M in acetone	+235.0	?	-179.5	(h)
Pr^n	Pr^n	0.01 M in CHCl_3	+254.3	+95.2	-174.5	(h)
		0.01 M in acetone	+248.6	+95.5	-180.9	(h)
		0.01 M in DMSO	+239.4	+94.8	-180.6	(h)
		0.01 M in $\text{CF}_3\text{CH}_2\text{OH}$	+249.4	+96.8	-175.6	(h)
cyclohexyl	$\text{CH}_2\text{CH}_2\text{F}$	1 M in CHCl_3	+238.2	+105.0	-176.7	(e,f)
$\text{CH}_2\text{CH}_2\text{F}$	$\text{CH}_2\text{CH}_2\text{F}$	1 M in CHCl_3	+262.8	+104.2	-178.8	(f)
$\text{CH}_2\text{CH}_2\text{OMe}$	$\text{CH}_2\text{CH}_2\text{OMe}$	0.01 M in CHCl_3	?	?	-178.0	(h)
cyclohexyl	$\text{CH}_2\text{CH}_2\text{OMe}$	0.01 M in CHCl_3	+238.6	?	-176.1	(h)
cyclohexyl	$\text{CH}_2\text{CH}_2\text{OH}$	1 M in CHCl_3	+236.9	+101.3	-176.9	(f)

Table 120 (continued)

$\text{Me}_2\text{N}-\text{C}(=\text{O})-\text{N}(\text{NO})\text{Me}$	1% in CHCl_3	+294.9 (Me_2N)	+118.0 (NMe)	-181.4 (NO)	(i)
$\text{Me}_2\text{N}-\text{C}(=\text{O})-\text{N}(\text{NO})\text{CH}_2\text{CH}_2\text{Cl}$	1 M in CHCl_3	+293.3 (Me N)	+113.3 (NCH_2)	-188.5 (NO)	(a)
$\text{EtO}-\text{C}(=\text{O})-\text{N}(\text{NO})\text{CH}_2\text{CH}_2\text{Cl}$	1 M in CHCl_3		+114.4 (NCH_2)	-201.9 (NO)	(a)
$\text{H}_2\text{N}-\text{C}(=\text{N}-\text{NO}_2)-\text{N}(\text{NO})\text{Me}$	3 M in DMSO	+286.1 (H_2N)	+124.6 (NMe)	+128.6 ($=\text{N}$)	+14.8 -186.6 (NO_2) (NO)

(a) Data from ref. 429, ^{15}N natural abundance spectra, 20.283 MHz, field parallel to sample tube, originally referred to neat HCONMe_2 , +277.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); originally reported relative to liquid NH_3 standard, taken at +103.8 ppm from the standard employed; this is incorrect since the latter value refers to field perpendicular to sample tube.

(b) See note (a), but ^{15}N labelled compounds; labelling sites indicated by nitrogen shieldings detected.

(c) Data from ref. 666, details in note (a).

(d) Data from ref. 666, details in note (b).

(e) Data from ref. 391, details in note (a).

(f) Data from ref. 430, details in note (a).

(g) Data from ref. 391, ^{15}N labelled NO group; details as in note (a).

(h) Data from ref. 430, details as in note (b).

(i) Data from ref. 284, ^{15}N natural abundance spectrum, 9.12 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk susceptibility effects.

TABLE 121

Nitrogen shieldings in some nitroso compounds, nitrites and thionitrites

Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
C-nitroso compounds,			
$\begin{array}{c} \text{R} \\ \diagdown \\ \text{N}=\text{O} \end{array}$			
Bu ^t -N=O	0.5 M in n-hexane	-590.5	(a)
	0.5 M in MeOH	-595.6	(a)
	in CHCl ₃	-593.8	(b)
its dimer (azodioxy compound)	see Table 117		
Ph-N=O	various	ca. -530	(c)
C ₆ F ₅ -N=O	satd. in CH ₂ Cl ₂	-513.1	(d)
<i>p</i> -(O=N-CMe ₂ CMe ₂ OOC-) ₂ C ₆ H ₄	in CHCl ₃	-603.0	(b)
CF ₃ CF ₂ CF ₂ C(CF ₃) ₂ -N=O	in CFCl ₃ /CCl ₄	-427.6	(b)
ClCF ₂ CF(CF ₃)-N=O	in CHCl ₃	-461.3	(b)
(CF ₃) ₂ CF-N=O	neat liquid	-458.9	(b)
CF ₃ CF ₂ CF ₂ -N=O	in CFCl ₂ CF ₂ Cl	-485.8	(b)
Covalent nitrites,			
$\begin{array}{ccc} \text{R}-\text{O} & & \text{R}-\text{O} \\ & \diagdown & \diagdown \\ & \text{N}=\text{O} & \text{N} \\ & & \\ \text{"trans"} & & \text{"cis"} \end{array}$			
Bu ^t -O-N=O (100% <i>trans</i>)	0.5 M in n-hexane	-201.8	(a)
	0.5 M in DMSO	-207.1	(a)
Bu ⁿ -O-N=O (<i>cis</i> and <i>trans</i>)	0.5 M in DMSO	-198.8	(a)
Thionitrites			
$\begin{array}{c} \text{RS} \\ \diagdown \\ \text{N}=\text{O} \end{array}$			
Et-S-N=O	neat liquid	ca. -405	(c)
$\begin{array}{c} \text{MeNH} \\ \diagdown \\ \text{C}=\text{S}-\text{N}=\text{O} \\ \text{MeNH}^+ \end{array}$	in EtOH/HCl, -10 °C	-382.7 (NO)	(e)
Nitrite ion, NO₂⁻, and related species			
NaNO ₂	0.3 M in H ₂ O	-227.6	(c)
	7.56 M in H ₂ O (satd.)	-228.9	(c)
	0.1 M in H ₂ O		
	+0.25 M phosphate	-229.7	(f)
	in 0.1 M HCl	-207.9	(e)
HO-N=O (nitrous acid)	in 0.1 M HCl	-180.5	(e)

TABLE 121—*cont.*

Compound	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
(H ₂ NO ₂) ⁺ (protonated nitrous acid)	in 0.1 M HCl	+26.2	(e)
Various species in NaNO ₂ solutions	see Table 122		
For additional data, see footnote (c)			

(a) Data from ref. 605; high-precision CW ¹⁴N spectra, 4.3342 MHz, differential saturation technique with full lineshape fitting; concentric spherical sample/standard containers in order to eliminate bulk-susceptibility effects; referred to neat nitromethane, 35.0 ± 0.2 °C.

(b) Data from ref. 387; ¹⁵N natural abundance spectra, 18.25 MHz and 40.55 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(c) See ref. 1, Tables 140 and 131 and references therein; see also Table 6 in the present account.

(d) Data from refs. 435, 624; ¹⁵N-labelled compound, ¹⁵N spectrum, 9.12 MHz, field perpendicular to sample tube, originally referred to liquid NH₃, +380.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(e) Data from ref. 391; ¹⁵N-enriched compounds, ¹⁵N spectra, frequency not reported, originally referred to liquid NH₃, +380.2 ppm from neat nitromethane (Table 6, value assumed for condition where field is perpendicular to sample tube), conversion scheme IV (Table 4); shielding quoted in the present table for HO—N=O was originally assigned to N₂O, which is erroneous (Tables 122, 123).

(f) Data from ref. 276; ¹⁵N-labelled nitrite, ¹⁵N spectrum, 30.42 MHz, field parallel to sample tube, originally referred to aqueous NaNO₃, +3.5 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

Table 122

Nitrogen shieldings in the nitrite ion (NO_2^-) and related species under acidic conditions in solutions

Starting concentration of NaNO_2	Solvent and conditions	Nitrogen shieldings (in ppm, referred to neat nitromethane) and their assignments			
		NO_2^-	HONO	NO_3^-	other
0.001 M	$\text{H}_2\text{O}/\text{acetone}$ (1:1), 0°C	-231.5			
0.002 M	acetone/0.01 M aqueous HCl (1:1), 0°C	-217.9		+4.5	
0.001 M	acetone/0.01 M aqueous HCl (1:1), 0°C	-222.8			
0.001 M	acetone/0.05 M aqueous HCl (1:1), 0°C		-205.7	+4.6	
0.001 M	acetone/0.1 M aqueous HCl (1:1), -5°C		-201.7	+4.8	
	0°C		-200.4	+4.6	
	25°C		-199.4		
0.001 M	acetone/1.0 M aqueous HCl (1:1), 0°C		-199.6	+4.6	
	5°C		-199.6	+4.6	-32.2 (?)
	25°C		-200.0		-32.0 (?)
0.001 M	acetone/ HCOOH (1:1), 0°C		-194.7	+8.6	

Table 122 (continued)

0.001 M	acetone/MeCOOH (1:1), 0°C	-195.8	-183.2 (MeCOONO ?)
0.001 M	acetone + 48% HBr, 5°C		+8.7 +25.3 (?)
Bu ⁿ -ONO	50% in acetone, 0°C	-191.8	(see also Table 121)

Data from ref. 392, ¹⁵N labelled nitrite, ¹⁵N spectra, 20.28 MHz, field parallel to sample tube, originally referred to neat dimethylformamide, +277.0 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4); originally reported relative to liquid NH₃ standard taken at +103.8 ppm from the standard employed; this is erroneous, since the latter value refers to field perpendicular to sample tube; shieldings marked with (?) were assigned originally to ClNO and BrNO, quite erroneously since the shieldings involved are -224 ppm and -352 ppm, respectively (ref. 3, p.336, and references therein).

Table 123

Nitrogen shieldings in nitrogen oxides, nitrogen-oxygen ions and related species

Molecule or ion	Solution or state	Nitrogen shielding referred to neat nitromethane (ppm)	Notes
$\text{N}^-=\text{N}^+=\text{O}$ (N_2O)	gaseous, 260-380 K	+147.6 (NO) +235.8 (N=)	(a) (a)
$\text{ON}-\text{NO}_2$ (N_2O_3)	in H_2O neat liquid	+45 (NO_2) ca.-60 (NO_2) ca.-300 (NO)	(b) (c) (c)
$\text{O}_2\text{N}-\text{NO}_2$ (N_2O_4)	various	+10 to +20	(c)
$\text{O}_2\text{N}-\text{O}-\text{NO}_2$ (N_2O_5)	various	+48 to +64	(c)
$\text{NO}^+ \text{AsF}_6^-$	in HF	+7.5	(d)
$\text{NO}^+ \text{BF}_4^-$	in SO_2 , -60°C	+3.2	(e)
$\text{NO}_2^+ \text{HSO}_4^-$	in $\text{HNO}_3/\text{H}_2\text{SO}_4$	+133 +132	(f) (d)

Table 123 (continued)

$\text{NO}_2^+ \text{AsF}_6^-$	in HF, -70°C	+136.3	(d)
$\text{H}_2\text{N}_2\text{O}_2$ (hyponitrous acid)	in H_2O , pH = 5.0	-32.0	(g)
	in 1 M HClO_4	-32.6	(g)
$\text{O}^- \text{N}=\text{N} \text{O}^-$ ($\text{N}_2\text{O}_2^{2-}$, hyponitrite)	in 1 M NaOH, 30°C	-48.5	(g)
	2°C	-47.1	(g)
$\text{ONNO}_2^{2-} \quad 2(\text{Na}^+)$	in H_2O , pH = 13	+25.0 (NO)	(h)
		+46.7 (NO_2)	(h)
$\text{ONNO}_2\text{H}^- \quad \text{Na}^+ \left(\begin{array}{c} \text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{H} \text{---} \text{N}=\text{N \text{---}} \text{O} \end{array} \right)^-$	in H_2O , pH = 6.8	+48.9 (NO)	(h)
		+40.6 (NO_2)	(h)
HONO (nitrous acid)	in $\text{H}_2\text{O}/\text{HCl}$	-180 to -200	(i)
$\text{NO}_2^- \quad \text{Na}^+$ (nitrite)	0.3 M in H_2O	-227.6	(i)
	satd. in H_2O	-228.9	(i)
HONO_2 (nitric acid)	neat liquid	+42.5	(j)
$\text{H}^+ \text{NO}_3^-$ (aqueous nitric acid)	in H_2O , various concentrations	+3.5 to +31.3	(j)

NO_3^- Na^+ or K^+ (nitrate)	0.3 M in H_2O	+3.5	(j)
	satd. in H_2O	+3.7	(j)
$\text{NO}_2^+ \text{AsF}_6^-$	in HF	+99.0	(k)
ClNO	neat liquid	ca.-220	(l)
BrNO	neat liquid	ca.-350	(l)
ClNO_2	neat liquid	ca.+65	(l)
FNO_2	neat liquid	ca.+70	(l)

(a) Data from ref. 56, ^{15}N natural abundance spectrum, 9.12 MHz, field perpendicular to sample tube, originally referred to neat nitromethane, uncorrected for bulk susceptibility effects.

(b) Data from ref. 393, ^{15}N labelled NO_2 moiety, as a product of denitrifying bacteria, ^{15}N spectrum, 40.57 MHz, referred originally to internal NaNO_2 , ca.-229 ppm from neat nitromethane (see this Table).

(c) See ref. 3, p.331, and references therein.

(d) Data from ref. 99, ^{14}N spectra, 28.9 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk susceptibility effects.

Table 123 (continued)

- (e) See ref. 1, Table 141 therein, and reference therein.
- (f) Data from ref. 374, ^{14}N spectrum, 5.8 MHz, field perpendicular to sample tube, originally referred to NH_4^+ in aqueous NH_4NO_3 , ca.+359 ppm from neat nitromethane (Table 6).
- (g) Data from ref. 234, ^{15}N labelled compounds, ^{15}N spectra, 10.14 MHz, field perpendicular to sample tube, originally referred to 6.6 M HNO_3 , +12.6 ppm from neat nitromethane (as can be calculated from Table 6), conversion scheme II (Table 4).
- (h) Data from ref. 235, selectively labelled species, ^{15}N spectra, 9.12 MHz, field perpendicular to sample tube, originally referred to 8.8 M HNO_3 , +14.3 ppm from neat nitromethane (as can be calculated from data in Table 6), conversion scheme II (Table 4).
- (i) See Tables 121 and 122.
- (j) See Table 114.
- (k) As in note (d), but 4.33 MHz spectra, field perpendicular to sample tube.
- (l) See ref. 3, p.336, and references therein.

Table 124

Nitrogen shieldings in dinitrogen and its complexes

Molecule	Solution or state	Nitrogen shielding referred to neat nitromethane	Notes
N_2	gas, 300 K	$+74.70 \pm 0.05$	(a)
	0.001 M in H_2O , $0^\circ C$	+74	(b)
$(Me_2PhP)_4Re(N\equiv N)Cl$ (α) (β)	in CH_2Cl_2 , $25^\circ C$	$+85.4 (N_\alpha)$, $+62.7 (N_\beta)$	(c)
	$-100^\circ C$	$+84.8 (N_\alpha)$, $+62.5 (N_\beta)$ $+81.3 (N_\alpha)$, $+63.5 (N_\beta)$	(c)
$[WH(N_2)(Ph_2PCH_2CH_2PPh_2)_2]HCl_2$	0.001 M in THF	$+78.7 (N_\alpha)$, $+52.7 (N_\beta)$	(d)
<u>trans</u> - $[ReCl(N_2)(PMe_2Ph)_4]$	0.001 M in THF	$+89.3 (N_\alpha)$, $+67.6 (N_\beta)$	(d)
	0.001 M in toluene	$+91.2 (N_\alpha)$, $+67.3 (N_\beta)$	(d)
<u>trans</u> - $[FeH(N_2)(Ph_2PCH_2CH_2PPh_2)_2]BPh_4$	0.001 M in THF	$+64.5 (N_\alpha)$, $+41.3 (N_\beta)$	(d)
<u>mer</u> - $[OsCl_2(N_2)(PMe_2Ph)_3]$	0.001 M in THF	$+118.5 (N_\alpha)$, $+63.7 (N_\beta)$	(d)
<u>mer</u> - $[OsHCl(N_2)(PMe_2Ph)_3]$	0.001 M in THF	$+119.2 (N_\alpha)$, $+65.9 (N_\beta)$	(d)
	+ $Cr(acac)_3$		
<u>mer</u> - $[OsBr_2(N_2)(PMe_2Ph)_3]$	0.001 M in THF	$+126.0 (N_\alpha)$, $+67.0 (N_\beta)$	(d)

Table 124 (continued)

$\text{mer-}[\text{OsHBr}(\text{N}_2)(\text{PMe}_2\text{Ph})_3]$	0.001 M in THF + $\text{Cr}(\text{acac})_3$	+120.9 (N_α), +65.6 (N_β)	(d)
$\text{mer-}[\text{OsCl}_2(\text{N}_2)(\text{PEt}_2\text{Ph})_3]$	0.001 M in THF	? (N_α), +61.7 (N_β)	(d)
$\text{mer-}[\text{OsBr}_2(\text{N}_2)(\text{PEt}_2\text{Ph})_3]$	0.001 M in THF	? (N_α), +61.1 (N_β)	(d)
$\text{trans-}[\text{RhCl}(\text{N}_2)(\text{Pcyclohexyl}_3)_2]$	0.001 M in CH_2Cl_2	+94.0 (N_α), +62.5 (N_β)	(d)
$[(\text{Bu}^t\text{CH=})(\text{Bu}^t\text{CH}_2)(\text{PMe}_3)_2\text{Ta=N-N=Ta}(\text{PMe}_3)_2(\text{CH}_2\text{Bu}^t)(=\text{CHBu}^t)]$ in toluene		-34	(e)

For additional data, see ref. 1, Table 142 therein

(a) Data from ref. 56, ^{15}N labelled N_2 , ^{15}N spectrum, 9.12 MHz, field perpendicular to sample tube, originally referred to neat nitromethane at 300 K, extrapolated to zero pressure, uncorrected for bulk susceptibility effects.

(b) Data from ref. 272, ^{15}N labelled N_2 , ^{15}N spectrum, 18.25 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk susceptibility effects.

(c) Data from ref. 376, ^{15}N labelled N_2 , ^{15}N spectra, 8.927 MHz, field perpendicular to sample tube originally referred to aqueous NaNO_3 , +3.7 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

(d) Data from ref. 394, ^{15}N labelled N_2 , ^{15}N spectra, 18.25 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk susceptibility effects.

(e) Data from ref. 395, ^{15}N labelled N_2 , ^{15}N spectrum, 25.4 MHz, field parallel to sample tube, originally referred to liquid NH_3 , ca. +380 ppm from neat nitromethane (Table 6).

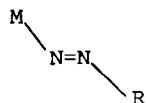
Table 125

Nitrogen shieldings in some diazenido, nitrene and nitrido ligands

Structure	Solution	Nitrogen shielding referred to neat nitromethane (ppm)	
Singly bent structure, $\begin{array}{c} \text{M}-\text{N}=\text{N} \\ \quad \diagdown \\ \quad \text{R} \end{array}$		M-N=	=N-R
<u>trans</u> -[ReCl (N=N-AlMe ₃) (PMe ₂ Ph) ₄]	0.001 M in toluene, -40°C	+88.8	+133.3
mer-[OsCl ₂ (N=N-AlMe ₃) (PMe ₂ Ph) ₃]	0.001 M in toluene, -40°C	+104.0	+139.6
<u>trans</u> -[WF (N=N-H) (Ph ₂ PCH ₂ CH ₂ PPh ₂) ₂]	0.001 M in THF	+24.6	+182.6
<u>trans</u> -[WBr (N=N-H) (Ph ₂ PCH ₂ CH ₂ PPh ₂) ₂]	0.001 M in THF -40°C	+25.9	+187.1

Table 125 (continued)

Doubly bent structure,



$\{[\text{Ru}(\text{NH}_3)_5]_2(\text{N}_2)\} \text{BF}_4$	0.001 M in H_2O	-210.8

Nitrene and nitrido structures

$[\text{ReCl}_2(\text{N})(\text{PPr}^n\text{Ph}_2)_2]$	0.001 M in CH_2Cl_2	-82.4
$[\text{ReCl}_2(\text{N})(\text{PMe}_2\text{Ph})_2]$	0.001 M in CH_2Cl_2	-64.8
$[\text{ReCl}(\text{N})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]\text{Cl}$	0.001 M in CH_2Cl_2	-63.7
$[\text{Mo}(\text{N})(\text{S}_2\text{CNet}_2)_3]$	0.001 M in CH_2Cl_2	-36.7
<u>trans</u> - $[\text{MoCl}(\text{NH})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]\text{Cl}$	0.001 M in CH_2Cl_2	-29.9

Data from ref. 394, ^{15}N labelled compounds, ^{15}N spectra, 18.25 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk susceptibility effects; additional data can be found in ref. 667; they have already been quoted in ref. 1, Table 143 therein.

TABLE 126

Nitrogen shieldings in some nitrosyl complexes

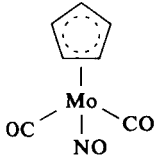
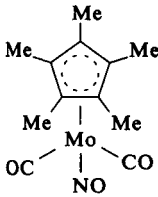
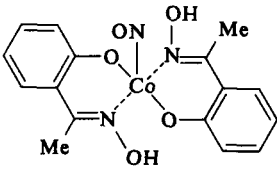
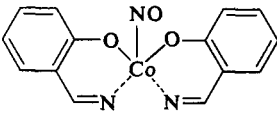
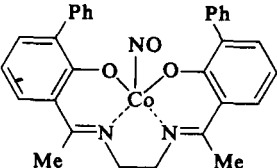
Structure	Solution	Nitrogen shielding referred to neat nitromethane	Notes
Linear nitrosyls, M-N-O angle = 180°			
[Os(NH ₃) ₅ (NO)]Cl ₃ (octahedral)	in H ₂ O	ca. +75 (NO)	(a)
<i>trans</i> -[RuCl ₃ (NO)(PPh ₃) ₂] (octahedral)	in CH ₂ Cl ₂	+36.7	(b)
<i>trans</i> -[RuCl ₂ (NO)(PMePh ₂) ₂] (octahedral)	in CH ₂ Cl ₂	+30.9	(d)
Na ₂ [Fe(CN) ₅ (NO)] (octahedral)	in H ₂ O	+13.5 (NO)	(e)
Bent nitrosyls, M-N-O angle = 180-160°			
[Os(NO) ₂ (PPh ₃) ₂] (tetrahedral)	in benzene	-10.6	(b)
[Ru(NO) ₂ (PPh ₃) ₂] (tetrahedral)	in benzene	-50.7	(b)
[Rh(NO) ₂ (PPh ₃) ₂]ClO ₄ (tetrahedral)	in CH ₂ Cl ₂	-81.4	(b)
[HB(pyrazolyl) ₃]Mo(CO) ₂ (NO)	in CH ₂ Cl ₂	-17 (NO)	(c)
[HB(3,5-Me ₂ -pyrazolyl) ₃]Mo(CO) ₂ (NO)	in CH ₂ Cl ₂	-18 (NO)	(c)
	in CH ₂ Cl ₂	-38	(c)
	in CH ₂ Cl ₂	-52	(c)
Strongly-bent nitrosyls, M-N-O angle < 160°			
<i>trans</i> -[RuCl(CO)(NO)(PPh ₃) ₂] (square-pyramidal)	in CH ₂ Cl ₂	-342.3	(b)
<i>trans</i> -[RhCl(CO)(NO)(PPr ⁱ ₃) ₂]ClO ₄	in CH ₂ Cl ₂	-368.2	(b, d)
<i>trans</i> -[RhCl(NO)(NO ₂)(PR ₃) ₂] (square-pyramidal)	in CH ₂ Cl ₂		

TABLE 126—*cont.*

Structure	Solution	Nitrogen shielding referred to neat nitromethane	Notes
R = cyclohexyl		−466.1 (NO)	(d)
Pr ⁱ		−467.6 (NO)	(d)
Ph		−481.5 (NO)	(d)
 (square-pyramidal)	in DMSO in CHCl ₃	−740.3 (NO) −717.3 (NO)	(d) (e)
 (square-pyramidal)	in DMSO	−736.9 (NO)	(d)
 (square-pyramidal)	in DMSO	−723.0 (NO)	(d)

For additional data see footnote (a)

(a) See ref. 1, Table 144 and references therein.

(b) Data from ref. 387; ¹⁵N-labelled NO, ¹⁵N spectra, 18.25 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk susceptibility effects.

(c) Data from ref. 398; ¹⁴N spectra, 18.1 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects; Mo-¹⁴N spin-spin coupling pattern observed.

(d) Data from ref. 397; ¹⁵N-labelled NO, ¹⁵N spectra, 40.55 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(e) Data from ref. 397; ¹⁵N natural abundance spectra, 18.25 MHz, field parallel to sample tube, calibration as in note (d).

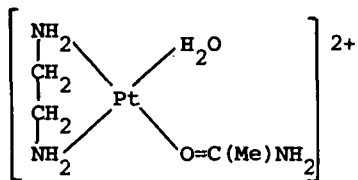
Table 127

Nitrogen shieldings in some ammino-type complexes of platinum

Structure	Solution	Nitrogen shielding referred to neat nitromethane (ppm)	Notes
<u>Pt(II) complexes</u>			
<u>cis</u> -[PtCl ₂ (NH ₃) ₂]	in H ₂ O	+428.3	(a)
	in HCONMe ₂	+426.8	(b)
[Pt(NH ₃)Cl ₃] ⁻	in H ₂ O	+426.6	(a)
[Pt(NH ₃) ₃ Cl] ⁺	in H ₂ O	+430.4 (<u>trans</u> to Cl) +426.6 (<u>trans</u> to NH ₃)	(a) (a)
[Pt(NH ₃) ₄] ²⁺	in H ₂ O	+427.4 +446.4 (?)	(a) (b)
<u>cis</u> -[Pt(NH ₃) ₂ (H ₂ O) ₂] ²⁺	in H ₂ O	+445.6 +446 +448.6 (?)	(b) (c) (d)

Table 127 (continued)

$[\text{Pt}(\text{NH}_3)(\text{H}_2\text{O})_3]^{2+}$	in H_2O	+448.6	(a)
$[\text{Pt}(\text{NH}_3)_2(\text{OH})_2]$	in H_2O	+437.8	(b)
<u>cis</u> - $[\text{Pt}(\text{NH}_3)_2(\text{OH})_2]^{2+}$	in H_2O	+446.4 +442.5 +441.2	(a) (b) (d)
$[\text{Pt}(\text{NH}_3)_2(\text{OH})_3]^{3+}$	in H_2O	+438.9 +438.7	(b) (d)
<u>cis</u> - $[\text{PtCl}(\text{H}_2\text{O})(\text{NH}_3)_2]^+$	in H_2O	+426.4 (<u>trans</u> to H_2O) +446.4 (<u>trans</u> to Cl) +464.6(?) (<u>trans</u> to H_2O) +445.5 (<u>trans</u> to Cl)	(a) (a) (b) (b)
$[\text{PtCl}(\text{OH})(\text{NH}_3)_2]$	in H_2O	+459.4 (<u>trans</u> to OH) +447.4 (<u>trans</u> to Cl)	(b) (b)
$\left[\begin{array}{c} \text{NH}_3 \quad \text{H}_2\text{O} \\ \diagdown \quad / \\ \text{Pt} \\ / \quad \diagdown \\ \text{NH}_3 \quad \text{O}=\text{C}(\text{Me})\text{NH}_2 \end{array} \right]^{2+}$	in H_2O	+444 (NH_3) +256 (amide)	(c) (c)



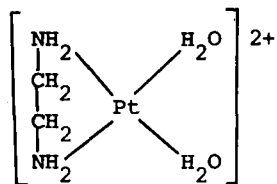
in H₂O

+406 (amine)

(c)

+256 (amide)

(c)



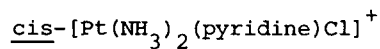
in H₂O

+408

(c)

+411.5

(d)



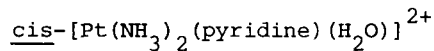
in H₂O

+423.8 (trans to Cl)

(a)

+429.7 (trans to py)

(a)



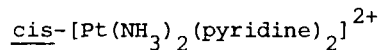
in H₂O

+427.5 (trans to py)

(a)

+443.0 (trans to H₂O)

(a)



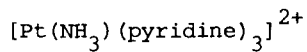
in H₂O

+425.8 (NH₃)

(a)

+180.8 (pyridine)

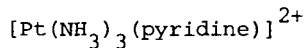
(a)



in H₂O

+420.9

(a)



in H₂O

+422.2 (trans to NH₃)

(a)

+430.9 (trans to py)

(a)

Table 127 (continued)

<u>cis</u> -[Pt(NH ₃) ₂ Cl(PhNH ₂)] ⁺	in H ₂ O	+424.6 (<u>trans</u> to Cl)	(a)
		+429.3 (<u>trans</u> to PhNH ₂)	(a)
		+384.3 (PhNH ₂)	(a)
<u>cis</u> -[Pt(NH ₃) ₂ (PhNH ₂) ₂] ²⁺	in H ₂ O	+424.6 (NH ₃)	(a)
		+386.8 (PhNH ₂)	(a)
<u>cis</u> -[Pt(NH ₃) ₂ (cytidine)Cl] ⁺	in H ₂ O	+426.9 (<u>trans</u> to Cl)	(a)
		+430.1 (<u>trans</u> to cyt)	(a)
<u>cis</u> -[Pt(NH ₃) ₂ (cytidine) ₂] ²⁺	in H ₂ O	+430.1	(a)
<u>cis</u> -[Pt(NH ₃) ₂ (guanosine/7-N)Cl] ⁺	in H ₂ O	+426.3 (<u>trans</u> to Cl)	(a)
		+429.0 (<u>trans</u> to guo)	(a)
<u>cis</u> -[Pt(NH ₃) ₂ (guanosine/7-N) ₂] ²⁺	in H ₂ O	+427.0	(a)
<u>cis</u> -[Pt(NH ₃) ₂ (guanosine/7-N)(H ₂ O)] ²⁺	in H ₂ O	+427.1 (<u>trans</u> to guo)	(a)
		+445.5 (<u>trans</u> to H ₂ O)	(a)
<u>cis</u> -[Pt(NH ₃) ₂ (guanosine/?-N)Cl] ⁺	in H ₂ O	+425.9 (<u>trans</u> to Cl)	(a)
		+430.3 (<u>trans</u> to guo)	(a)
<u>cis</u> -[Pt(NH ₃) ₂ (guanosine/?-N)(H ₂ O)] ²⁺	in H ₂ O	+424.4 (<u>trans</u> to guo)	(a)
		+444.7 (<u>trans</u> to H ₂ O)	(a)
<u>cis</u> -[Pt(NH ₃) ₂ (guanosine/?-N) ₂] ²⁺	in H ₂ O	+430.1	(a)

Pt(IV) complexes

<u>cis-cis-trans</u> -[Pt(NH ₃) ₂ (OH) ₂]	in H ₂ O	+397.5	(d)
<u>cis</u> -[Pt(NH ₃) ₂ Cl ₄]	in H ₂ O	+390.1	(d)

(a) Data from ref. 276, ¹⁵N labelled NH₃, ¹⁵N spectra, 18.25 MHz, field parallel to sample tube, originally referred to 1 M HNO₃, +6.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(b) Data from ref. 407, ¹⁵N labelled NH₃, ¹⁵N spectra, 27.4 MHz, field parallel to sample tube, originally referred to NH₄⁺ in 5M NH₄NO₃ in 2 M HNO₃, +359.0 (NH₄) and +4.6 ppm (NO₃) from neat nitromethane (Table 6), conversion scheme II (Table 4).

(c) Data from ref. 408, ¹⁵N labelled compounds, ¹⁵N spectra, 18.24 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk susceptibility effects; proton-coupled spectra.

(d) Data from ref. 415, ¹⁵N labelled NH₃, ¹⁵N spectra, 20.3 and 40.55 MHz, field parallel to sample tube; originally referred to what was reported as 2.4 M NH₄Cl in 1 M HCl, +352.5 ppm from neat nitromethane (Table 6); however, the latter value gives systematic deviations from other shieldings reported in this Table which suggest that probably NH₄NO₃ was actually employed as standard, +359.6 ppm from neat nitromethane; the latter conversion constant was used here.

Table 128

Ligand effects on nitrogen shielding in some Pt(II) ammino-complexes

$\begin{array}{c} \text{X} \\ \\ \text{X}-\text{Pt}-\text{NH}_3 \\ \\ \text{X} \end{array}$	Effect on nitrogen shielding in NH_3 ligand referred to nitrogen shielding in $[\text{Pt}(\text{NH}_3)\text{Cl}_3]^-$, +426.6 ppm from neat nitromethane (Table 127), exerted by single ligand X in position specified	
	X <u>trans</u> to NH_3	X <u>cis</u> to NH_3
X = H_2O	+19.2 to +21.1 ppm	-3.0 to -0.9 ppm
pyridine	+0.5 to +2.0	-6.4 to -3.9
aniline	0.0 to +1.0	-4.7 to -3.7
Cl^-	0 (reference)	0 (reference)
NH_3	-3.0 to -0.7	+0.8 to +2.1

Data from ref. 276, based on shieldings reported in Table 127, note (a).

TABLE 129

Nitrogen shieldings in some miscellaneous metal complexes

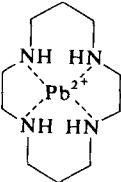
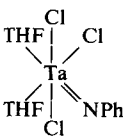
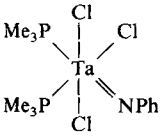
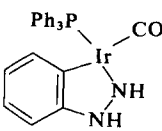
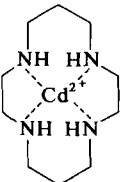
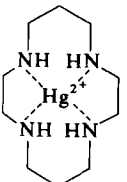
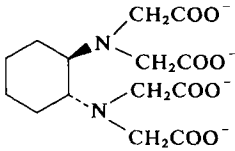
Structure	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	(NO ₃ ⁻) ₂ 0.9 M in DMSO	+325.5 (axial NH) +318.8 (equatorial NH) +11.8 (NO ₃ ⁻)	(a) (a) (a)
	in Et ₂ O	+11	(b)
	in Et ₂ O	+27	(b)
	in CDCl ₃	+332.0 (Ir—NH—)	(c)
	(NO ₃ ⁻) ₂ 0.9 M in DMSO	+349.7 (trigonal-bipyramidal structure, axial and equatorial NH) +348.2 (square-planar)	(d) (d)
	(ClO ₄ ⁻) ₂ 1.7 M in DMSO	+335.8	(d)

TABLE 129—*cont.*

Structure	Solution	Nitrogen shielding referred to neat nitromethane	Notes
	0.7 M in H ₂ O pH = 12 pH = 7	+344.4 +399.4	(d) (d)
(trans-1,2-diaminocyclohexane- <i>N,N,N',N'</i> -tetraacetate ion = cydta)			
[Pb(cydta)] ²⁻	0.5 M in H ₂ O	+312.3	(d)
[Cd(cydta)] ²⁻	0.5 M in H ₂ O	+341.5	(d)
[Ag(cydta)] ³⁻	0.5 M in H ₂ O	+345.2	(d)
[Hg(cydta)] ²⁻	0.7 M in H ₂ O	+329.1	(d)
[Hg(H-cydta)(OH)] ²⁻	0.5 M in H ₂ O	+331.2	(d)
[Hg(H-cydta)Cl] ²⁻	0.5 M in H ₂ O	+328.8	(d)

(a) Data from ref. 668; ¹⁵N natural abundance spectrum, 18.25 MHz, field parallel to sample tube, originally referred to neat nitromethane, uncorrected for bulk-susceptibility effects.

(b) Data from ref. 669; ¹⁵N-labelled complexes, ¹⁵N spectra, 9.04 MHz, field perpendicular to sample tube, originally referred to liquid NH₃, +380.2 ppm from neat nitromethane (Table 6), conversion scheme IV (Table 4).

(c) Data from ref. 417; ¹⁵N-labelled Ir—NH moiety, ¹⁵N spectrum, 10.14 MHz, field perpendicular to sample tube, originally referred to aqueous NH₄Cl, +352.9 ppm from neat nitromethane (Table 6), conversion scheme II (Table 4).

(d) Data from ref. 273; details as in note (a).

TABLE 130

Some ^{15}N - ^1H couplings across one bond (signs of couplings in parentheses are unmeasured)

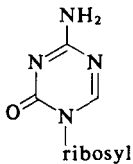
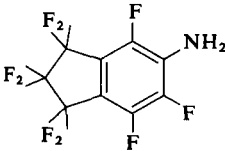
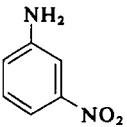
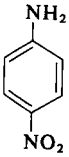
Compound	Solvent	$^1J(^{15}\text{N}-^1\text{H})$ (Mz)	Ref.
$\text{PhN}=\text{NC}_6\text{H}_4\text{-}p\text{-NH}_2$	DMSO-d_6	(-)88.2	382
	DMSO (1 M)	(-)87	378
	H_2SO_4 (95%)	(-)76.2	382
 ribosyl	(methylsulphonyl)-methane	(-)91	349
$\text{C}_6\text{F}_5\text{CONH}_2$	CH_2Cl_2	(-)90.7	435
$2,6\text{-F}_2\text{C}_6\text{H}_3\text{CONH}_2$	CH_2Cl_2	(-)90.6	435
$4\text{-NH}_2\text{C}_6\text{F}_4\text{NH}_2$	CH_2Cl_2	(-)80.3	435
$4\text{-MeOC}_6\text{F}_4\text{NH}_2$	CH_2Cl_2	(-)85.0	435
$4\text{-MeC}_6\text{F}_4\text{NH}_2$	CH_2Cl_2	(-)80.3	435
$4\text{-CF}_3\text{C}_6\text{F}_4\text{NH}_2$	CH_2Cl_2	(-)90.6	435
$4\text{-CNC}_6\text{F}_4\text{NH}_2$	CH_2Cl_2	(-)87.9	435
$4\text{-NO}_2\text{C}_6\text{F}_4\text{NH}_2$	CH_2Cl_2	(-)90.4	435
	CH_2Cl_2	(-)87.9	435
$2\text{-NO}_2\text{C}_6\text{F}_4\text{NH}_2$	CH_2Cl_2	(-)90.4	435
$2\text{-NO}_2\text{-5-CF}_3\text{C}_6\text{F}_3\text{NH}_2$	CH_2Cl_2	(-)90.2	435
	CH_2Cl_2	(-)87.9	435
	acetone- d_6	(-)85.4	670
	acetone- d_6	(-)91.0	670
$\text{PhNH}_3^+\text{OSO}_3\text{F}^-$	CH_2Cl_2	(-)70.5	435
$2,6\text{-F}_2\text{C}_6\text{H}_3\text{NH}_2$	CH_2Cl_2	(-)81.7	435

TABLE 130—*cont.*

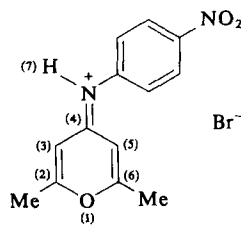
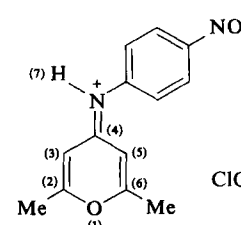
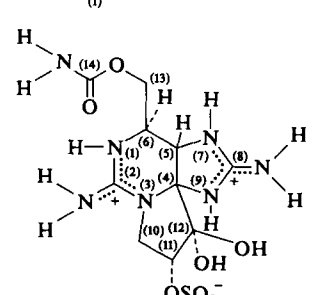
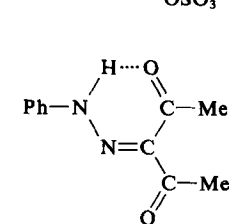
Compound	Solvent	$^1J(^{15}\text{N}-^1\text{H})$ (Mz)	Ref.
$t[^{15}\text{N}]\text{RNA}_1^{\text{fMet}}$	H_2O	(-)87.5 to (-)93.4 (imino protons)	438
$\text{PhN}=\text{NC}(\text{SH})=\text{NNHPh}$ $\updownarrow$ $\text{PhNHN}=\text{C}(\text{SH})\text{N}=\text{NPh}$	CDCl_3	(-)90.8	440
2',3'- <i>O</i> -isopropylidene- 5'- <i>O</i> - <i>t</i> -butyldimethyl- silylquanosine	DMSO	(-)94	147
	CDCl_3 CD_3CN	(-)91.2 (H7) (-)89.7 (H7)	461 461
	CD_3CN CD_3NO_2	(-)94.3 (H7) (-)94.9 (H7)	461 461
	H_2O	(-)92.8 ($\text{NH}_2\text{-C2}$) (-)93.2 ($\text{NH}_2\text{-C8}$) (-)90.9 ($\text{NH}_2\text{-C14}$) (-)95.5 (N1) (-)99.6 (N7) (-)99.1 (N9)	285 285 285 285 285 285
	CDCl_3	(-)95.2	436

TABLE 130—*cont.*

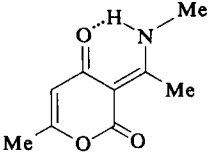
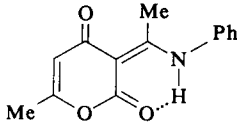
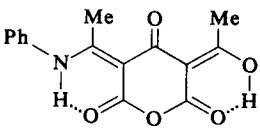
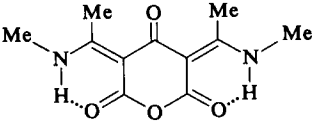
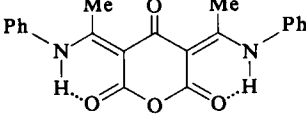
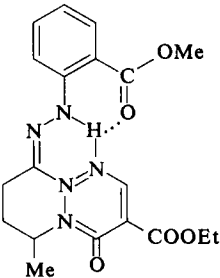
Compound	Solvent	$^1J(^{15}\text{N}-^1\text{H})$ (Mz)	Ref.
	DMSO CDCl ₃	(-)89.1 (-)86	437 437
	CDCl ₃ DMSO	(-)84 (-)83.3	437 437
	CDCl ₃ DMSO	(-)87.5 (-)91.6	437 437
	CDCl ₃ DMSO	(-)87 (-)88.5	437 437
	CDCl ₃ DMSO	(-)85.5 (-)85.2	437 437
	CDCl ₃	(-)97	437

TABLE 130—*cont.*

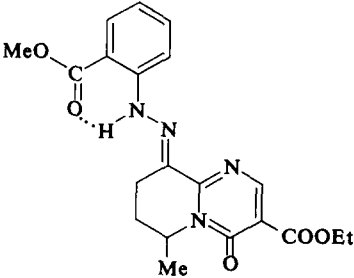
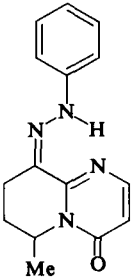
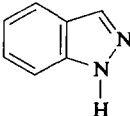
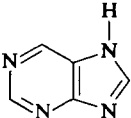
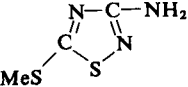
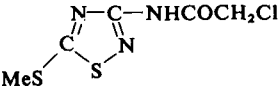
Compound	Solvent	$^1J(^{15}\text{N}-^1\text{H})$ (Mz)	Ref.
	CDCl_3	(-)96.4	254
	CDCl_3	(-)94	254
	DMSO-d_6	(-)106.4	326
	HSO_3F	(-)103.2	159
	$\text{CDCl}_3/\text{DMSO-d}_6$ (1:1 v/v)	(-)87.0	331
	$\text{CDCl}_3/\text{DMSO-d}_6$ (1:1 v/v)	(-)89.4	331

TABLE 130—*cont.*

Compound	Solvent	$^1J(^{15}\text{N}-^1\text{H})$ (Mz)	Ref.
	$\text{CDCl}_3/\text{DMSO}-d_6$ (1:1 v/v)	(-)90.8	331
	$\text{CDCl}_3/\text{DMSO}-d_6$ (1:1 v/v)	(-)90.4	331
	$\text{CDCl}_3/\text{DMSO}-d_6$ (1:1 v/v)	(-)91.1	331
	$\text{CDCl}_3/\text{DMSO}-d_6$ (1:1 v/v)	(-)89.3 (NH—Me)	331
MeCONHMe	none	(-)93.0	431
	CCl_4	(-)92.9	431
	H_2O	(-)93.0	431
EtCONHMe	none	(-)92.9	431
	CCl_4	(-)92.7	431
	H_2O	(-)93.0	431
Pr ⁱ CONHMe	none	(-)92.7	431
	CCl_4	(-)92.8	431
	H_2O	(-)92.9	431
Bu ⁱ CONHMe	CCl_4	(-)92.7	431
	H_2O	(-)92.9	431
$\overline{\text{CO}(\text{CH}_2)_3}\text{NH}$	none	(-)92.4	431
	CCl_4	(-)92.7	431
$\overline{\text{CO}(\text{CH}_2)_4}\text{NH}$	CCl_4	(-)89.2	431
	H_2O	(-)89.9	431
$\overline{\text{CO}(\text{CH}_2)_5}\text{NH}$	CCl_4	(-)89.5	431
	H_2O	(-)90.0	431
	CDCl_3	(-)92.8	118
	CD_3CN	(-)93.0	118
	DMSO	-93.35 ± 0.02	433

TABLE 130—*cont.*

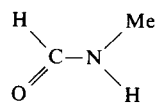
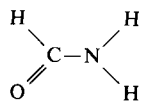
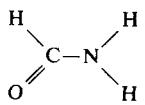
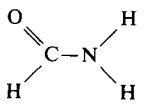
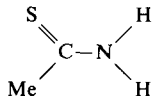
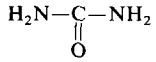
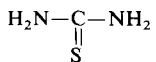
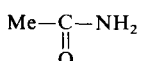
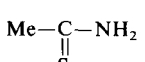
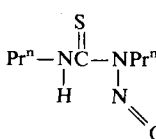
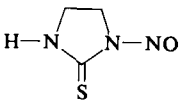
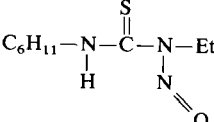
Compound	Solvent	$^1J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	DMSO	-90.13 ± 0.06	433
	DMSO	-87.80 ± 0.10 (<i>Z</i>)	433
	DMSO	-90.35 ± 0.10 (<i>E</i>)	433
	DMSO-d ₆	$(-)90.4$ (<i>E</i>)	145
	DMSO-d ₆	$(-)87.7$ (<i>Z</i>)	145
	acetone	-90.2 (<i>E</i>)	434
	acetone	-88.2 (<i>Z</i>)	434
	acetone-d ₆	$(-)90.8$ (<i>Z</i>)	214
	acetone-d ₆	$(-)89.2$ (<i>E</i>)	214
	H ₂ O	$(-)89.7$	215
	H ₂ O	$(-)91.5$	215
	H ₂ O	$(-)90.5$	215
	H ₂ O	$(-)92.0$	215
	CHCl ₃	$(-)89.2$	430
	acetone	$(-)92.7$	430
	DMSO	$(-)91.2$	430
	CF ₃ CH ₂ OH	$(-)91.0$	430
	acetone	$(-)100.0$	430
	CDCl ₃	$(-)90.0$	430
	acetone	$(-)91.0$	430

TABLE 130—*cont.*

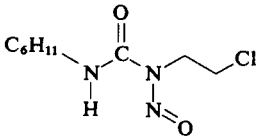
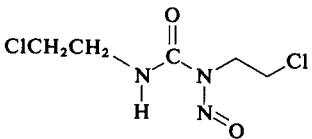
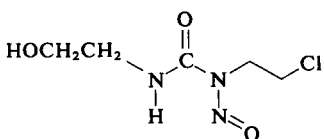
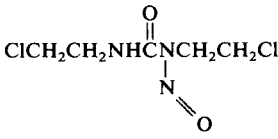
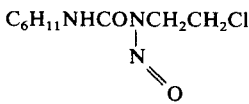
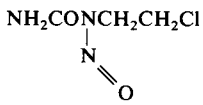
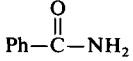
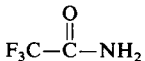
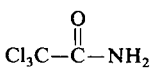
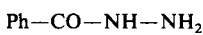
Compound	Solvent	$^1J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	DMSO CDCl ₃	(-)92.5 (-)90.6	429 429
	DMSO CDCl ₃	(-)92.6 (-)93.5	429 429
	DMSO CDCl ₃	(-)90.1 (-)91.5	429 429
	CDCl ₃	(-)93.5	429
	CF ₃ CH ₂ OH	(-)94.0	429
	DMSO-d ₆	(-)92.6	429
	pyridine	(-)92.3	429
	dioxan + phosphate buffer (pH = 5.0)	(-)93.8	429
	dioxan + phosphate buffer (pH = 7.0)	(-)93.8	429
	CDCl ₃	(-)90.6	429
	CF ₃ CH ₂ OH	(-)92.0	429
	DMSO-d ₆	(-)92.5	429
	CDCl ₃	(-)91.5	429
	CF ₃ CH ₂ OH	(-)73.5	429
	DMSO-d ₆	(-)90.0	429
	DMSO	(-)87.8 ± 0.2 (<i>Z</i>)	671
		(-)98.2 ± 0.2 (<i>E</i>)	671
	DMSO	(-)88.6 (<i>Z</i>)	671
		(-)90.1 (<i>E</i>)	671
	DMSO	(-)88.8 (<i>Z</i>)	671
		(-)90.8 (<i>E</i>)	671
	DMSO (1 M)	(-)101 (NH)	378
		(-)68 (NH ₂)	378

TABLE 130—*cont.*

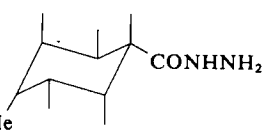
Compound	Solvent	$^1J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	DMSO (1 M)	(-)101 (NH) (-)73 (NH ₂)	378 378
EtO-CO-NHNH ₂	DMSO (2 M)	(-)102 (NH) (-)70 (NH ₂)	378 378
Ph-NHNH-CO-NHNH-Ph	DMSO (1 M)	(-)101 (CONH) (-)90 (PhNH)	378 378
Ph-NH-NH ₂	DMSO (20% v/v)	(-)88 (NH)	378
Ph-NHNH-CO-NH ₂	DMSO (1 M)	(-)98 (NH) (-)91 (PhNH) (-)89 (NH ₂)	378 378 378
Ph-NHNH-CO-N=N-Ph	DMSO (1 M)	(-)99 (CONH) (-)90 (PhNH)	378 378
Lysine and hydroxymethyl derivatives	H ₂ O	(-)74-75	647
arginine and derivatives	H ₂ O	(-)92-94	647
H ₂ N·C(=NH)NH(CH ₂) ₃ CH(NH ₂)COOH	H ₂ O	(-)93 (C=NH)	647
Val and Thr (amide protons)	CDCl ₃	92.5 ± 0.3	242
Cyclo(Pro-Phe-gly-Phe-Gly) _n (n = 1, 2)			
Phe-4	DMSO-d ₆	(-)92.7	441
Phe-2		(-)93.2	441
Gly-3		(-)93.7	441
Gly-5		(-)93.2	441
Tyr-gly-Gly-Phe Residue			
Gly ²	DMSO	(-)97	447
Gly ³		(-)94	447
Phe		(-)92	447
Tyr-Gly-Gly-Phe-Leu Residue			
Gly ³	DMSO	(-)92.5	447
Phe		(-)91	447
Leu		(-)91	447

TABLE 130—*cont.*

Compound	Solvent	$^1J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
<i>cis</i> -cyclo(L-Ala-L-Phe)			
Residue			
Ala	0.1 M DMSO- d_6	(-)89.4	446
Phe		(-)89.5	446
<i>trans</i> -cyclo(D-Ala-L-Phe)			
Residue			
Ala	0.1 M DMSO- d_6	(-)89.9	446
Phe		(-)89.9	446
Asn ¹ Arg ² Val ³ Tyr ⁴ Val ⁵ His ⁶ Pro ⁷ Phe ⁸ (angiotensin amide)			
Val ³	H ₂ O	(-)93.5	237
Tyr ⁴	H ₂ O	(-)93.3	237
Val ⁵	H ₂ O	(-)92.00	237
Phe ⁸	H ₂ O	(-)93.3	237
<i>N</i> -formylalanine, methyl ester	CDCl ₃	(-)92.04	308
<i>N</i> -acetylalanine, methyl ester	CDCl ₃	(-)91.31	308
G-G-C-Up nucleotide	aqueous solution (70 mM in 0.1 M in NaCl)	(-)90	659
Guanine (imino proton)			
$\text{Na}_4^{+2-} \text{O}_2\text{P} \begin{array}{c} \text{O} \\ \parallel \\ \text{N} \end{array} \begin{array}{c} \text{O} \\ \parallel \\ \text{PO}_2^{2-} \\ \\ \text{H} \end{array}$	H ₂ O	(-)73	625
(imidodiphosphate)			
$\text{AMP-O-P} \begin{array}{c} \text{O} \\ \parallel \\ \text{O} \end{array} \text{N} \begin{array}{c} \text{O}^- \\ \parallel \\ \text{P-OH} \\ \\ \text{O}^- \end{array}$	H ₂ O	(-71)	625
(5'-adenyl imidodiphosphate)			
B(NHMe) ₃	C ₆ D ₆	-80.1	126
Et ₃ SiNH ₂	benzene- d_6	(-)61.9	427
Pr ₃ GeNH ₂	benzene- d_6	(-)65.6	427
[Me ₃ Ge] ₂ NH ₂	benzene- d_6	(-)67.8	427
[Pr ₃ Ge] ₂ NH	benzene- d_6	(-)67.1	427
Bu ₃ SnNH ₂	benzene- d_6	(-)62.6	427
[Pr ₃ Sn] ₂ NH	benzene- d_6	(-)60.6	427
Bu ₃ PbNH ₂	benzene- d_6	(-)56.4	427
MeNH ₂	benzene- d_6	(-)64.5	427
PhNH ₂	benzene- d_6	(-)79.0	427
<i>trans</i> -[WBr(¹⁵ N2-H)(dppe) ₂]	THF (-40 °C)	(-)60.5	394
<i>trans</i> -[MoCl(¹⁵ N1-H)dppe) ₂]Cl	CH ₂ Cl ₂	(-)72	394

TABLE 130—*cont.*

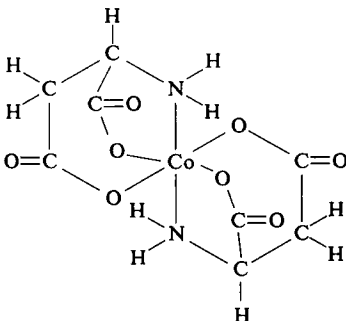
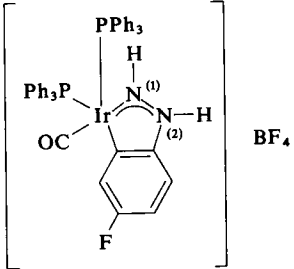
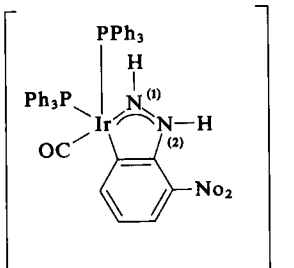
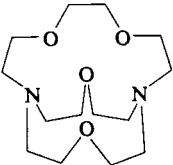
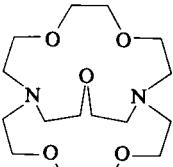
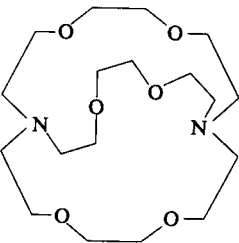
Compound	Solvent	$^1J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	H ₂ O	(-)75	405
	CDCl ₃	(-)84 (N1-H)	417
	CDCl ₃	(-)86 (N1-H)	417
aminodiazonium ion, RHNN ₂ ⁺			
HHNN ₂ ⁺	SO ₂ ClF (-78 °C)	(-)100.0	317
MeHNN ₂ ⁺	SO ₂ ClF (-78 °C)	(-)107.3	317
EtHNN ₂ ⁺	SO ₂ ClF (-78 °C)	(-)105.1	317
NH ₄ ⁺ AsF ₆ ⁻	HF	(-)76.2	99
NH ₄ ⁺ NO ₃ ⁻ (5M)	HNO ₃ (aq) (2 M)	(-)72.9	99
NH ₃ F ⁺ ·O ₃ SCF ₃	CF ₃ SO ₃ H	(-)43.2	99

TABLE 130—*cont.*

Compound	Solvent	$^1J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	MeOH	(-)81.1	267
	MeOH	(-)83.5	267
	MeOH	(-)80	267

* Nitrogen atom involved in coupling.

TABLE 131

Some ^{15}N - ^1H couplings across two bonds (absolute values if sign not given)

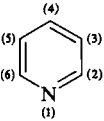
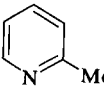
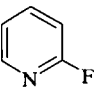
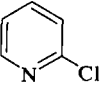
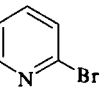
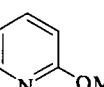
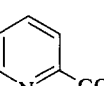
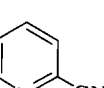
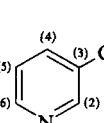
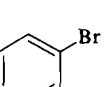
Compound	Solvent	$^2J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	acetone- d_6	-10.93	117
	acetone- d_6	11.01	123
	acetone- d_6	-11.35	117
	acetone- d_6	-11.35	123
	acetone- d_6	-11.76	117
	acetone- d_6	11.82	123
	acetone- d_6	-11.84	117
	acetone- d_6	-11.52	117
	acetone- d_6	11.52	123
	acetone- d_6	11.13	123
	acetone- d_6	-11.72	117
	acetone- d_6	-10.75 (N-H2)	117
	acetone- d_6	-11.28 (N-H6)	117
	acetone- d_6	-10.88 (N-H2)	117
		-11.31 (N-H6)	117

TABLE 131—*cont.*

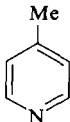
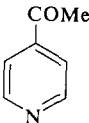
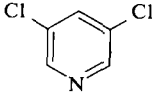
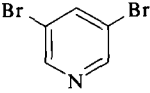
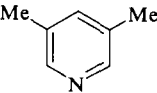
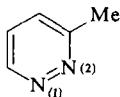
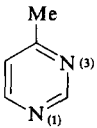
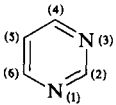
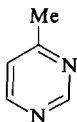
Compound	Solvent	$^2J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	acetone- d_6	~ 10.81	117
	acetone- d_6	~ 10.96	117
	acetone- d_6	~ 11.21	117
	acetone- d_6	~ 11.32	117
	acetone- d_6	~ 10.83	117
	DMSO	11.2	25
	DMSO	12.9 (N3-H2)	25
	DMSO	12.31 (N1-H2) 13.41 (N1-H6)	123 123
	DMSO	13.45 (H1-H2) 10.78 (N1-H6) 14.55 (N3-H2)	123 123 123

TABLE 131—*cont.*

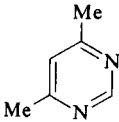
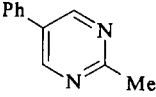
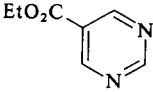
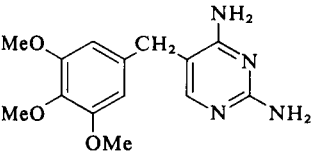
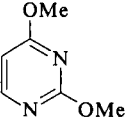
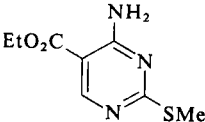
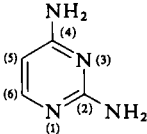
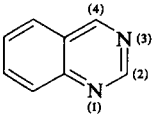
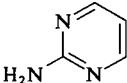
Compound	Solvent	$^2J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	DMSO	14.58 (N1-H2)	123
	DMSO	11.60 (N1-H6)	123
	DMSO	10.90 (N1-H6)	123
	DMSO	11.20 (N1-H6)	123
	DMSO	11.80 (N1-H6)	123
	DMSO	11.80 (N1-H6)	(123)
	H ₂ O (pH = 11)	11.0 (N1-H6)	345
	H ₂ O (pH = 11)	15.9 (N1-H2)	345
		10.9 (N3-H2)	345
		14.5 (N3-H4)	345
	H ₂ O (pH = 11)	9.8	345

TABLE 131—*cont.*

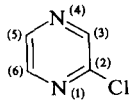
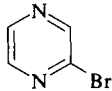
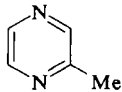
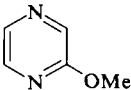
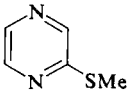
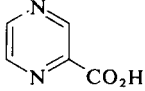
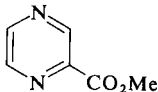
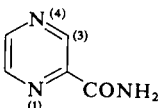
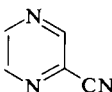
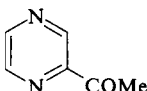
Compound	Solvent	$^2J(^{15}\text{N}-^1\text{H})$ (Hz)	ref.
	DMSO	10.3 (N1-H6) 10.5 (N4-H?)	338 338
	DMSO	11.2 (N1-H6) 10.7 (N4-H?)	338 338
	DMSO	12.1 (N1-H6) 10.3 (N4-H?)	338 338
	DMSO	9.2 (N1-H6) 11.0 (N4-H?)	338 338
	DMSO	11.8 (N1-H6)	338
	DMSO	11.4 (N1-H6)	338
	DMSO	11.4 (N1-H6) 10.7 (N4-H?)	338 338
	DMSO	11.0 (N1-H6) 10.3 (N4-H?)	338 338
	DMSO	11.0 (N1-H6) 11.0 (N4-H?)	338 338
	DMSO	11.2 (N1-H6) 9.8 (N4-H?)	338 338
	DMSO	11.0 (N1-H6) 11.0 (N4-H?)	338 338

TABLE 131—*cont.*

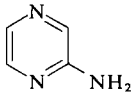
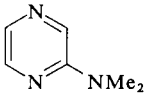
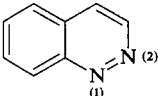
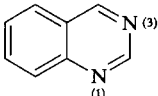
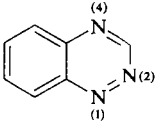
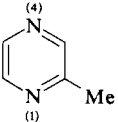
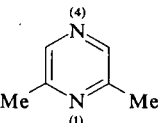
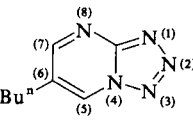
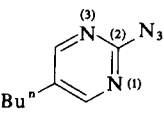
Compound	Solvent	$^2J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	DMSO	11.0 (N1-H6) 10.6 (N4-H?)	338 338
	DMSO	12.2 (N1-H6) 10.4 (N4-H?)	338 338
	DMSO	10.3 (N2-H3)	25
	DMSO	13.8 (N1-H2)	25
	DMSO	11.2	25
	DMSO	13.2 (N2-H3) 11.5 (N4-H3)	25 25
	DMSO	9.8 (N1-H6)	25
	DMSO	10.3	25
	acetone-d ₆	12.0 (N8-H7)	314
	acetone-d ₆	11.5 (N1-H ₆)	314

TABLE 131—*cont.*

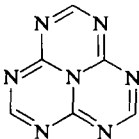
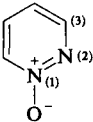
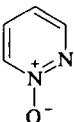
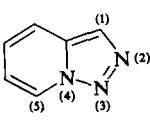
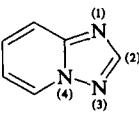
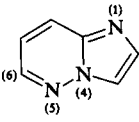
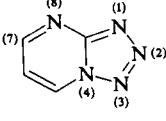
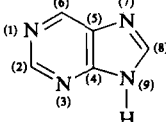
Compound	Solvent	$^2J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	DMSO	14.0	351
	acetone- d_6	-0.81 (N1-H6)	141
	acetone- d_6	-14.46 (N2-H3)	141
	DMSO	8.9 (N2-H1) 6.2 (N4-H5)	24 24
	DMSO	11.2 (N3-H2)	24
	DMSO	7.7 (N5-H6)	24
	DMSO	6.6 (N8-H7)	24
	NaOH (5%)	13.9 (N1-H2) 9.7 (N1-H6) 13.4 (N3-H2) 12.6 (N7-H8) 12.6 (N9-H8)	125 125 125 125 125
	H ₂ O	14.1 (N1-H2) 9.6 (N1-H6) 14.1 (N3-H2)	125 125 125

TABLE 131—*cont.*

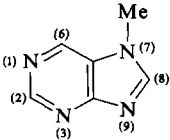
Compound	Solvent	$^2J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	D_2O	14.3 (N1-H?)	327
		14.0 (N3-H2)	327
		10.3 (N7-H8)	327
		9.1 (N9-H8)	327
	D_2SO_4 (20%)	8.3 (N1-H2)	125
		2.6 (N1-H6)	125
		12.7 (N3-H2)	125
		8.4 (N7-H8)	125
		9.2 (N9-H8)	125
	H_2SO_4 (90%)	8.8 (N1-H2)	125
		≤ 3 (N1-H6)	125
		13.3 (N3-H2)	125
		6.3 (N7-H8)	125
		6.3 (N9-H8)	125
	$\text{DMSO}-d_6$	14.9 (N1-H2)	125
		10.9 (N1-H6)	125
		15.1 (N3-H2)	125
		11.9 (N7-H8)	125
		9.7 (N9-H8)	125
	DMSO	16.5 (N1-H?)	327
		15.2 (N3-H2)	327
		9.7 (N7-H8)	327
		9.7 (N9-H8)	327
	TFA	8.9 (N1-H2)	125
		≤ 3 (N1-H6)	125
		13.0 (N3-H2)	125
		10.2 (N7-H8)	125
		8.3 (N9-H8)	125
	$\text{H}_2\text{SO}_3\text{F}$	7.3 (N1-H2)	125
		≤ 3 (N1-H6)	125
		12.8 (N3-H2)	125
		≤ 3 (N7-H8)	125
		3.7 (N9-H8)	125
	D_2O	11.9 (N1-H2)	125
		11.9 (N1-H6)	125
		14.0 (N3-H2)	125
		9.6 (N7-H8)	125
		13.5 (N9-H8)	125
	D_2O	13.8 (N1-H?)	327
		13.7 (N3-H2)	327
		9.4 (N7-H8)	327
		11.7 (N9-H8)	327

TABLE 131—*cont.*

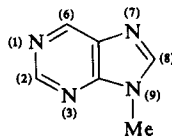
Compound	Solvent	$^2J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	D_2SO_4 (20%)	11.8 (N1-H2)	125
		≤ 3 (N1-H6)	125
		12.3 (N3-H2)	125
		9.3 (N7-H8)	125
		10.9 (N9-H8)	125
	D_2SO_4 (90%)	8.7 (N1-H2)	125
		≤ 3 (N1-H6)	125
		13.3 (N3-H2)	125
		7.8 (N7-H8)	125
		5.7 (N9-H8)	125
	$\text{DMSO}-d_6$	12.9 (N1-H2)	125
		12.9 (N1-H6)	125
		14.9 (N3-H2)	125
		9.6 (N7-H8)	125
	TFA	12.4 (N9-H8)	125
		10.9 (N1-H2)	125
		≤ 3 (N1-H6)	125
		12.9 (N3-H2)	125
		8.9 (N7-H8)	125
	D_2O	11.4 (N9-H8)	125
		13.8 (N1-H2)	125
		9.7 (N1-H6)	125
		14.6 (N3-H2)	125
		11.4 (N7-H8)	125
	D_2O	9.9 (N9-H8)	125
		14.6 (N1-H?)	327
		14.6 (N3-H2)	327
		11.1 (N7-H8)	327
	D_2SO_4 (20%)	8.5 (N9-H8)	327
		7.9 (N1-H2)	125
		2.6 (N1-H6)	125
		12.9 (N3-H2)	125
		11.1 (N7-H8)	125
	D_2SO_4 (90%)	11.1 (N9-H8)	125
		9.3 (N1-H2)	125
		≤ 3 (N1-H6)	125
		13.5 (N3-H2)	125
		5.8 (N7-H8)	125
	$\text{DMSO}-d_6$	7.7 (N9-H8)	125
		13.1 (N1-H2)	125
		13.1 (N1-H6)	125
		15.6 (N3-H2)	125
		12.4 (N7-H8)	125
		10.4 (N9-H8)	125

TABLE 131—*cont.*

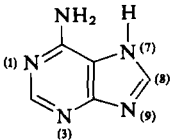
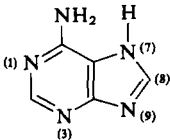
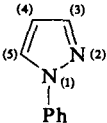
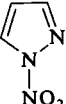
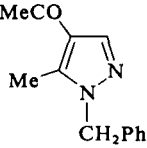
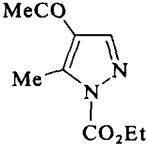
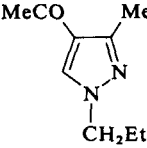
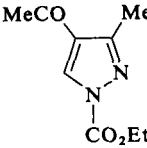
Compound	Solvent	$^2J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	TFA	9.5 (N1-H2)	125
		≤ 3 (N1-H6)	125
		13.4 (N3-H2)	125
		9.7 (N7-H8)	125
		9.0 (N9-H8)	125
	D_2O	14 (N1-H2)	672
		13 (N3-H2)	672
		12.5 (N7-H8)	672
		12.5 (N9-H8)	672
	benzene- d_6	-4.52 (N1-H5)	91
		-13.27 (N2-H3)	91
	DMSO	3.1 (N1-H5)	120
		13.5 (N2-H3)	120
	DMSO	12.0 (N2-H3)	120
	DMSO	13.7 (N2-H3)	120
	DMSO	3.6 (N1-H5)	120
	DMSO	3.4 (N1-H5)	120

TABLE 131—*cont.*

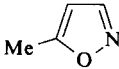
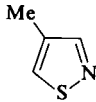
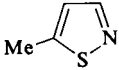
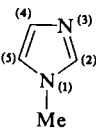
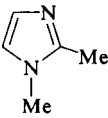
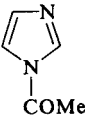
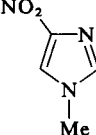
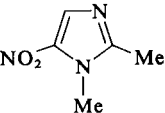
Compound	Solvent	$^2J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	DMSO	14.7	120
	CDCl_3	14.4	120
	DMSO	14.4	120
	acetone- d_6	-14.2	445
	DMSO	-14.2	120
	DMSO	14.4	120
	DMSO	14.5	120
	H_2O	-7.6 (N1-H2)	120
		-5.5 (N1-H5)	120
		-10.8 (N3-N2)	120
		-9.0 (N3-H4)	120
	DMSO	8.1 (N1-H2)	120
		4.7 (N1-H5)	120
	DMSO	10.0 (N3-H4)	120
		8.2 (N1-H2)	120
		4.1 (N1-H5)	120
		11.5 (N3-H2)	120
		10.0 (N3-H4)	120
		7.8 (N1-H2)	120
		3.3 (N1-H5)	120
		12.4 (N3-H2)	120
	DMSO	9.5 (N3-H4)	120

TABLE 131—*cont.*

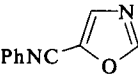
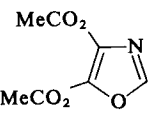
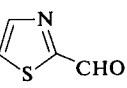
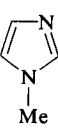
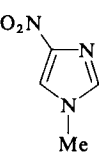
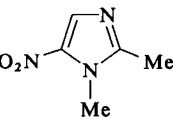
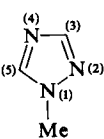
Compound	Solvent	$^2J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	DMSO	13.4 (N3-H2) 10.4 (N3-H4)	120 120
	DMSO	13.4 (N3-H2) 10.4 (N3-H4)	120 120
	DMSO CDCl ₃	13.7 13.7	120 120
	DMSO	14.6 (N3-H2)	120
	CDCl ₃ CS ₂	10.5 (N3-H2) 10.5 (N3-H4) -10.6 (N3-H2) -10.6 (N3-H4)	120 120 120 120
	acetone	-10.5	120
	H ₂ O	-1.6 (N1-Me)	120
	DMSO	1.7 (N1-Me)	120
	DMSO	1.8 (N1-Me1)	120
	DMSO	10.6 (N1-H5) 13.8 (N2-H3)	26 26

TABLE 131—*cont.*

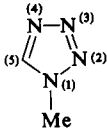
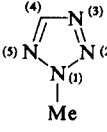
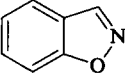
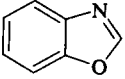
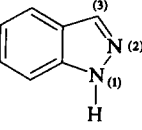
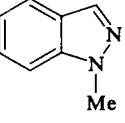
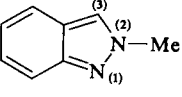
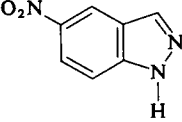
Compound	Solvent	$^2J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	DMSO	9.9 (N1-H5) 12.2 (N4-H5)	26 26
	DMSO	10.1 (N3-H4)	26
	DMSO	14.6	26
	DMSO	12.0	26
	DMSO	9.9 (N3-H4)	26
	DMSO-d ₆ acetone	12.8 (N2-H3) 12.9 (N2-H3)	326 326
	DMSO-d ₆	12.8 (N2-H3)	326
	DMSO-d ₆	4.3 (N2-H3) 2.1 (N2-Me)	326 326
	DMSO-d ₆ acetone	12.9 (N2-H3) 12.9 (N2-H3)	326 326

TABLE 131—*cont.*

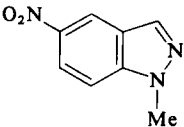
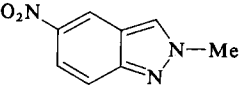
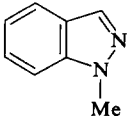
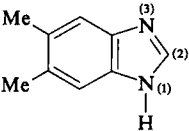
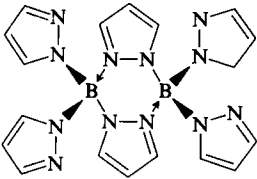
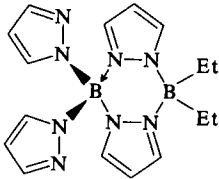
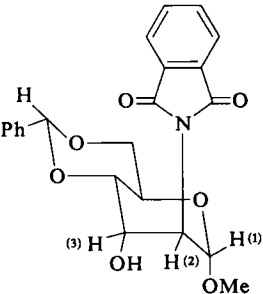
Compound	Solvent	$^2J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	DMSO- d_6 acetone	13.2 (N2-H3) 13.0 (N2-H3)	326 326
	DMSO- d_6	4.1 (N2-H3) 2.1 (N2-Me)	326 326
	DMSO- d_6	1.7 (N1-Me)	326
	CDCl_3	10.3 (N3-H2)	443
	CDCl_3	<i>ca.</i> 12	653
	CDCl_3	<i>ca.</i> 12	653
	acetone- d_6	2.1 (N-H2)	453

TABLE 131—*cont.*

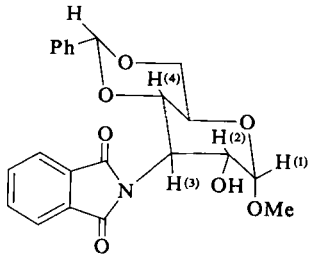
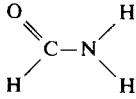
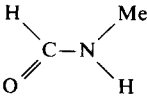
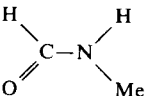
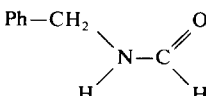
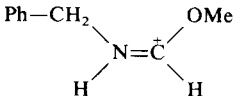
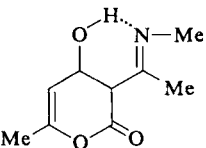
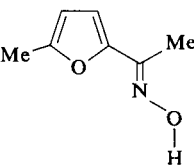
Compound	Solvent	$^2J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	acetone- d_6	$<0.5(\text{N}-\text{H}_3)$	453
	acetone- d_6	-15.6	434
	DMSO- d_6	14.4	145
	DMSO	-14.25	433
	DMSO	-13.63 (N-COH)	433
	DMSO	-15.67 (N-COH)	433
	CDCl_3	15.4 (N-COH) 0.6 (N- CH_2)	118 118
	CD_3CN	6.25 (N=CH) 1.7 (N- CH_2)	118 118
	CDCl_3	1.0 (N-Me)	437
	acetone	2.0	365

TABLE 131—*cont.*

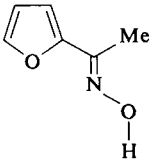
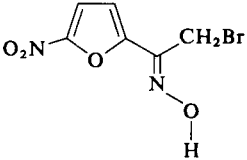
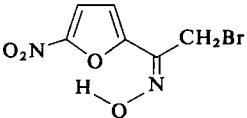
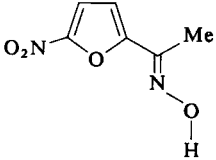
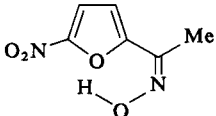
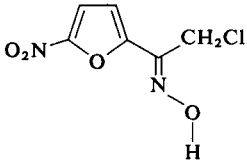
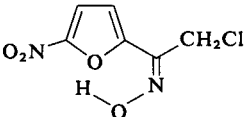
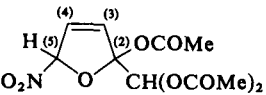
Compound	Solvent	$^2J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	acetone	1.9	365
	acetone	1.8	365
	acetone	1.2	365
	acetone	1.9	365
	acetone	1.2	365
	acetone	2.0	365
	acetone	1.2	365
HCN	neat	-8.6 ± 0.1	673

TABLE 131—*cont.*

Compound	Solvent	$^2J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
$\text{ClCH}_2\text{CH}_2\overset{*}{\text{N}}\text{HCNCH}_2\text{CH}_2\text{Cl}$ $\begin{array}{c} \\ \text{N} \\ // \\ \text{O} \end{array}$	CDCl_3	1.5	429
	$\text{CF}_3\text{CH}_2\text{OH}$	1.6	429
	DMSO-d_6	0.6	429
	pyridine	0.6	429
$\text{C}_6\text{H}_{11}\overset{*}{\text{N}}\text{HCONCH}_2\text{CH}_2\text{Cl}$ $\begin{array}{c} \\ \text{N} \\ // \\ \text{O} \end{array}$	CDCl_3	1.8	429
	$\text{CF}_3\text{CH}_2\text{OH}$	1.5	429
	DMSO-d_6	0.6	429
Methyl ester of <i>N</i> -formylalanine	CDCl_3	16.4	308
2-coscyanomethyl propionate	CDCl_3	2.6	308
Tyr-Gly-Gly-Phe Residue			
Gly ²	DMSO	0.7	447
Gly ³	DMSO	1	447
Phr	DMSO	1.5	447
Tyr-Gly-Gly-Phe-Leu Residue			
Gly ²	DMSO	0	447
Gly ³	DMSO	1	447
Phe	DMSO	1.5	447
	DMSO-d_6	1.3	370
$\text{B}(\text{OCH}_2\text{CH}_2)_3\text{N}$	CDCl_3	-0.5	268
$\text{Ph}(\text{Me})\text{Si}(\text{OCH}_2\text{CH}_2)_2\text{NMe}$	CDCl_3 (10%)	0	268

* Nitrogen atom involved in coupling.

TABLE 132

Some ^{15}N - ^1H couplings across three bonds (absolute values if sign not given)

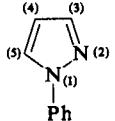
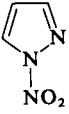
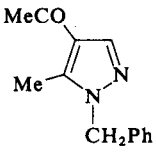
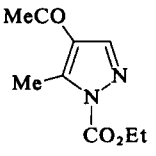
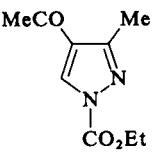
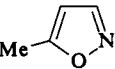
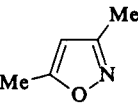
Compound	Solvent	$^3J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	benzene- d_6 (37% w/w)	-8.72 (N1-H3)	91
		-5.91 (N1-H4)	91
		-0.99 (N2-H4)	91
		+0.13 (N2-H5)	91
	DMSO- d_6	10.3 (N1-H3)	120
		7.4 (N1-H4)	120
		≤ 1 (N2-H4)	120
		≤ 1 (N2-H5)	120
	DMSO- d_6	10.5 (N1-H3)	120
	DMSO- d_6	9.0 (N1-H3)	120
	DMSO- d_6	1.9 (N2-H3)	120
	DMSO- d_6	1.6 (N2-H4)	120
		<1 (N2-H5)	120
	CDCl_3	1.8 (N2-H4)	120
	DMSO- d_6	1.4 (N2-H4)	120
	CDCl_3	1.3 (N2-H4)	120
	acetone- d_6	-1.86 (N2-H4)	120
		+1.32 (N2-H5)	120

TABLE 132—*cont.*

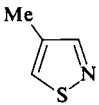
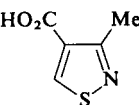
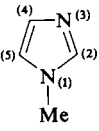
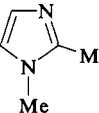
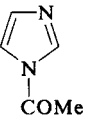
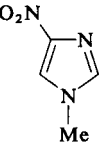
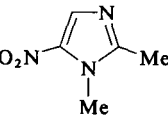
Compound	Solvent	$^3J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	DMSO	1.3 (N2-H5)	120
	DMSO	2.2 (N2-H4)	120
	DMSO	1.5 (N2-H5)	120
	H ₂ O	-3.5 (N1-H4)	120
	DMSO	-1.7 (N3-H5)	120
	DMSO	3.4 (N1-H4)	120
	DMSO	1.0 (H3-H5)	120
	DMSO	4.1 (N1-H4)	120
		1.6 (N3-H5)	120
	DMSO	1.5 (N3-H5)	120
		1.5 (NO ₂ -H5)	120
	DMSO	1.8 (N1-H4)	120
		2.0 (N1-Me2)	120
		2.5 (N3-Me2)	120
		2.8 (NO ₂ -H4)	120
	DMSO	1.2 (N3-H5)	120
	CDCl ₃	2.2 (N3-H5)	120
	CS ₂	-1.97 (N3-H5)	120

TABLE 132—*cont.*

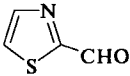
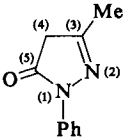
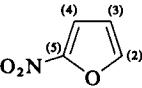
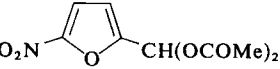
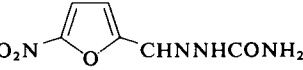
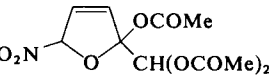
Compound	Solvent	$^3J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	acetone (90%)	-1.93 (N3-H5) +0.36 (N3-CHO)	120 120
	CF ₃ CHOHCF ₃	3.0 (N2-Me)	674
	DMF-d ₇	3.0 (N2-Me)	674
	DMF-d ₇ (-30 °C)	3.0 (N2-Me)	674
	DMF-d ₇ (-55 °C)	3.0 (N2-Me)	674
	THF-d ₈ (-50 °C)	3.2 (N2-Me)	674
	THF-d ₈ (-90 °C)	3.2 (N2-Me)	674
	DMSO	3.5 (N2-Me)	674
	CF ₃ CH ₂ OH	3.0 (N2-Me)	674
	HMPT	3.0 (N2-Me)	674
	CDCl ₃	3.5 (N2-Me)	674
	acetone-d ₆	3.6 (N2-Me)	674
	pyridine	3.6 (N2-Me)	674
	MeOH	2.6 (N2-Me)	674
	CDCl ₃	<0.5 (N1-H4)	674
	acetone-d ₆	5.0 (N1-H4)	674
	THF	5.0 (N1-H4)	674
	DMF	5.0 (N1-H4)	674
	DMF (-60 °C)	5.0 (N1-H4)	674
	DMSO	5.0 (N1-H4)	674
	pyridine	5.0 (N1-H4)	674
	HMPT	5.1 (N1-H4)	674
	CF ₃ CH ₂ OH	3.6 (N2-H4)	
	HMPT	<0.5 (N2-H4)	674
	CDCl ₃	<0.5 (N2-H4)	674
	DMSO-d ₆	0 (NO ₂ -H4)	370
	DMSO-d ₆	0 (NO ₂ -H4)	370
	DMSO-d ₆	0 (NO ₂ -H4)	370
	DMSO-d ₆	0.6 (NO ₂ -H4)	370

TABLE 132—*cont.*

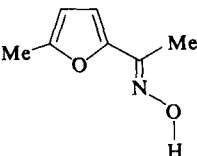
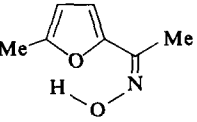
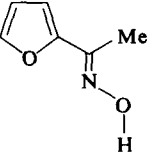
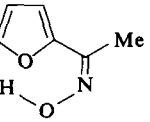
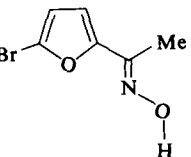
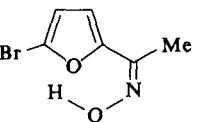
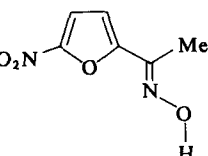
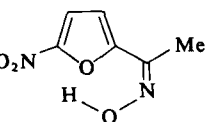
Compound	Solvent	$^3J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	acetone	2.0 (N-Me)	365
	acetone-TFA (2:1 v/v)	3.0 (N-Me)	365
	acetone-TFA (2:1 v/v)	4.4 (N-Me)	365
	acetone	2.1 (N-Me)	365
	acetone-TFA (2:1 v/v)	2.6 (N-Me)	365
	acetone-TFA (2:1 v/v)	4.4 (N-Me)	365
	acetone	2.0 (N-Me)	365
	acetone	4.3 (N-Me)	365
	acetone	2.1 (N-Me)	365
	acetone-TFA (2:1 v/v)	2.1 (N-Me)	365
	acetone	4.7 (N-Me)	365
	acetone-TFA (2:1 v/v)	4.1 (N-Me)	365

TABLE 132—*cont.*

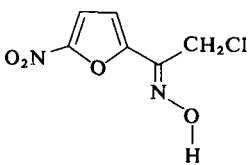
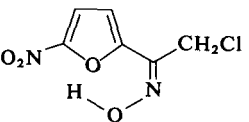
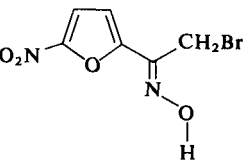
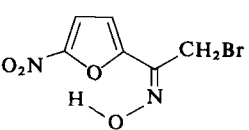
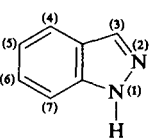
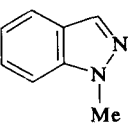
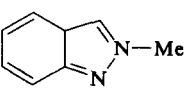
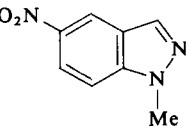
Compound	Solvent	$^3J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	acetone	1.2 (N-CH ₂ Cl)	365
	acetone	4.4 (N-CH ₂ Cl)	365
	acetone	1.1 (N-CH ₂ Br)	365
	acetone	4.1 (N-CH ₂ Br)	365
	DMSO-d ₆	7.4 (N1-H3) 1.0 (N1-H7)	326 326
	DMSO-d ₆	7.6 (N1-H3) 1.0 (N1-H7)	326 326
	DMSO-d ₆	<0.5 (N1-H3) 0.3 (N1-H7) 2.1 (N1-Me)	326 326 326
	DMSO-d ₆	2.0 (N2-Me)	326

TABLE 132—*cont.*

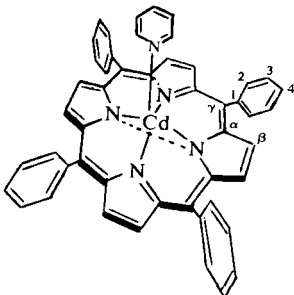
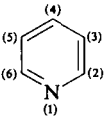
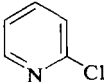
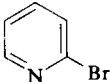
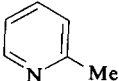
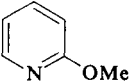
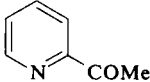
Compound	Solvent	$^3J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	CDCl_3	~ 0.5 (H-H β)	401
	acetone- d_6	-1.47 (N-H3)	117
	acetone- d_6	-1.48 (N-H3)	123
	acetone- d_6	-0.69 (N-H3)	117
	acetone- d_6	-1.94 (N-H5)	117
	acetone- d_6	-0.69 (N-H3)	123
	acetone- d_6	-0.83 (N-H3)	117
	acetone- d_6	-1.80 (N-H5)	117
	acetone- d_6	0.88 (N-H3)	123
	acetone- d_6	1.83 (N-H5)	123
	acetone- d_6	-0.99 (N-H3)	117
	acetone- d_6	-1.79 (N-H5)	117
	acetone- d_6	1.15 (N-H3)	123
	acetone- d_6	1.52 (N-H5)	123
	acetone- d_6	2.91 (N-Me)	123
	acetone- d_6	-0.70 (N-H3)	117
	acetone- d_6	-1.82 (N-H5)	117
	acetone- d_6	0.72 (N-H3)	123
	acetone- d_6	1.85 (N-H5)	123
	acetone- d_6	0.92 (N-H3)	123
	acetone- d_6	1.67 (N-H5)	123

TABLE 132—*cont.*

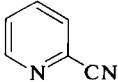
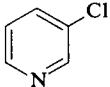
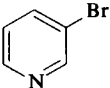
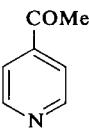
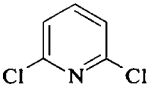
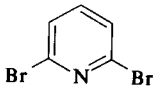
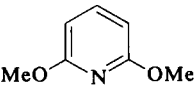
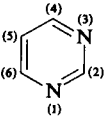
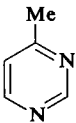
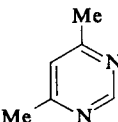
Compound	Solvent	$^3J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	acetone- d_6	-0.73 (N-H3) -1.70 (N-H5)	117 117
	acetone- d_6	-1.57 (N-H5)	117
	acetone- d_6	-1.54 (N-H5)	117
	acetone- d_6	-1.52 (N-H3) -1.52 (N-H5)	117 117
	acetone- d_6	-1.01 (N-H3) -1.01 (N-H5)	117 117
	acetone- d_6	-1.15 (N-H3) -1.15 (N-H5)	117 117
	acetone- d_6	-0.89 (N-H3) -0.89 (N-H5)	117 117
	DMSO	1.20 (N1, 3-H5)	123
	DMSO	1.08 (N1-H5) 0.86 (N3-H5) 2.88 (N3-Me)	123 123 123
	DMSO	0.81 (N1-H5) 2.73 (N3-Me4)	123 123

TABLE 132—*cont.*

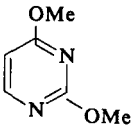
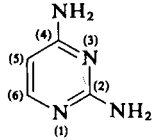
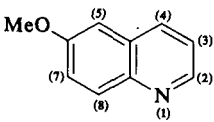
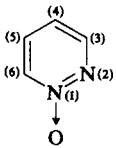
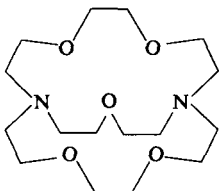
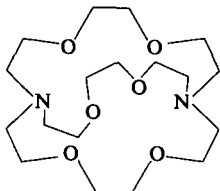
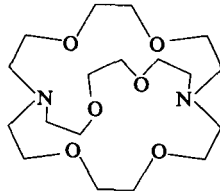
Compound	Solvent	$^3J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	DMSO	1.40 (N1-H5)	123
	H ₂ O (pH = 11)	1.8 (N1-H5) 3.7 (N3-H5)	345 345
	CDCl ₃	1.7 (N-H8) 1.5 (N-H3)	119 119
	DMSO	-8.30 (N1-H3) -5.04 (N1-H5) -1.85 (N2-H4) -0.33 (N2-H6)	141 141 141 141
	CHCl ₃	3.3	267
	CHCl ₃	3.1	267
	CHCl ₃	2.6	267
Sr(NO ₃) ₂ complex			

TABLE 132—*cont.*

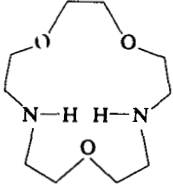
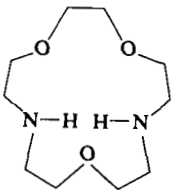
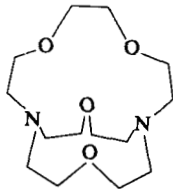
Compound	Solvent	$^3J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
 2HCl	CHCl_3	3.3	267
 2HCl + KSCN complex	CHCl_3	3.5	267
 $\text{B}(\text{OCH}_2\text{CH}_2)_3\text{N}$	CHCl_3	3.6	267
$\text{MeSi}(\text{OCH}_2\text{CH}_2)_3\text{N}$	CDCl_3	2.6	268
$\alpha\text{-C}_{10}\text{H}_7\text{Ge}(\text{OCH}_2\text{CH}_2)_3\text{N}$	CDCl_3	2.4	268
$\beta\text{-C}_{10}\text{H}_7\text{Ge}(\text{OCH}_2\text{CH}_2)_3\text{N}$	CDCl_3	2.2	268
$\text{O}=\text{V}(\text{OCH}_2\text{CH}_2)_3\text{N}$	CDCl_3	2.3	268
$\text{O}=\text{V}(\text{OCH}_2\text{CH}_2)_3\text{N}$	DMSO	2.2	268
$\text{MeGe}(\text{OCH}_2\text{CH}_2)_3\text{N}$	DMSO	3.2	268
$\text{EtGe}(\text{OCH}_2\text{CH}_2)_3\text{N}$	CDCl_3	2.1	139
$\alpha\text{-C}_{10}\text{H}_7\text{Ge}(\text{OCH}_2\text{CH}_2)_3\text{N}$	CDCl_3	2.2	139
$\beta\text{-C}_{10}\text{H}_7\text{Ge}(\text{OCH}_2\text{CH}_2)_3\text{N}$	CDCl_3	2.2	139
$\text{EtOGe}(\text{OCH}_2\text{CH}_2)_3\text{N}$	CDCl_3	2.3	139
$\text{PhOGe}(\text{OCH}_2\text{CH}_2)_3\text{N}$	CDCl_3	2.1	139
$\text{ClGe}(\text{OCH}_2\text{CH}_2)_3\text{N}$	CDCl_3	2.1	139
$\text{ClGe}(\text{OCH}_2\text{CH}_2)_3\text{N}$	DMSO	2.1	139
$\text{trans-}[\text{FeH}(\text{N}_2)]-$	THF	2.1	139
$-(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{BPh}_4$	THF	3.0	394
MeCSNH_2	acetone- d_6	2.0	214

TABLE 132—*cont.*

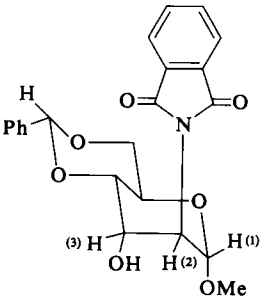
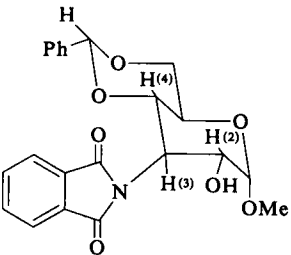
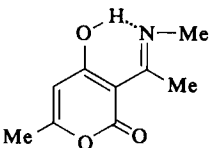
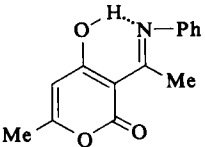
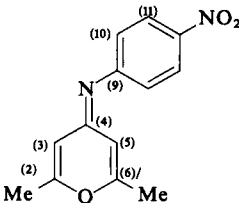
Compound	Solvent	$^3J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	acetone- d_6	1.5 (N-H1)	453
	acetone- d_6	0.9 (N-H2) <0.5 (N-H4)	453 453
	CDCl_3	2.5 (N=CMe)	437
	CDCl_3	2.25 (N=CMe)	437
	CDCl_3 CD_3CN	1.1 (N-H10) 1.1 (N-H10)	461 461

TABLE 132—*cont.*

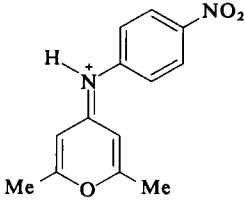
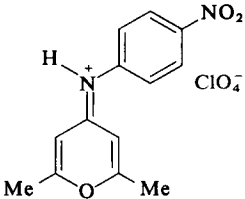
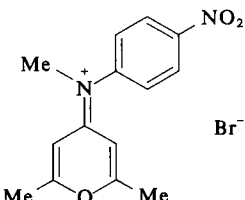
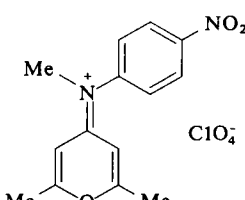
Compound	Solvent	$^3J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	CDCl ₃ CD ₃ CN	2.0 (N-H10) 2.0 (N-H10)	461 461
	CD ₃ CN CD ₃ NO ₂	2.0 (N-H10) 2.0 (N-H10)	461 461
	CDCl ₃ CD ₃ CN	2.0 (N-H10) 2.0 (N-H10)	461 461
	CD ₃ CN CD ₃ NO ₂	2.0 (N-H10) 2.0 (N-H10)	461 461
Tyr-Gly-Gly-Phe Residue			
Tyr ¹	DMSO	0.5 (N2-H1α)	447
Gly ²		0.5 (N3-H2α)	447
Gly ³		1.5 (N4-H3α)	447
Phe ⁴		2.75 (N4-H4β)-A (from ¹⁵ N spectrum)	447
		3 (N4-H4β)-A (from ¹ H spectrum)	447
		2.25 (N4-H4β)-B (from ¹⁵ N and ¹ H spectra)	447

TABLE 132—*cont.*

Compound	Solvent	$^3J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
Tyr-Gly-Gly-Phe-Leu			
Residue			
Tyr ¹	DMSO	0 (N2-H1 α)	447
Gly ²		0.5 (N3-H2 α)	447
Gly ³		1.7 (N4-H3 α)	447
Phe ⁴		1 (N5-H4 α)	447
		2.7 (N4-H4 β)-A	447
		(from ^{15}N spectrum)	
		3.7 (N4-H4 β)-A	447
		(from ^1H spectrum)	
		1.1 (N4-H4 β)-B ₁	447
		(from ^{15}N and ^1H spectra)	
Leu ⁵	DMSO	3.5 (N5-H5 β)-A	447
		(from ^{15}N spectrum)	
		0 (N5-H5 β)-B	447
		(from ^{15}N spectrum)	
<i>cis</i> -cyclo(α -Ala- α -Phe)			
Ala/Phe	DMSO-d ₆	0 (N1-H2 α)	446
Phe/Ala		0 (N2-H1 α)	446
Ala		3.0 (N1-H1 β)	446
Phe		4.6 (N2-H2 β)-A	446
		1.8 (N2-H2 β)-B	
<i>trans</i> -cyclo(D-Ala- α -Phe)			
Ala/Phe	DMSO-d ₆	0 (N1-H2 α)	446
Phe/Ala		0 (N2-H1 α)	446
Ala		3.0 (N1-H1 β)	446
Phe		4.2 (N2-H2 β)-A	446
		2.0 (N2-H2 β)-B	446
Methyl ester of			
N-formylalanine	CDCl ₃	2.69	308
2-isocyanomethyl			
propionate	CDCl ₃	2.69	308

TABLE 133

Some ^{15}N - ^1H couplings across four bonds (absolute values if sign not given)

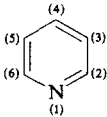
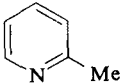
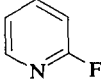
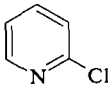
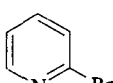
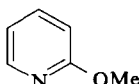
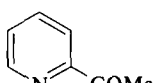
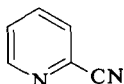
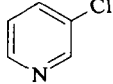
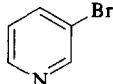
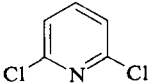
Compound	Solvent	$^4J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	acetone- d_6	$\text{N2} + 0.27$ (N1-H4)	117
	acetone- d_6	0.27 (N1-H4)	123
	acetone- d_6	0.37 (N1-H4)	123
	acetone- d_6	$+0.69$ (N1-H4)	117
	acetone- d_6	0.69 (N1-H4)	123
	acetone- d_6	$+0.58$ (N1-H4)	117
	acetone- d_6	0.57 (N1-H4)	123
	acetone- d_6	$+0.60$ (N1-H4)	117
	acetone- d_6	$+0.59$ (N1-H4)	117
	acetone- d_6	0.54 (N1-H4)	123
		0.13 (N-Me)	123
	acetone- d_6	0.25 (N1-H4)	123
		0.51 (N-Me)	123
	acetone- d_6	$+0.22$ (N1-H4)	117
	acetone- d_6	<0.2 (N1-H4)	117
	acetone- d_6	<0.2 (N1-H4)	117
	acetone- d_6	$+0.71$ (N1-H4)	117

TABLE 133—*cont.*

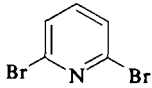
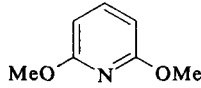
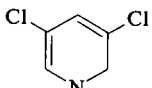
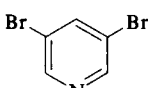
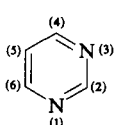
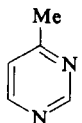
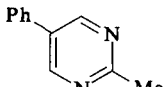
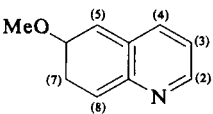
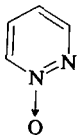
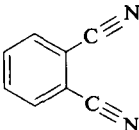
Compound	Solvent	$^4J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	acetone- d_6	+0.79 (N1-H4)	117
	acetone- d_6	+0.66 (N1-H4)	117
	acetone- d_6	<0.2 (N1-H4)	117
	acetone- d_6	<0.2 (N1-H4)	117
	DMSO	0.95 (N1-H4)	123
	DMSO	0.52 (N3-H6)	123
	DMSO	1.40 (N1-H4)	123
	CDCl_3	0.38 (N-H4)	119
		0.29 (N-H7)	119
	acetone- d_6	0.81 (N1-H4)	141
		0.38 (N2-H5)	141
	acetone- d_6	0	144

TABLE 133—*cont.*

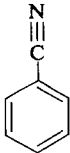
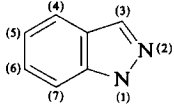
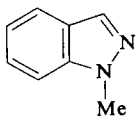
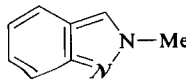
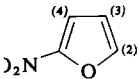
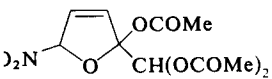
Compound	Solvent	$^4J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
	<i>acetone-d</i> ₆	0	675
	DMSO- <i>d</i> ₆	0.9 (N1-H6)	326
	DMSO- <i>d</i> ₆	0.8 (N1-H6)	326
	DMSO- <i>d</i> ₆	0.7 (N1-H6)	326
	DMSO- <i>d</i> ₆	0.7 (N-H2)	370
	DMSO- <i>d</i> ₆	0 (N-H3)	370

TABLE 134

Some ^{15}N - ^1H couplings across five and six bonds (absolute values if sign not given)

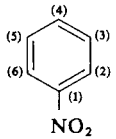
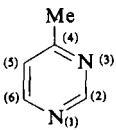
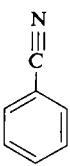
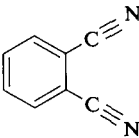
Compound	Solvent	$^{5,6}J(^{15}\text{N}-^1\text{H})$ (Hz)	Ref.
 <chem>O=[N+]([O-])c1ccccc1</chem>	acetone- d_6	$(^5J) -0.3$ (N-H4)	1
 <chem>Cn1ccccc1</chem>	DMSO	$(^5J) 0.42$ (N1-Me)	123
 <chem>N#Cc1ccccc1</chem>	acetone- d_6	$(^5J) 0$ $(^6J) 0$	675 675
 <chem>N#Cc1ccccc1C#N</chem>	acetone- d_6	$(^5J) 0$ $(^6J) 0$	144 144

Table 135

D/H isotope effects on $^1\text{J}(\text{N-H})$ in the ammonium ion ²²⁹

	$^1\text{J}(^{14}\text{N}-^1\text{H})$	$^1\text{J}(^{14}\text{N}-\text{D})$	$^1\text{J}(^{14}\text{N}-^1\text{H})^{\text{a}}$
	in Hz		
NH_4^+	52.52 ± 0.02	-	-
NH_3D^+	52.47 ± 0.02	8.09 ± 0.03	52.7 ± 0.2
NH_2D_2^+	52.41 ± 0.02	8.07 ± 0.02	52.6 ± 0.15
NHD_3^+	52.37 ± 0.03	8.08 ± 0.03	52.6 ± 0.2
ND_4^+	-	8.06 ± 0.02	52.5 ± 0.15

^a Calculated using $^1\text{J}(^{14}\text{N}-\text{H}) = 6.5144 \text{ } ^1\text{J}(^{14}\text{N}-\text{D})$

TABLE 136

Some ^{15}N - ^{13}C couplings across one bond (absolute values if sign not given)

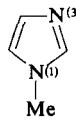
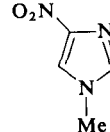
Compound	Solvent	$^1J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
MeCN	acetone- d_6 (90% v/v)	-17.5	484
	CDCl_3	-17.8	676
diamagnetic cyano complexes			
species			
CN^-	D_2O	6.1	399
	H_2O	6.1	323
HCN	gas (condensed and sealed)	18.5	399
		18.6	673
octahedral hexacyano complexes			
$[\text{Fe}(\text{CN})_6]^{4-}$	H_2O	6.8	323
$[\text{Ru}(\text{CN})_6]^{4-}$	H_2O	8.4	323
$[\text{Os}(\text{CN})_6]^{4-}$	H_2O	9.1	323
square-planar tetracyano complexes			
$[\text{Ni}(\text{CN})_4]^{2-}$	H_2O	9.7	323
	D_2O	9.8	399
$[\text{Pd}(\text{CN})_4]^{2-}$	H_2O	9.5	323
	D_2O	8.3	399
$[\text{Pt}(\text{CN})_4]^{2-}$	H_2O	11.1	323
	D_2O	11.4	399
Linear dicyano complexes			
$[\text{Ag}(\text{CN})_2]^-$	H_2O	9.2	323
$[\text{Au}(\text{CN})_2]^-$	H_2O	11.1	323
$[\text{Hg}(\text{CN})_2]^-$	H_2O	10.8	323
Tetrahedral tetracyano complexes			
$[\text{Cu}(\text{CN})_4]^{3-}$	H_2O	7.8	323
$[\text{Zn}(\text{CN})_4]^{2-}$	H_2O	8.9	323
	D_2O	8.9	399
$[\text{Cd}(\text{CN})_4]^{2-}$	H_2O	7.7	323
	D_2O	7.4	399
$[\text{Hg}(\text{CN})_4]^{2-}$	H_2O	7.2	323
	D_2O	7.2	399
2,4,6- $\text{Me}_3\text{C}_6\text{H}_2\text{CNO}$	CDCl_3	73	448
Me_3SiCNO	CDCl_3	50	448
Me_3CCNO	CDCl_3	770	448
Ph_3SiCCNO	CDCl_3	734	448
	H_2O	1.6 (N1-Me)	120
	DMSO	1.7 (N1-Me)	120

TABLE 136—*cont.*

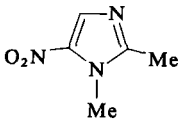
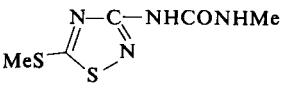
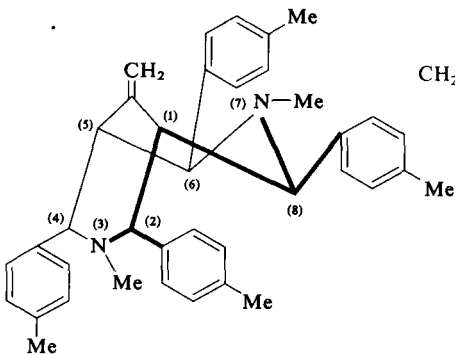
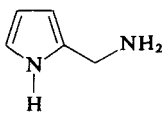
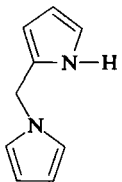
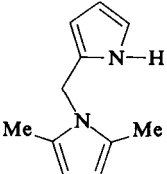
Compound	Solvent	$^1J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	DMSO	1.8 (N1-Me)	120
	1:1 DMSO- d_6 /CDCl $_3$	12.2 (N-Me)	331
	CH $_2$ Cl $_2$	4.6 (N3-Me) 4.6 (N7-Me) 3.7 (N3-C2) 3.7 (N3-C4) 4.5 (N7-C6) 4.5 (N7-C8)	471 471 471 471 471 471
	CDCl $_3$	3.9 (N-CH $_2$)	677
	CDCl $_3$	11.0 (N-CH $_2$)	677
	CDCl $_3$	11.2 (N-CH $_2$)	677

TABLE 136—*cont.*

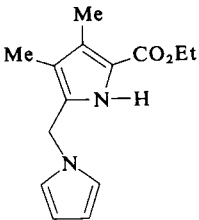
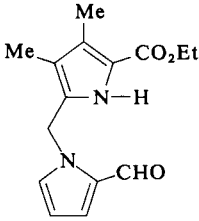
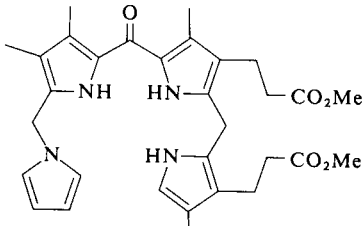
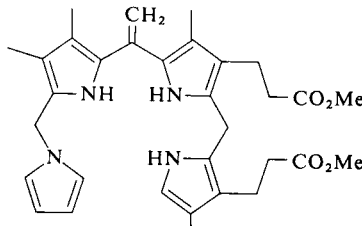
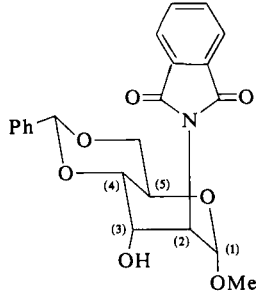
Compound	Solvent	$^1J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	CDCl_3	11.3 (N-CH ₂)	677
	CDCl_3	9.6 (N-CH ₂)	677
	CDCl_3	10.4 (N-CH ₂)	677
	CDCl_3	10.7 (N-CH ₂)	677
	DMSO	9.8 (N-C2) 12.2 (N-CO)	453 453

TABLE 136—cont.

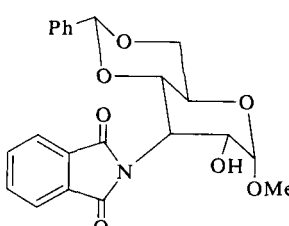
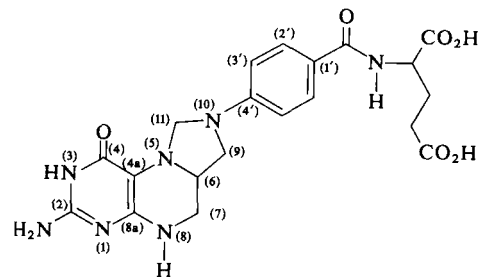
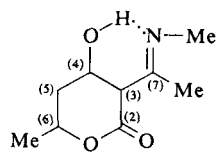
Compound	Solvent	$^1J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	DMSO	9.8 (N-C3)	453
		12.2 (N-CO)	453
$\text{Me}_2\text{N}-\dot{\text{C}}\text{H}-\text{NMe}_2$	DMSO- d_6	19.8 (N-CH)	449
$\text{Me}_2\text{N}-\dot{\text{C}}\text{H}-\text{CH}=\text{CH}-\text{NMe}_2$	DMSO- d_6	17.6 (N-CH)	449
$\text{Me}_2\text{N}-\dot{\text{C}}\text{H}-(\text{CH}=\text{CH})_2-\text{NMe}_2$	DMSO- d_6	17.6 (N-CH)	449
$\text{Me}_2\text{N}-\dot{\text{C}}\text{H}-(\text{CH}=\text{CH})_3-\text{NMe}_2$	DMSO- d_6	16.5 (N-CH)	449
$\text{Me}_2\text{N}-\text{CHO}$	benzene- d_6 (50% v/v)	14.3 (N-CH)	32
		12.1 (N-Me)	32
		10.4 (N-Me)	32
$\text{Me}_2\text{N}-\text{CH}=\text{CH}-\text{CHO}$	CDCl_3 (50% v/v)	15.9 (N-CH)	32
$\text{Me}_2\text{N}-(\text{CH}=\text{CH})_2-\text{CHO}$	CDCl_3 (2 M)	15.9 (N-CH)	32
$\text{Me}_2\text{N}-(\text{CH}=\text{CH})_3-\text{CHO}$	CDCl_3	15.3 (N-CH)	32
		11.0 (N-Me)	32
	D_2O (0.1 M)	8.0 (N5-C4a)	286
		3.6 (N5-C6)	286
		4.7 (N5-C11)	286
		16.0 (N10-C4')	286
		9.9 (N10-C9)	286
		10.8 (N10-C11)	286
	CDCl_3	4.75 (N-Me)	437

TABLE 136—*cont.*

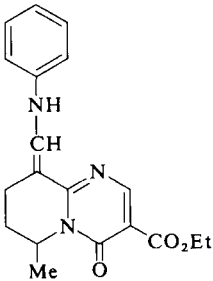
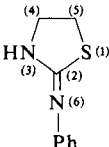
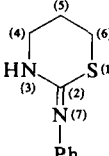
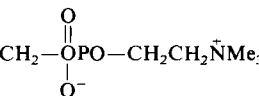
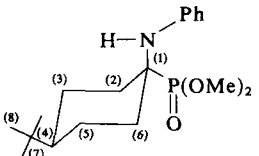
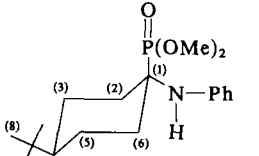
Compound	Solvent	$^1J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	CDCl_3	13.0 (NH-CH)	643
	CDCl_3	6.5 (N3-C4) 14.5 (N3-C2) 14.5 (N6-C2) 8.5 (N6-Ph)	460 460 460 460
	CDCl_3	12.8 (N3-C2) 6.7 (N3-C4) 12.0 (N7-C2) 6.5 (N7-Ph)	460 460 460 460
$\text{CH}_2-\text{O}-\text{CH}_2-\text{C}_{15}\text{H}_{31}$ 	$\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$ (50:50:15 v/v/v)	4.9 (N-CH ₂) 5.1 (N-Me)	678 678
	CD_2Cl_2	6.4 (N-C1) 10.2 (N-Ph)	464 464
	CD_2Cl_2	4.9 (N-C1) 11.5 (N-Ph)	464

TABLE 136—*cont.*

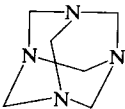
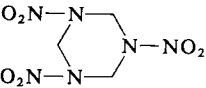
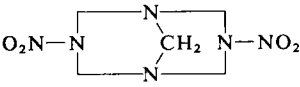
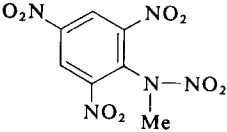
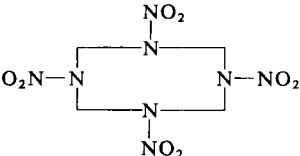
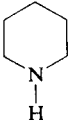
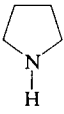
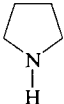
Compound	Solvent	$^1J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	acetone- d_6	0 (N- CH_2)	462
	acetone- d_6	3.6 (N- CH_2)	462
	DMSO- d_6	0 (N- CH_2)	462
$\text{MeN}(\text{NO}_2)_2$	acetone- d_6	0 (N-Me)	462
MeNHNO_2	acetone- d_6	8.5 (N-Me)	462
Me_2NNO_2	acetone- d_6	9.2 (N-Me)	462
	acetone- d_6	8.9 (N-Me)	462
	acetone- d_6	10.2 (N- CH_2)	462
$\text{Me}_2\text{CHCH}_2\text{NH}_2$	neat	5.3 ^a	492
Et_2NH	neat	5.5 ^a	492
	neat	4.9 ^a	492
	neat	3.8 ^a	492
	water (99%)	3.9 ^a	492

TABLE 136—*cont.*

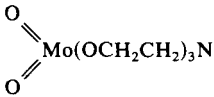
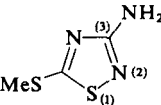
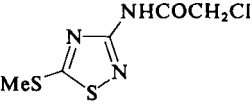
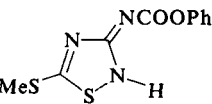
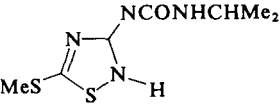
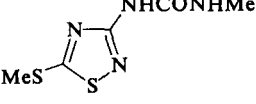
Compound	Solvent	$^1J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
Et_3N	neat	5.1 ^a	492
$\text{PhMeSi}(\text{OCH}_2\text{CH}_2)_3\text{NMe}$	CDCl_3 (10%)	6.6 (N-Me) 6.5 (N-CH ₂)	269 269
$\text{B}(\text{OCH}_2\text{CH}_2)_3\text{N}$	CDCl_3	6.7	268
$\text{MeSi}(\text{OCH}_2\text{CH}_2)_3\text{N}$	CDCl_3	7.8	268
$\alpha\text{-C}_{10}\text{H}_7\text{Ge}(\text{OCH}_2\text{CH}_2)_3\text{N}$	CDCl_3	7.0	268
$\beta\text{-C}_{10}\text{H}_7\text{Ge}(\text{OCH}_2\text{CH}_2)_3\text{N}$	CDCl_3	7.3	268
$\text{O}=\text{V}(\text{OCH}_2\text{CH}_2)_3\text{N}$	DMSO	5.9	268
	DMSO	4.7	268
$\text{MeGe}(\text{OCH}_2\text{CH}_2)_3\text{N}$	CDCl_3	7.3	139
$\text{EtGe}(\text{OCH}_2\text{CH}_2)_3\text{N}$	CDCl_3	6.6	139
$\alpha\text{-C}_{10}\text{H}_7\text{Ge}(\text{OCH}_2\text{CH}_2)_3\text{N}$	CDCl_3	7.0	139
$\beta\text{-C}_{10}\text{H}_7\text{Ge}(\text{OCH}_2\text{CH}_2)_3\text{N}$	CDCl_3	7.3	139
$\text{EtOGe}(\text{OCH}_2\text{CH}_2)_3\text{N}$	CDCl_3	6.6	139
$\text{PhOGe}(\text{OCH}_2\text{CH}_2)_3\text{N}$	CDCl_3	6.6	139
$\text{ClGe}(\text{OCH}_2\text{CH}_2)_3\text{N}$	DMSO	5.9	139
	$\text{CDCl}_3/\text{DMSO}$ 1:1 v/v	20.8 (N2-C3)	331
	$\text{CDCl}_3/\text{DMSO}$ 1:1 v/v	23.2 (N2-C3)	331
	$\text{CDCl}_3/\text{DMSO}$ 1:1 v/v	25.8 (N2-C3)	331
	$\text{CDCl}_3/\text{DMSO}$ 1:1 v/v	22.5 (N2-C3)	331
	$\text{CDCl}_3/\text{DMSO}$ 1:1 v/v	23.2 (N2-C3)	331

TABLE 136—*cont.*

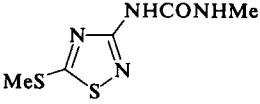
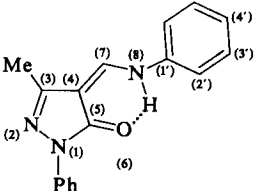
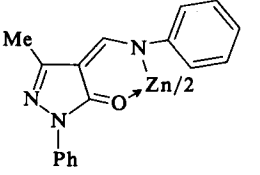
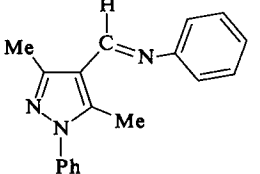
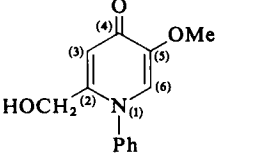
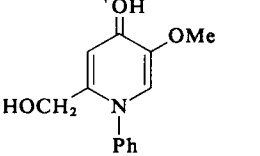
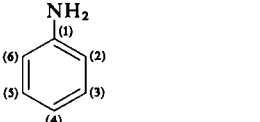
Compound	Solvent	$^1J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	CDCl ₃ /DMSO 1:1 v/v	23.2 (N2-C3)	331
	CDCl ₃	16.5 (N8-C7) 16.5 (N8-C1')	452 452
	CDCl ₃	9.9 (N8-C7) 7.7 (N8-C1')	452 452
	CDCl ₃	6.6 (N8-C7)	452
	DMSO (3% w/v)	13.2 (N-Ph) 15.4 (N-C2) 14.6 (N-C6)	639 639 639
	DMSO (3% v/v)	13.8 (N-Ph) 13.5 (N-C2) ~14 (N-C6)	639 639 629
	DMSO-d ₆ (1 M)	-12.1 (N-C1)	87

TABLE 136—*cont.*

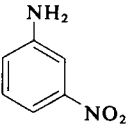
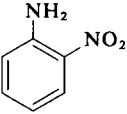
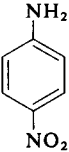
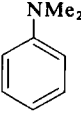
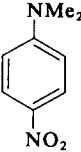
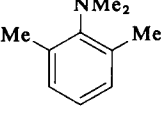
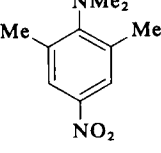
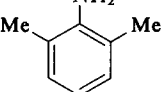
Compound	Solvent	$^1J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	acetone-d ₆	12.5 (N-C1) ^a	670
	acetone-d ₆	15.3 (N-C1) ^a	670
	DMSO-d ₆ (1 M) acetone-d ₆	-14.7 (N-C1) 14.7 (N-C1)	87
	acetone-d ₆	-13.2 (N-C1)	87
	acetone-d ₆	-15.6 (N-C1)	87
	acetone-d ₆	-12.9 (N-C1)	87
	acetone-d ₆	-14.2 (N-C1)	87
	acetone-d ₆	-11.9 (N-C1)	87

TABLE 136—*cont.*

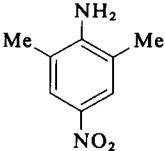
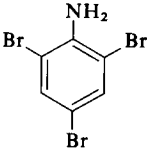
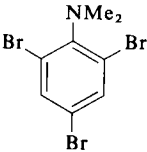
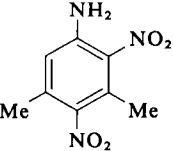
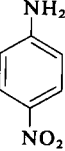
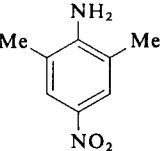
Compound	Solvent	$^1J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	DMSO- d_6 (1 M)	-14.8 (N-C1)	87
	DMSO- d_6 (1 M)	-17.6 (N-C1)	87
	DMSO- d_6 (1 M)	-16.3 (N-C1)	87
	DMSO- d_6 (1 M)	-14.8 (N-C1)	87
	DMSO- d_6 (1 M)	-15.8 (N-C1)	87
	DMSO- d_6 (1 M)	-16.2 (N-C1)	87
	DMSO- d_6 (1 M)	-15.8 (N-C1)	87

TABLE 136—*cont.*

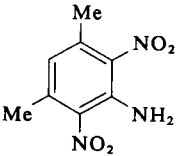
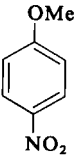
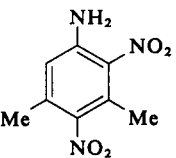
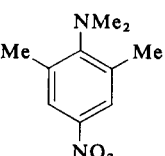
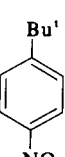
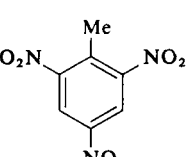
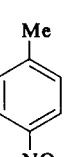
Compound	Solvent	$^1J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	DMSO- d_6 (1 M)	-15.6 (N-C1)	87
	DMSO- d_6 (1 M)	-15.9 (N-C1)	87
	DMSO- d_6 (1 M)	-16.6 (N-C1)	87
	DMSO- d_6 (1 M)	-14.7 (N-C1)	87
	DMSO- d_6 (1 M)	-15.0 (N-C1)	87
	DMSO- d_6 (1 M)	-18.0 (N-C1)	87
	DMSO- d_6 (1 M)	-14.9 (N-C1)	87

TABLE 136—*cont.*

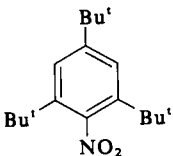
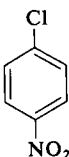
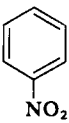
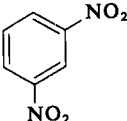
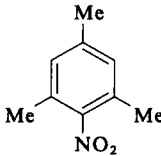
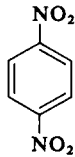
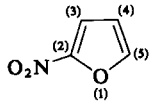
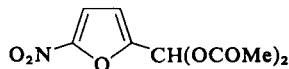
Compound	Solvent	$^1J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	DMSO- d_6 (1 M) (measured at 70 °C)	-13.7 (N-C1)	87
	DMSO- d_6 (1 M)	-15.4 (N-C1)	87
	DMSO- d_6 (1 M)	-14.7 (N-C1)	87
	DMSO- d_6 (1 M)	-15.9 (N-C1)	87
	DMSO- d_6 (1 M)	-14.7 (N-C1)	87
	DMSO- d_6 (1 M)	-15.3 (N-C1)	87
	DMSO- d_6 (1 M)	26.6 (N-C2)	370
	DMSO- d_6	27.2 (N-C2)	370

TABLE 136—*cont.*

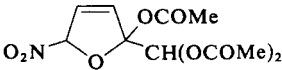
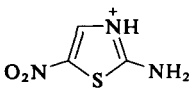
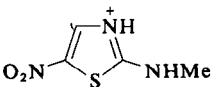
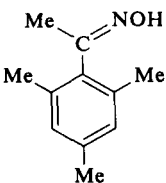
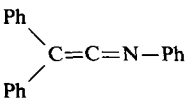
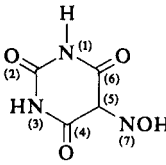
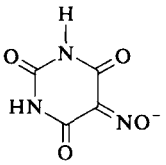
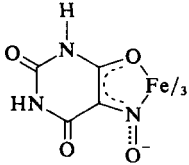
Compound	Solvent	$^1J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	DMSO- d_6	8.8 (N-C2)	370
	D ₂ SO ₄ (92%)	25.0 (N-C2)	332
	D ₂ SO ₄ (92%)	23 (N-C2)	332
	not specified	3.3	450
	CH ₂ Cl ₂	18.8 (?)	360
	DMSO	2.55 (N7-C5)	454
	DMSO	5.51 (N7-C5)	454
	DMSO	4.19 (N1-C5)	454

TABLE 136—*cont.*

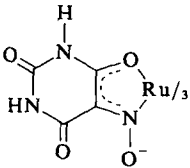
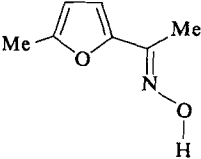
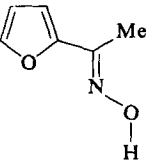
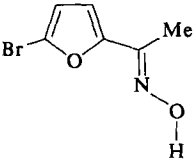
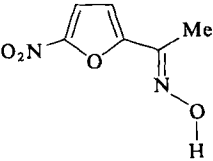
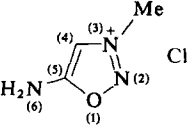
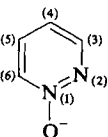
Compound	Solvent	$^1J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	DMSO	5.13 (N7-C5)	454
	acetone- d_6	3.9	365
	acetone- d_6	3.9	365
	acetone- d_6	3.9	365
	acetone- d_6	3.9	365
	CD ₃ OD/D ₂ O 1:1 v/v	-7.6 (N3-Me) -12.4 (N3-C4) -23.5 (N6-C5)	336 336 336
	acetone- d_6	15 (N1-C6)	141

TABLE 136—*cont.*

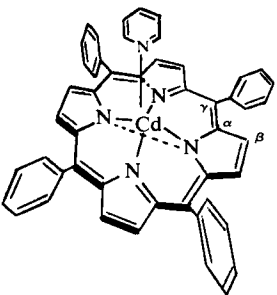
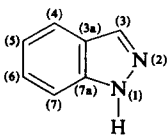
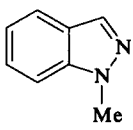
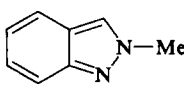
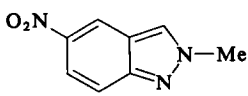
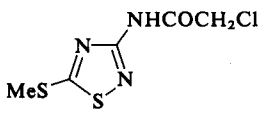
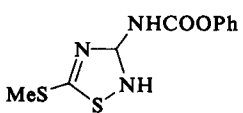
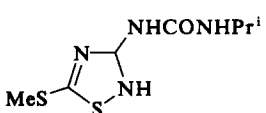
Compound	Solvent	$^1J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	CDCl_3	<2.0 (N—C α)	401
	$\text{DMSO}-d_6$	13.56 (N1—C7a)	326
	$\text{DMSO}-d_6$	15.03 (N1—C7a) 13.8 (N1—Me)	326 326
	$\text{DMSO}-d_6$	1.83 (N1—C7a) 13.20 (N2—C3) 12.8 (N2—Me)	326 326 326
	$\text{DMSO}-d_6$	13.37 (N2—C3) 12.8 (N2—Me)	326 326
	$\text{CDCl}_3/\text{DMSO}-d_6$ 1:1 v/v	12.8 (N—CO)	331
	$\text{CDCl}_3/\text{DMSO}-d_6$ 1:1 v/v	27.5 (N—CO)	331
	$\text{CDCl}_3/\text{DMSO}-d_6$ 1:1 v/v	18.8 (N—CO)	331

TABLE 136—*cont.*

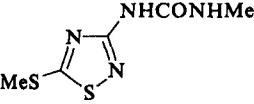
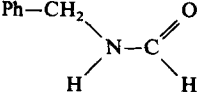
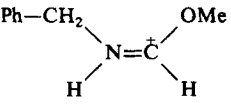
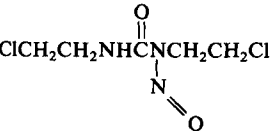
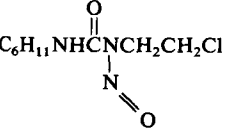
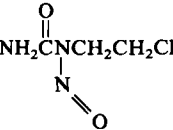
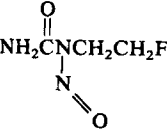
Compound	Solvent	$^1J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	$\text{CDCl}_3/\text{DMSO-d}_6$ 1:1 v/v	19.3 (N-CO)	331
		22.0 (NMe-CO)	331
	CDCl_3	13.5 (N-CO)	118
		10.5 (N-CH ₂)	118
	CD_3CN	20.5 (N-CO)	118
OSO_2F^-		7.0 (N-CH ₂)	118
	CDCl_3	12.0 (NH-CH ₂)	429
		17.2 [N(NO)-CO]	429
		22.5 (NH-CO)	429
		7.5 [N(NO)-CH ₂]	429
	DMSO	11.0 (NH-CH ₂)	429
		17.6 [N(NO)-CO]	429
		21.5 (NH-CO)	429
		7.5 [N(NO)-CH ₂]	429
	CDCl_3	10.5 (NH-CH ₂)	429
		16.2 [N(NO)-CO]	429
		24.0 (NH-CO)	429
		7.3 [N(NO)-CH ₂]	429
	DMSO-d ₆	11.6 (NH-CH ₂)	429
		16.2 [N(NO)-CO]	429
		23.8 (NH-CO)	429
		8.5 [N(NO)-CH ₂]	429
	CDCl_3	24.2 (NH ₂ -CO)	429
		4.5 [(NO)-CH ₂]	429
	DMSO-d ₆	24.5 [NH ₂ -CO]	429
	CDCl_3	18.3 [N(NO)-CO]	429
		8.0 [N(NO)-CH ₂]	429
	DMSO-d ₆	16.2 [N(NO)-CO]	429
		7.3 [N(NO)-CH ₂]	429

TABLE 136—*cont.*

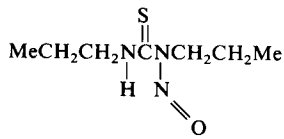
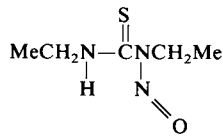
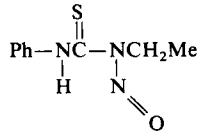
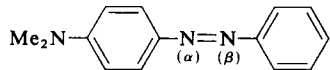
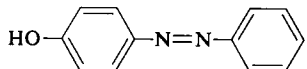
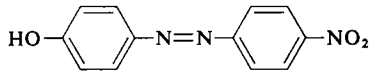
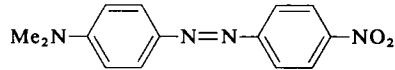
Compound	Solvent	$^1J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	CHCl ₃	11.1 (NH-CH ₂)	430
		18.2 (NH-CS)	430
		12.5 [N(NO)-CS]	430
		8.0 [N(NO)-CH ₂]	430
	acetone	11.4 (NH-CH ₂)	430
		17.5 (NH-CS)	430
		12.7 [N(NO)-CS]	430
		8.1 [N(NO)-CH ₂]	430
	CHCl ₃	11.4 (NH-CH ₂)	430
		16.2 (NH-CS)	430
		13.6 [N(NO)-CS]	430
		7.8 [N(NO)-CH ₂]	430
	acetone	10.5 (NH-Ph)	430
		18.4 (NH-CS)	430
PhN=NPh	CDCl ₃	1.8	379
		+1.9	465
	CCl ₄ + C ₆ D ₁₂	+2.0	468
	D ₂ SO ₄ 22 N (+15% EtOH)	-7.1	468
Z-isomer	CDCl ₃	3.9	467
E-isomer	CDCl ₃	1.9	467
E-isomer	D ₂ SO ₄ 22 N-EtOH (7:1 v/v)	-7.1	467
	CDCl ₃	0.6 (N α)	379
	DMSO	1.76 (N β)	379
	DMSO-d ₆	1.76 (N β)	463
		1.17 (N α)	463
	DMSO	0.8 (N α)	379
	CDCl ₃	0.8 (N α)	379

TABLE 136—*cont.*

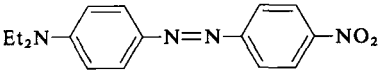
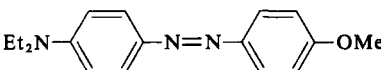
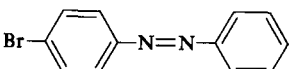
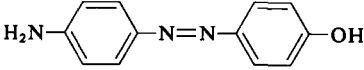
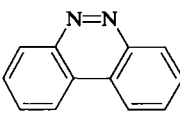
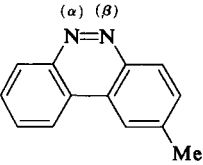
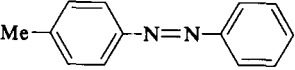
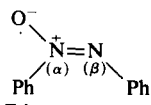
Compound	Solvent	$^1J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	CDCl_3	0 ($\text{N}\alpha$)	679
<i>E</i> -isomer			
	CDCl_3	0 ($\text{N}\alpha$)	679
	CDCl_3	1.5 ($\text{N}\beta$)	379
	DMSO	0.6 ($\text{N}\beta$)	379
	CDCl_3	3.4	467
		+7.3	468
	D_2SO_4 -EtOH (7:1 v/v)	-3.7	467
	$\text{CCl}_4 + \text{C}_6\text{D}_{12}$	+8.3	468
	D_2SO_4 16 N (+10% EtOH)	-4.4	468
	CDCl_3	+7.2 ($\text{N}\alpha$)	468
	strong-acid media	-6.3 (-6.3)	468
		obs. 55 °C($\text{N}\alpha$)	
	strong-acid	-10.6 (-10.3)	468
		obs. 55 °C($\text{N}\beta$)	
	CDCl_3	+1.8 ($\text{N}\beta$)	468
<i>E</i> -isomer	CDCl_3	1.2 ($\text{N}\alpha$)	679
<i>Z</i> -isomer	CDCl_3	+9.3 ($\text{N}\alpha$)	679
	CDCl_3	3.7 ($\text{N}\beta$)	679
<i>Z</i> -isomer			
<i>Z</i> -isomer	CDCl_3	-12.5 ($\text{N}\alpha$)	679
<i>E</i> -isomer	pyridine- d_6	1.3 ($\text{N}\beta$)	679

TABLE 136—*cont.*

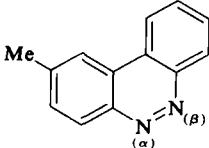
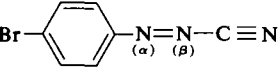
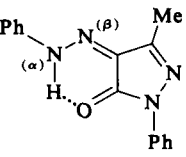
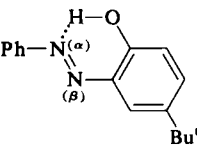
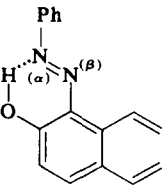
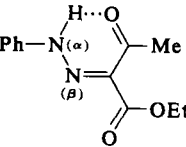
Compound	Solvent	$^1J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	CDCl_3	7.2 ($\text{N}\alpha$)	679
	CDCl_3	8.8 ($\text{N}\alpha$)	679
<i>Z</i> -isomer			
<i>Z</i> -isomer	CDCl_3	18.3 ($\text{N}\beta$)	679
<i>E</i> -isomer	CDCl_3	0 ($\text{N}\alpha$)	679
<i>E</i> -isomer	CDCl_3	0 ($\text{N}\beta$)	679
	CDCl_3	18.77 ($\text{N}\alpha$) 5.13 ($\text{N}\beta$)	463 463
	CDCl_3	1.61 ($\text{N}\alpha$) 1.17 ($\text{N}\beta$)	463 463
	CDCl_3	13.28 ($\text{N}\alpha$) 8.24 ($\text{N}\beta$)	463 463
	CDCl_3	18.7 ($\text{N}\alpha$) 3.4 ($\text{N}\beta$)	679 679

TABLE 136—*cont.*

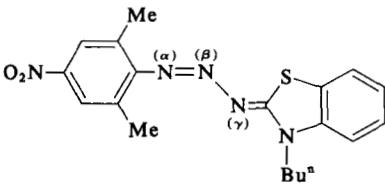
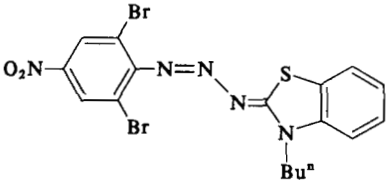
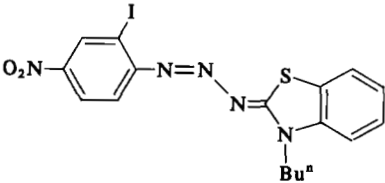
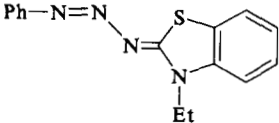
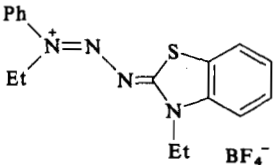
Compound	Solvent	$^1J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	pyridine- d_5	+8.2 ($\text{N}\alpha$)	679
<i>Z</i> -isomer			
<i>E</i> -isomer	pyridine- d_5	0 ($\text{N}\alpha$)	679
	pyridine- d_5	0 ($\text{N}\alpha$)	679
<i>E</i> -isomer			
	pyridine- d_5	0 ($\text{N}\alpha$)	679
<i>E</i> -isomer			
	pyridine- d_5	7.7 ($\text{N}\alpha$) 4.4 ($\text{N}\gamma$)	664 664
<i>Z</i> -isomer			
	CDCl_3	11.0 ($\text{N}\alpha\text{-CH}_2$) 9.9 ($\text{N}\alpha\text{-Ph}$) 2.2 ($\text{N}\gamma$)	664 664 664
<i>Z</i> -isomer			

TABLE 136—*cont.*

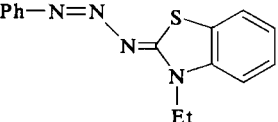
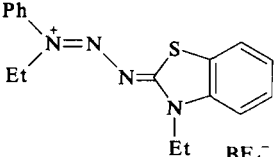
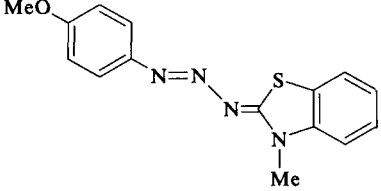
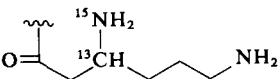
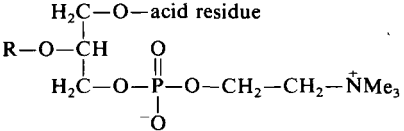
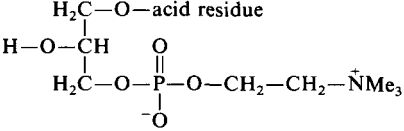
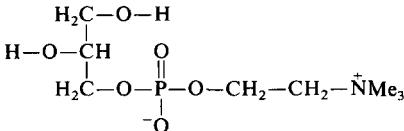
Compound	Solvent	$^1J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	pyridine- d_5	0 ($\text{N}\alpha$) 4.4 ($\text{N}\gamma$)	664 664
<i>E</i> -isomer			
	DMSO- d_6	16.0 ($\text{N}\alpha$ -Ph) 4.4 ($\text{N}\alpha$ - CH_2) 3.3 ($\text{N}\gamma$)	664 664 664
<i>E</i> -isomer			
	pyridine	0 ($\text{N}\alpha$) 5.5 ($\text{N}\gamma$)	451 451
Streptothricin F	pyridine 2%/D $_2$ O	3.4	459
			
	CDCl $_3$ /CD $_3$ OD/D $_2$ O 50:50:15 v/v/v	5.0 (N-Me) 5.0 (N-CH_2)	459 459
	CDCl $_3$ /CD $_3$ OD/D $_2$ O 50:50:15 v/v/v	5.2 (N-Me)	500
	CDCl $_3$ /CD $_3$ OD/D $_2$ O 50:50:15 v/v/v D $_2$ O	5.0 (N-Me) 5.2 (N-Me)	500 500

TABLE 136—*cont.*

Compound	Solvent	$^1J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
choline chloride	$\text{CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$ 50:50:15 v/v/v	5.3 (N-Me)	500
	D_2O	5.5 (N-Me)	500
gonyautoxin II (see Table 42)	$\text{D}_2\text{O}/\text{H}_2\text{O}$ (5:95 v/v)	9.4 (N7-C5)	285
		7.8 (N1-C6)	285
		8.4 (N3-C10)	285
neosaxitoxin (see Table 42)	$\text{D}_2\text{O}/\text{H}_2\text{O}$ (5:95 v/v)	6.4 (N3-C10)	285
Tyr¹-Gly²Gly³-Phe⁴			
Residue			
Tyr ¹	DMSO at 27 °C	14 (N-CO)	447
Gly ²	DMSO at 27 °C	14.1 (N-CO)	447
Gly ³	DMSO at 27 °C	15.5 (N-CO)	447
Tyr¹-Gly²-Gly³-Phe⁴-Leu			
Residue			
Tyr ¹	DMSO at 27 °C	14 (N-CO)	447
Gly ²	DMSO at 27 °C	15.5 (N-CO)	447
Gly ³	DMSO at 27 °C	14.5 (N-CO)	447
Phe ⁴	DMSO at 27 °C	14.7 (N-CO)	447
<i>cis</i> -cyclo(L-Ala-L-Phe)	DMSO-d_6	14.9 (N-CO, Ala)	446
		8.0 (N-C α , Ala)	446
		15.0 (N-CO, Phe)	446
		8.1 (N-C α , Phe)	446
<i>trans</i> -cyclo(D-Ala-L-Phe)	DMSO-d_6	14.4 (N-CO, Ala)	446
		8.0 (N-C α , Ala)	446
		14.6 (N-CO, Phe)	446
		8.1 (N-C α , Phe)	446
cyclo(Ala-gly)	DMSO	6.8 (N-C α)	114
		15.0 (N-CO, Ala)	114
	$\text{H}_2\text{O}/\text{D}_2\text{O}$ (4:1 v/v)	5.0 (N-C α)	114
		16.4 (N-CO, Ala)	114
Bu ¹ OCO-Ala-GlyOMe	DMSO	9.0 (N-C α)	114
		14.3 (N-CO, Ala)	114
Ala-GlyOMe	$\text{H}_2\text{O}/\text{D}_2\text{O}$ (4:1 v/v)	9.3 (N-C α)	114
		16.6 (N-CO, Ala)	114

TABLE 136—*cont.*

Compound	Solvent	$^1J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
<i>Asn</i> ¹ - <i>Arg</i> ² - <i>Val</i> ³ - <i>Tyr</i> ⁴ - <i>Val</i> ⁵ - <i>His</i> ⁶ - <i>Pro</i> ⁷ - <i>Phe</i> ⁸ (angiotensin)			
<i>Val</i> ³	H ₂ O (0.1 M)	13.5 (N-CO)	237
		10.3 (N-C α)	237
<i>Tyr</i> ⁴	H ₂ O (0.1 M)	11.6 (N-CO)	237
		10.5 (N-C α)	237
<i>Val</i> ⁵	H ₂ O (0.1 M)	12.1 (N-CO)	237
		10.0 (N-C α)	237
<i>Phe</i> ⁸	H ₂ O (0.1 M)	13.0 (N-CO)	237
		11.2 (N-C α)	237
<i>streptomyces subtilisin</i> inhibitor			
<i>Met</i> ⁷³	D ₂ O	15.4 (N-CO)	457
$\begin{array}{c} \text{H} \\ \\ \text{Me}-\text{C}-\text{NHCOH} \\ \\ \text{COOMe} \end{array}$	CDCl ₃	11.91 (N-C α)	308
		13.40 (N-CO)	308
$\begin{array}{c} \text{H} \\ \\ \text{Me}-\text{C}-\text{NH}=\text{C} \\ \\ \text{COOMe} \end{array}$	CDCl ₃	10.68 (N-C α)	308
		6.10 (N=C)	308

(a) Recalculated from ^{14}N - ^1H data.

TABLE 137

Some ^{15}N - ^{13}C couplings across two bonds (absolute values if sign not given)

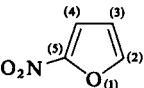
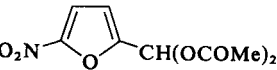
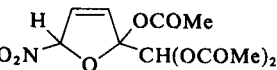
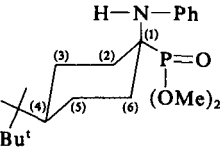
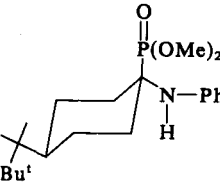
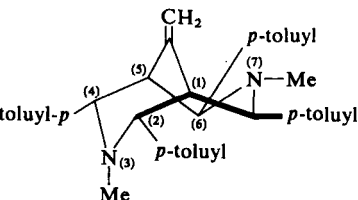
Compound	Solvent	$^2J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
MeCN	CDCl_3	2.9	676
$\text{Me}_2\text{N}-\text{CH}=\text{CH}-\text{CHO}$	CDCl_3 (1:1v/v)	0 (N-CH)	32
$\text{Me}_2\text{N}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CHO}$	CDCl_3 (2 M)	0 (N-CH)	32
$\text{Me}_2\text{N}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CHO}$	CDCl_3	1.8 (N-CH)	32
	$\text{DMSO}-d_6$	3.2 (N-C4)	370
	$\text{DMSO}-d_6$	3.5 (N-C4)	370
	$\text{DMSO}-d_6$	0 (N-C4)	370
	CD_2Cl_2	1.8 (N-C2,6)	464
	CD_2Cl_2	1.9 (N-C2,6)	464
	CH_2Cl_2	3.4 (N7-Tol) 2.5 (N3-Tol)	471 471

TABLE 137—*cont.*

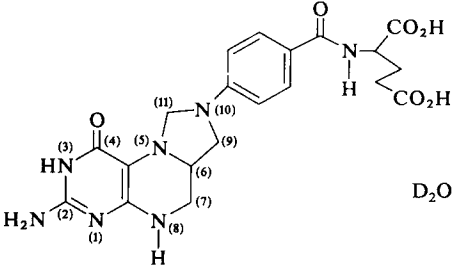
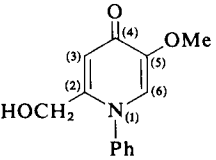
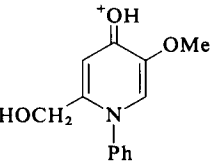
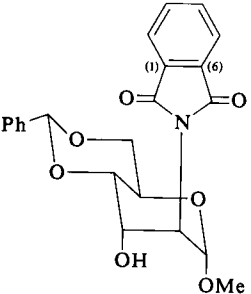
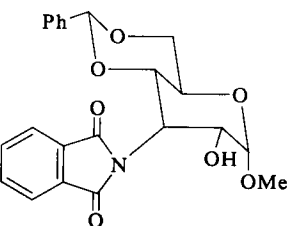
Compound	Solvent	$^2J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	D ₂ O (0.1 M)	2.0 (N5-C9)	286
	DMSO (3% w/v)	~1.2 (N-C3) <1 (N-C5)	639 639
	DMSO (3% w/v)	<1 (N-C3)	639
	DMSO	7.3 (N-C1,6)	453
	DMSO	8.5 (N-C1,6)	453

TABLE 137—*cont.*

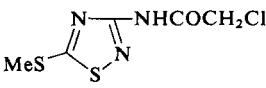
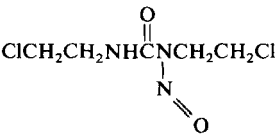
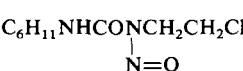
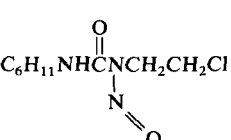
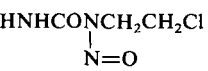
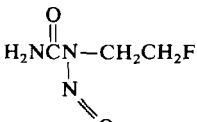
Compound	Solvent	$^2J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	CDCl ₃ /DMSO-d ₆ (1:1 v/v)	12.0 (NH-CH ₂)	331
MeGe(OCH ₂ CH ₂) ₃ N	CDCl ₃	0.6	139
EtGe(OCH ₂ CH ₂) ₃ N	CDCl ₃	0.6	139
α -naphthyl-Ge(OCH ₂ CH ₂) ₃ N	CDCl ₃	0.8	139
β -naphthyl-Ge(OCH ₂ CH ₂) ₃ N	CDCl ₃	0.6	139
EtOGGe(OCH ₂ CH ₂) ₃ N	CDCl ₃	0.6	139
PhOGGe(OCH ₂ CH ₂) ₃ N	CDCl ₃	0.6	139
ClGe(OCH ₂ CH ₂) ₃ N	DMSO	0.6	139
B(OCH ₂ CH ₂ N)	CDCl ₃	1.2	268
MeSi(OCH ₂ CH ₂) ₃ N	CDCl ₃	1.5	268
O=V(OCH ₂ CH ₂) ₃ N	DMSO	0.8	268
PhMeSi(OCH ₂ CH ₂) ₂ NMe	CDCl ₃ (10%)	2.6	269
	CDCl ₃ DMSO-d ₆	4.5 (NO-CO) 5.0 (NO-CO)	429 429
	CDCl ₃ DMSO-d ₆	4.5 (NO-CO) 4.5 (NO-CO)	429 429
	CDCl ₃ DMSO-d ₆ dioxan + phosphate buffer (pH = 5.0) dioxan + phosphate buffer (pH = 7.2)	3.7 (NO-CO) 4.5 (NO-CO) 4.5 (NO-CO) 4.5 (NO-CO)	429 429 429 429
	CDCl ₃ DMSO-d ₆	4.5 (NO-CO) 5.0 (NO-CO)	429 429
	CDCl ₃ DMSO-d ₆	5.1 (NO-CO) 5.1 (NO-CO)	429 429

TABLE 137—*cont.*

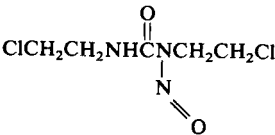
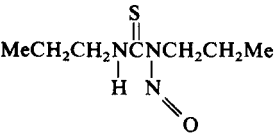
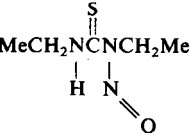
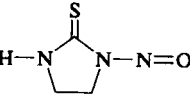
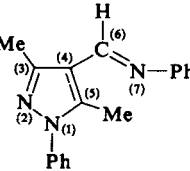
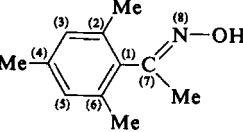
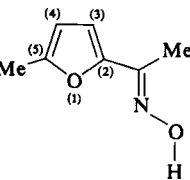
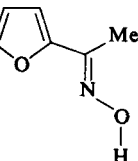
Compound	Solvent	$^2J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	CDCl_3 $\text{DMSO}-d_6$	1.4 (NO-CH ₂) 1.2 (NO-CH ₂)	429 429
	CHCl_3 acetone DMSO	3.6 (NO-CS) 3.7 (NO-CS) 4.0 (NO-CS)	430 430 430
	CHCl_3	3.2 (NO-CS)	430
	acetone	4.1 (NO-CS)	430
	CDCl_3	6.6 (N7-C4) 3.3 (N7-Ph)	452 452
	not specified	8.0 (N8-C1) <0.6 (N8-Me)	450 450
	acetone- d_6	<0.3 (N-Me) 10.7 (N-C2)	365 365
	acetone- d_6	<0.3 (N-Me) 10.7 (N-C2)	365 365

TABLE 137—*cont.*

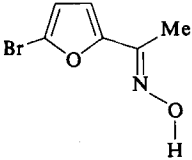
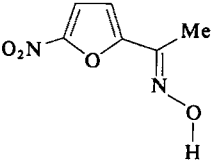
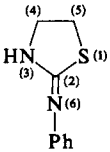
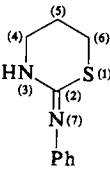
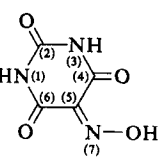
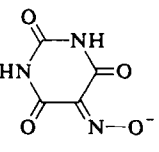
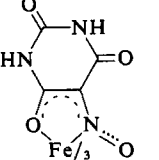
Compound	Solvent	$^2J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	acetone- d_6	<0.3 (N-Me) 10.7 (N-C2)	365 365
	acetone- d_6	<0.3 (N-Me) 10.7 (N-C2)	365 365
	CDCl_3	2.0 (N6-Ph)	460
	CDCl_3	5.5 (N7-Ph)	460
	DMSO	10.47 (N7-C4,6)	454
	DMSO	9.18 (N7-C4,6)	454
	DMSO	5.86 (N7-C6)	454

TABLE 137—*cont.*

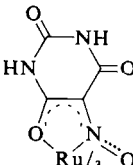
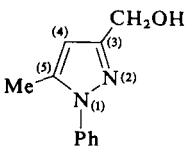
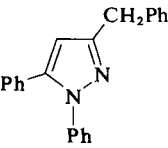
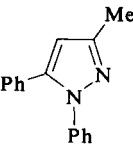
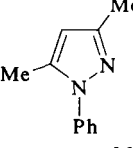
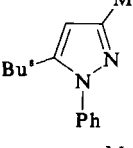
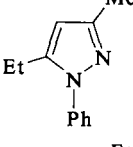
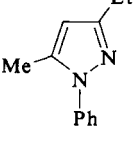
Compound	Solvent	$^2J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	DMSO	5.61 (N7-C6)	454
	CDCl ₃	4.9 (N2-Ph) 8.5 (N2-CH ₂) 1.8 (N2-C4)	465 465 465
	CDCl ₃	4.6 (N2-Ph) 8.2 (N2-CH ₂) 1.8 (N2-C4)	465 465 465
	CDCl ₃	4.6 (N2-Ph) 8.5 (N2-Me) 1.8 (N2-C4)	465 465 465
	CDCl ₃	4.6 (N2-Ph) 8.7 (N2-Me) 1.9 (N2-C4)	465 465 465
	CDCl ₃	4.6 (N2-Ph) 8.5 (N2-Me) 1.8 (N2-C4)	465 465 465
	CDCl ₃	4.3 (N2-Ph) 8.8 (N2-Me) 1.5 (N2-C4)	465 465 465
	CDCl ₃	8.8 (N2-Et) 1.5 (N2-C4)	465 465

TABLE 137—*cont.*

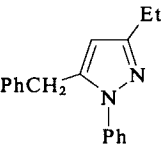
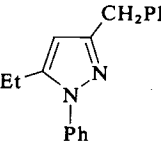
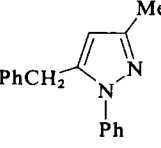
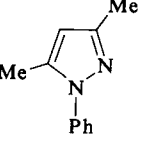
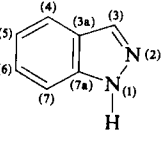
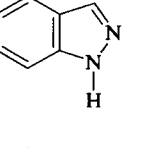
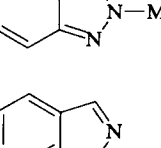
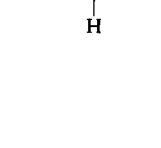
Compound	Solvent	$^2J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	CDCl_3	4.6 (N2-Ph) 8.2 (N2-Et) 1.8 (N2-C4)	465 465 465
	CDCl_3	4.6 (N2-Ph) 8.2 (N2-CH ₂) 1.8 (N2-C4)	465 465 465
	CDCl_3	8.6 (N2-Me) 1.8 (N2-C4)	465 465
	CDCl_2	0.7 (N1-Me) 6.4 (N1-C4)	465 465
	DMSO-d_6	1.83 (N1-C7) 5.87 (N1-C3a)	326 326
	DMSO-d_6	1.10 (N1-C7) 6.60 (N1-C3a)	326 326
	DMSO-d_6	7.33 (N1-C7) 0.73 (N1-C3a) 6.4 (N1-Me)	326 326 326
	DMSO-d_6	1.83 (N2-C3a) 1.1 (N2-C7a)	326 326

TABLE 137—*cont.*

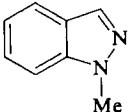
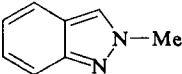
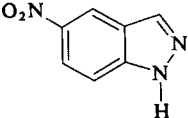
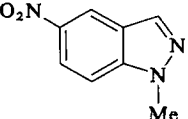
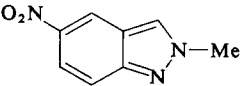
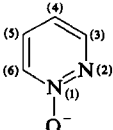
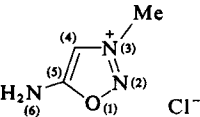
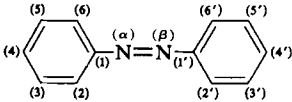
Compound	Solvent	$^2J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	DMSO- d_6	1.83 (N2-C3a)	326
		0.8 (N2-C7a)	326
		5.5 (N2-Me)	326
	DMSO- d_6	4.95 (N2-C3a)	326
		1.28 (N2-C7a)	326
	DMSO- d_6	1.83 (N2-C3a)	326
		1.28 (N2-C7a)	326
	DMSO- d_6	1.83 (N2-C3a)	326
		1.28 (N2-C7a)	326
		5.9 (N2-Me)	326
	DMSO- d_6	4.76 (N2-C3a)	326
		0.73 (N2-C7a)	326
	acetone- d_6	6.3 (N1-C3)	141
	CD ₃ OD/D ₂ O (1.5 M 1:1 v/v)	2.2 (N2-C5)	336
		5.9 (N2-Me)	336
		<i>ca.</i> 0 (N2-C4)	336
		2.2 (N3-C5)	336
		<i>ca.</i> 0 (N6-C4)	336
	CDCl ₃	4.0 (N α -C2,6)	379
		5.2 (N α -C1')	379
	CDCl ₃	-5.3 (N α -C1')	468
	CCl ₄ + C ₆ D ₁₂	-5.6 (N α -C1')	468
	D ₂ SO ₄ (22 N) + EtOH (15%)	-0.9 (N α -C1')	468
	CDCl ₃	-5.4 (N α -C1')	467
		-3.9 (N α -C2,6)	467
<i>E</i> -isomer	D ₂ SO ₄ /EtOH	-0.8 (N α -C1')	467
	(7:1 v/v)	-3.3 (N α -C2,6)	467

TABLE 137—*cont.*

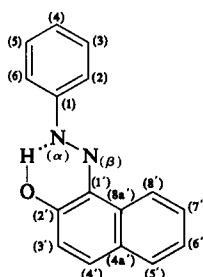
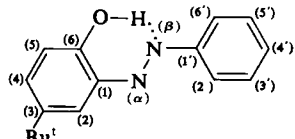
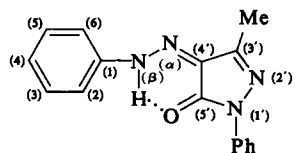
Compound	Solvent	$^2J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
<i>Z</i> -isomer	CDCl_3	+10.0 ($\text{N}\alpha\text{-C1}'$) -2.5 ($\text{N}\alpha\text{-C2,6}$)	467 467
$\text{Me-}p\text{-C}_6\text{H}_4\text{-N=N-Ph}$	strong-acid media	$\begin{cases} <1.0 (\text{N}\beta\text{-C1}) \\ -2.4 (\text{N}\beta\text{-C2',6'}) \end{cases}$	468 468
	CDCl_3	-5.4 ($\text{N}\beta\text{-C1}$) -3.9 ($\text{N}\beta\text{-C2',6'}$)	468 468
$\text{HO-}p\text{-C}_6\text{H}_4\text{-N=N-Ph}$	DMSO-d_6	5.13 ($\text{N}\beta\text{-C1}$) 3.81 ($\text{N}\beta\text{-C2',6'}$) 4.25 ($\text{N}\alpha\text{-C2,6}$) 5.42 ($\text{N}\alpha\text{-C1}'$)	379 379 379 379
$\text{Br-}p\text{-C}_6\text{H}_4\text{-N=N-Ph}$	CDCl_3	5.5 ($\text{N}\beta\text{-C1}$) 4.0 ($\text{N}\beta\text{-C2',6'}$)	379 379
$\text{H}_2\text{N-}p\text{-C}_6\text{H}_4\text{-N=N-C}_6\text{H}_4\text{-}p\text{-OH}$	DMSO	5.1 ($\text{N}\beta\text{-C1}$) 4.3 ($\text{N}\beta\text{-C2',6'}$)	379 379
$\text{HO-}p\text{-C}_6\text{H}_4\text{-N=N-C}_6\text{H}_4\text{-}p\text{-NO}_2$	DMSO	4.6 ($\text{N}\alpha\text{-C2,6}$) 5.8 ($\text{N}\alpha\text{-C1}'$)	379 379
$\text{Me}_2\text{N-}p\text{-C}_6\text{H}_4\text{-N=N-C}_6\text{H}_4\text{-}p\text{-NO}_2$	CDCl_3	4.3 ($\text{N}\alpha\text{-C2,6}$) 6.0 ($\text{N}\alpha\text{-C1}'$)	379 379
$\text{Me}_2\text{N-}p\text{-C}_6\text{H}_4\text{-N=N-Ph}$	CDCl_3	4.6 ($\text{N}\alpha\text{-C2,6}$) 5.3 ($\text{N}\alpha\text{-C1}'$)	379 379
	CDCl_3	2.74 ($\text{N}\alpha\text{-C1}'$) 2.44 ($\text{N}\alpha\text{-C2,6}$) 0.40 ($\text{N}\beta\text{-C2'}$) 2.56 ($\text{N}\beta\text{-C8a'}$) 6.14 ($\text{N}\beta\text{-C1}$)	463 463 463 463 463
	CDCl_3	1.32 ($\text{N}\beta\text{-C1}$) 3.37 ($\text{N}\beta\text{-C2',6'}$) 0.58 ($\text{N}\alpha\text{-C2}$) 9.38 ($\text{N}\alpha\text{-C6}$) 5.00 ($\text{N}\alpha\text{-C1}'$)	463 463 463 463 463
	CDCl_3	4 ($\text{N}\alpha\text{-C4'}$) 1.83 ($\text{N}\alpha\text{-C2, 6}$) 8.64 ($\text{N}\beta\text{-C3'}$) <0.5 ($\text{N}\beta\text{-C5'}$) 5.71 ($\text{N}\beta\text{-C1}$)	463 463 463 463 463

TABLE 137—*cont.*

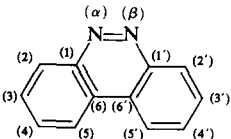
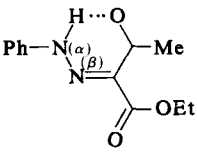
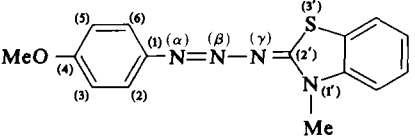
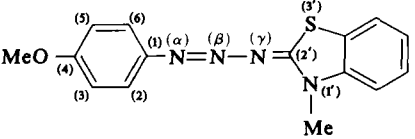
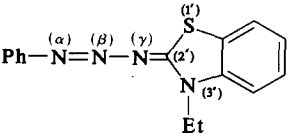
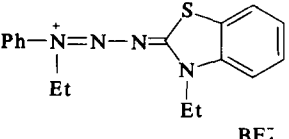
Compound	Solvent	$^2J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	CDCl_3	+7.3 (Nβ-C1) -9.7 (Nα-C2)	467 467
	$\text{D}_2\text{SO}_4/\text{EtOH}$ (7:1 v/v)	+4.5 (Nα-C6) +4.6 (Nβ-C1) -7.2 (Nα-C2) +0.3 (Nα-C6)	467 467 467 467
	CDCl_3	+3.5 (Nβ-C1) -9.7 (Nβ-C2')	468 468
	Strong-acid media (obs. 55 °C)	+4.5 (Nβ-C6') +3.6 (Nβ-C1) -5.2 (Nβ-C2') +0.3 (Nβ-C6')	468 468 468 468
	CDCl_3	6.6 (Nβ-C1) 0.3 (Nβ-COMe) 10.5 (Nβ-COOEt) 2.0 (Nα-C2,6) 1.3 (Nα-C=)	466 466 466 466 466
	CDCl_3	6.6 (Nβ-C1) 1.0 (Nβ-COOEt) 12.6 (Nβ-COMe)	466 466 466
	pyridine	8.8 (Nβ-C2') 6.6 (Nβ-C1) 5.5 (Nα-C2,6)	451 451 451
	pyridine- d_6	1.6 (Nα-C2,6) 8.8 (Nβ-C2') 2.7 (Nβ-C1)	664 664 664
Z-isomer			
	CDCl_3	12.1 (Nβ-C2') 2.2 (Nβ-C1) 6.6 (Nβ-Et)	664 664 664
Z-isomer	BF_4^-		

TABLE 137—*cont.*

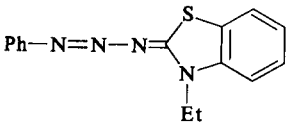
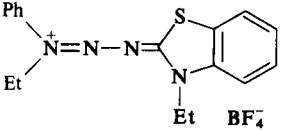
Compound	Solvent	$^2J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	pyridine- d_6	3.8 ($\text{N}\alpha\text{-C2,6}$) 9.3 ($\text{N}\beta\text{-C2'}$) 6.0 ($\text{N}\beta\text{-C1}$)	664 664 664
<i>E</i> -isomer			
	DMSO- d_6	12.1 ($\text{N}\beta\text{-C2'}$) 6.6 ($\text{N}\beta\text{-C1}$)	664 664
<i>E</i> -isomer			
<i>cis</i> -cyclo(α -Ala- α -Phe)	DMSO- d_6 (0.1 M)	6.3 ($\text{N2-C1}\alpha$) 6.6 ($\text{N1-C2}\alpha$)	446 446
<i>trans</i> -cyclo(D-Ala- α -Phe)	DMSO- d_6 (0.1 M)	6.3 ($\text{N2-C1}\alpha$) 6.6 ($\text{N1-C2}\alpha$)	446 446
Cyclo(Ala-Gly)	DMSO $\text{H}_2\text{O}/\text{D}_2\text{O}$ (4:1 v/v)	6.8 ($\text{N1-C2}\alpha$) 5.0 ($\text{N2-C1}\alpha$)	114 114
Bu ^t OCO-Ala-GlyOMe	DMSO	9.0 ($\text{N1-C2}\alpha$)	114
Ala-GlyOMe	$\text{H}_2\text{O}/\text{D}_2\text{O}$ (4:1 v/v)	9.3 ($\text{N1-C2}\alpha$)	114
Asn ¹ -Arg ² -Val ³ -Tyr ⁴ -Val ⁵ -His ⁶ -Pro ⁷ -Phe ⁸ (angiotensin)			
Val ³	H_2O (0.1 M)	7.6 ($\text{N-C2}\alpha$) 4.1 (N-CO)	237 237
Tyr ⁴	H_2O (0.1 M)	7.9 ($\text{N-C3}\alpha$) 2.0 (N-CO)	237 237
Val ⁵	H_2O (0.1 M)	6.9 ($\text{N-C4}\alpha$) 5.5 (N-CO)	237 237
Phe ⁸	H_2O (0.1 M)	8.2 ($\text{N-C7}\alpha$) 3.8 (N-CO)	237 237

TABLE 138

Some ^{15}N - ^{13}C couplings across three bonds (absolute values if sign not given)

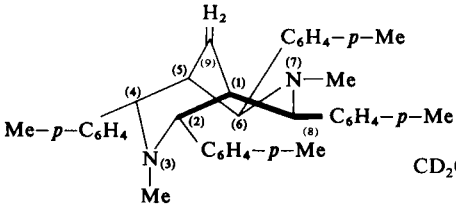
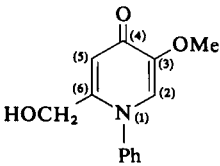
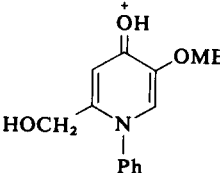
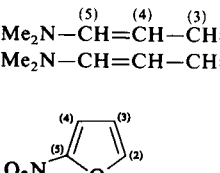
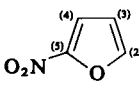
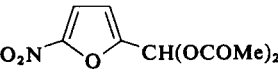
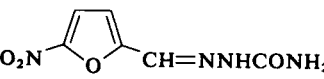
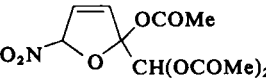
Compound	Solvent	$^3J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
$\text{Me}_2\text{H}-\overset{+}{\text{C}}\text{H}-\text{CH}=\text{CH}-\text{NMe}_2$	DMSO- d_6	4.4	449
$\text{Me}_2\text{N}-\overset{+}{\text{C}}\text{H}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{NMe}_2$	DMSO- d_6	3.3	449
	CD_2Cl_2	0-1 (N3-C9) 4.6 (N7-C9)	471 471
	DMSO (3% w/v)	1.9 (N-C4)	639
	DMSO (3% w/v)	3.0 (N-C4)	639
	CDCl_3 (50% v/v)	3.7 (N-C1)	32
$\text{Me}_2\text{N}-\overset{(5)}{\text{CH}}=\overset{(4)}{\text{CH}}-\overset{(3)}{\text{CH}}=\overset{(2)}{\text{CH}}-\overset{(1)}{\text{CHO}}$	CDCl_3 (2 M)	3.7 (N-C3)	32
$\text{Me}_2\text{N}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CHO}$	CDCl_3	2.4 (N-C5)	32
	DMSO- d_6	1.8 (N-C3) 1.5 (N-C2)	370 370
	DMSO- d_6	1.8 (N-C3) 1.8 (N-C2)	370 370
	DMSO- d_6	0 (N-C3) 0 (N-C2)	370 370
	DMSO- d_6	0 (N-C3) 0 (N-C2)	370 370

TABLE 138—*cont.*

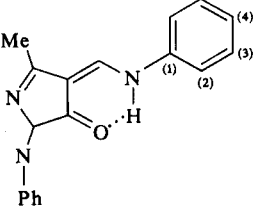
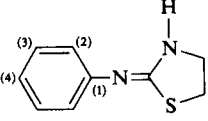
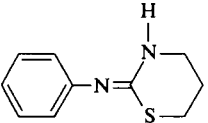
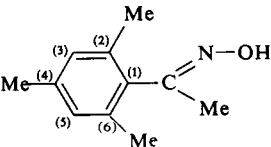
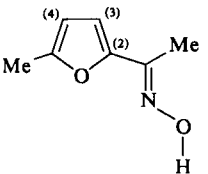
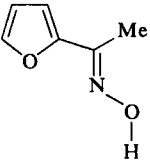
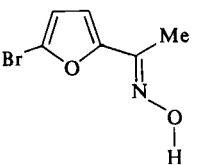
Compound	Solvent	$3J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	CDCl_3	2.2 (N-C3)	452
	CDCl_3	2.0 (N-C3)	460
	CDCl_3	1.8 (N-C3)	460
	not specified	1.2 (N-C2,6)	450
	acetone- d_6	1.9 (N-C3)	365
	acetone- d_6	1.5 (N-C3)	365
	acetone- d_6	2.9 (N-C3)	365

TABLE 138—*cont.*

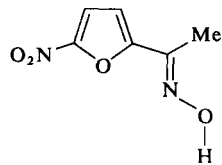
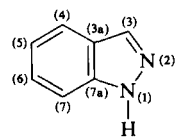
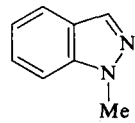
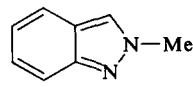
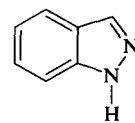
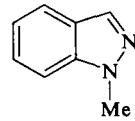
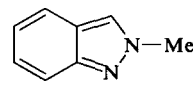
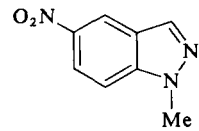
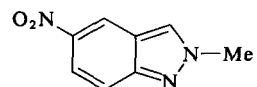
Compound	Solvent	$^3J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	acetone- d_6	<0.3 (N-C3)	365
	DMSO- d_6	1.47 (N1-C4) 2.02 (N1-C6)	326 326
	DMSO- d_6	1.65 (N1-C4) 1.83 (N1-C6)	326 326
	DMSO- d_6	3.12 (N1-C6)	326
	DMSO- d_6	1.10 (N2-C4)	326
	DMSO- d_6	0.92 (N2-C4)	326
	DMSO- d_6	3.30 (N2-C4) 4.22 (N2-C7)	326 326
	DMSO- d_6	1.28 (N2-C4)	326
	DMSO- d_6	3.48 (N2-C4) 4.03 (N2-C7)	326 326

TABLE 138—*cont.*

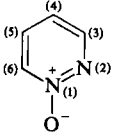
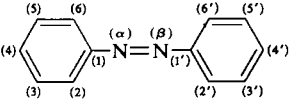
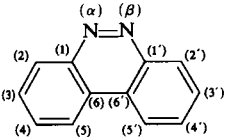
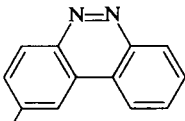
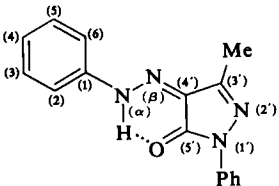
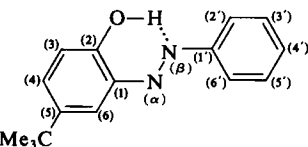
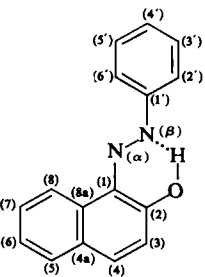
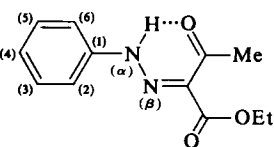
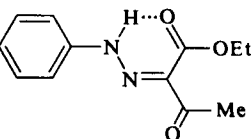
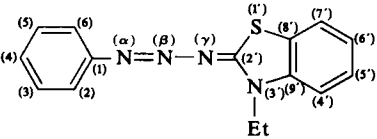
Compound	Solvent	$^3J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	acetone- d_6	19.4 (N1-C4)	141
	CDCl_3	1.8 (N α -C3,5) 4.0 (N α -C2',6')	379 379
<i>E</i> -isomer	CDCl_3	-3.9 (N α -C2',6')	467
		2.0 (N α -C3,5)	467
	D_2SO_4 (22 N)-EtOH (7:1 v/v)	-3.3 (N α -C2',6')	467
<i>Z</i> -isomer	CDCl_3	-2.5 (N α -C2',6')	467
Me- <i>p</i> -C ₆ H ₄ -N=N-Ph	strong-acid media	-4.0 (N β -C2,6)	468
	CDCl_3	-4.2 (N β -C2,6)	468
		2.0 (N β -C3',5')	468
Me ₂ N- <i>p</i> -C ₆ H ₄ -N=N-C ₆ H ₄ - <i>p</i> -OH	CDCl_3	2.1 (N α -C3,5)	379
		4.3 (N α -C2',6')	379
HO- <i>p</i> -C ₆ H ₄ -N=N-Ph	DMSO	2.05 (N α -C3,5)	379
		4.10 (N α -C2',6')	379
		1.76 (N β -C3',5')	379
		4.25 (N β -C2,6)	379
Br- <i>p</i> -C ₆ H ₄ -N=N-Ph	CDCl_3	1.6 (N β -C3',5')	379
		4.2 (N β -C2,6)	379
HO- <i>p</i> -C ₆ H ₄ -N=N-C ₆ H ₄ - <i>p</i> -NO ₂	DMSO	2.3 (N α -C3,5)	379
		3.9 (N α -C2',6')	379
H ₂ N- <i>p</i> -C ₆ H ₄ -N=N-C ₆ H ₄ - <i>p</i> -OH	DMSO	2.1 (N β -C3',5')	379
		4.3 (N β -C2,6)	379
Me ₂ N- <i>p</i> -C ₆ H ₄ -N=N-C ₆ H ₄ - <i>p</i> -NO ₂	CDCl_3	2.2 (N α -C3,5)	379
		4.0 (N α -C2',6')	379
	CDCl_3	-3.1 (N α -C2')	467
		3.5 (N α -C3)	467
		-0.8 (N α -C6')	467
	D_2SO_4 (22 N)-EtOH (7:1 v/v)	-1.8 (N α -C2')	467
		3.1 (N α -C3)	467
		-3.9 (N α -C6')	467
	CDCl_3	-3.3 (N β -C2)	468
		-0.9 (N β -C6)	468
		3.5 (N β -C3')	468
		<0.8 (N β -C5')	468
	strong-acid media	-4.2 (N β -C6)	468
	obs. 55 °C	-3.1 (N β -C2)	468

TABLE 138—*cont.*

Compound	Solvent	$^3J(^5\text{N}-^{13}\text{C})$ (Hz)	Ref.
	CDCl ₃	2.9 (Nα-C3') 1.68 (Nα-C5') 2.44 (Nα-C3,5) 2.34 (Nβ-C2,6)	463 463 463 463
	CDCl ₃	1.98 (Nβ-C2) 3.22 (Nβ-C6) 2.05 (Nβ-C3',5') <0.4 (Nα-C3) 3.22 (Nα-C5) 4.10 (Nα-C2',6')	463 463 463 463 463 463
	CDCl ₃	1.76 (Nβ-C2) 0.4 (Nβ-C8a) 2.34 (Nβ-C3',5') <0.4 (Nα-C3) 2.00 (Nα-C4a) 4.21 (Nα-C8) 3.21 (Nα-C2',6')	463 463 463 463 463 463
	CDCl ₃	2.4 (Nβ-C2,6) 2.1 (Nα-C3,5) 1.0 (Nα-COMe) 3.4 (Nα-COOEt)	466 466 466 466
	CDCl ₃	2.4 (Nβ-C2,6) 2.1 (Nα-C3,5) 0.9 (Nα-COMe) 3.7 (Nα-COOEt)	466 466 466 466
	pyridine-d ₅	4.4 (Nα-C2') 5.5 (Nγ-C1)	664 664

Z-isomer

TABLE 138—*cont.*

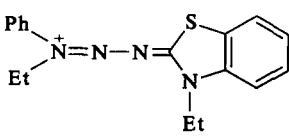
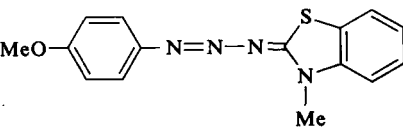
Compound	Solvent	$3J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
<i>E</i> -isomer	pyridine- d_5	7.7 ($\text{N}\gamma\text{-C1}$)	664
		7.1 ($\text{N}\alpha\text{-C2'}$)	664
		1.1 ($\text{N}\alpha\text{-C3,5}$)	664
		3.8 ($\text{N}\beta\text{-C2,6}$)	664
	CDCl_3	8.8 ($\text{N}\alpha\text{-C2'}$)	664
<i>Z</i> -isomer	BF_4^-	8.9 ($\text{N}\alpha\text{-C2'}$)	664
<i>E</i> -isomer	$\text{DMSO-}d_6$	2.2 ($\text{N}\beta\text{-C2,6}$)	664
	pyridine- d_5	6.6 ($\text{N}\alpha\text{-C2'}$)	451
		6.6 ($\text{N}\gamma\text{-C1}$)	451
		5.5 ($\text{N}\beta\text{-C2,6}$)	451
		2.2 ($\text{N}\gamma\text{-Me}$)	451
L-Val			
cation $\text{pD} = 0.9$	D_2O	0.5 (N-Me)	470
		1.0 (N-Me)	470
amphion $\text{pD} = 6.2$		0.6 (N-Me)	470
		0.9 (N-Me)	470
anion $\text{pD} = 13.5$		0.7 (N-Me)	470
		0.7 (N-Me)	470
L-Ile			
cation $\text{pD} = 1.1$	D_2O	0.4 (N-Me)	470
		1.1 (N-Et)	470
amphion $\text{pD} = 5.9$		0.5 (N-Me)	470
		1.0 (N-Et)	470
anion $\text{pD} = 13.8$		0.6 (N-Me)	470
		0.8 (N-Et)	470
L-Leu			
cation $\text{pD} = 1.1$	D_2O	0.8 (N-Pr^i)	470
amphion $\text{pD} = 5.9$		0.7 (N-Pr^i)	470
anion $\text{pD} = 13.2$		1.0 (N-Pr^i)	470
L-Thr			
cation $\text{pH} = 0.6$	D_2O	0.6 (N-Me)	470
amphion $\text{pD} = 6.2$		0.7 (N-Me)	470
anion $\text{PD} = 13.0$		0.6 (N-Me)	470

TABLE 139

Some ^{15}N - ^{13}C coupling across four bonds (absolute values if sign not given)

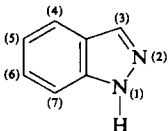
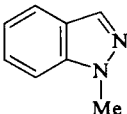
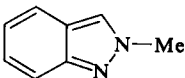
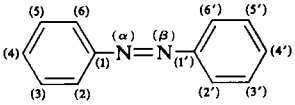
Compound	Solvent	$^4J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
$\text{Me}_2\text{B}-\overset{(5)}{\text{CH}}=\overset{(4)}{\text{CH}}-\overset{(3)}{\text{CH}}=\overset{(2)}{\text{CH}}-\overset{(1)}{\text{CHO}}$	CDCl_3 (2M)	0 (N-C2)	32
$\text{Me}_2\text{N}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CHO}$	CDCl_3	1.2 (N-C4)	32
		0.55 (N2-C6)	326
		0.55 (N2-C6)	326
		0.55 (N2-C6)	326
	CDCl_3	0.6 (N α -C4) 0.5 (N α -C3',5')	379 379
<i>E</i> -isomer	CDCl_3	0.8 (N α -C4)	467
$\text{Me}-p\text{-C}_6\text{H}_4-\text{N}=\text{N}-\text{Ph}$	CDCl_3	<0.6 (N β -C3,5) 0.7 (N β -C4')	468 468
$\text{MeN}-p\text{-C}_6\text{H}_4-\text{N}=\text{N}-\text{Ph}$	CDCl_3	0.5 (N α -C4) 0.5 (N α -C3',5')	379 379
$\text{OH}-p\text{-C}_6\text{H}_4-\text{N}=\text{N}-\text{Ph}$	DMSO	0.5 (N β -C3,5) 0.88 (N α -C4) 0.5 (N α -C3',5') 0.90 (N β -C4')	379 379 379 379
$\text{Br}-p\text{-C}_6\text{H}_4-\text{N}=\text{N}-\text{Ph}$	CDCl_3	0.5 (N β -C3,5) 0.5 (N β -C4')	379 379
$\text{HO}-p\text{-C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4-p\text{-NO}_2$	DMSO	0.5 (N α -C4) 0.5 (N α -C3',5')	379 379
$\text{H}_2\text{N}-p\text{-C}_6\text{H}_4-\text{H}=\text{N}-\text{C}_6\text{H}_4-p\text{-OH}$	DMSO	0.5 (N β -C3,5) 0.7 (N β -C4')	379 379
$\text{Me}_2\text{N}-p\text{-C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4-p\text{-NO}_2$	CDCl_3	0.8 (N α -C4) 0.5 (N α -C3',5')	379 379

TABLE 139—*cont.*

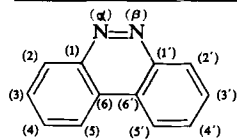
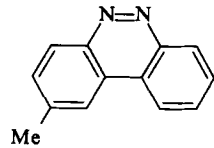
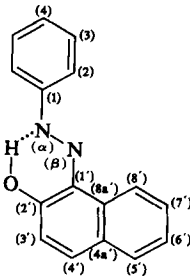
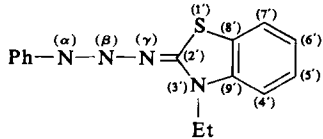
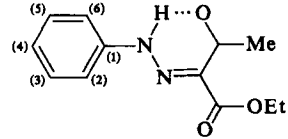
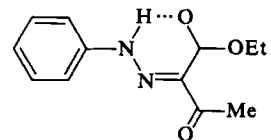
Compound	Solvent	$^4J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	CDCl_3	0.4 ($\text{N}\alpha\text{-C3'}$) 0.8 ($\text{N}\alpha\text{-C4}$)	467 467
	CDCl_3	<0.8 ($\text{N}\beta\text{-C3}$) <0.8 ($\text{N}\beta\text{-C5}$) 0.9 ($\text{N}\beta\text{-C4'}$)	468 468 468
	CDCl_3	<0.4 ($\text{N}\alpha\text{-C3'}$) 0.6 ($\text{N}\alpha\text{-C4a'}$) <0.4 ($\text{N}\alpha\text{-C8'}$) 0.78 ($\text{N}\alpha\text{-C4}$) <0.4 ($\text{N}\beta\text{-C4'}$) <0.4 ($\text{N}\beta\text{-C5'}$) <0.4 ($\text{N}\beta\text{-C7'}$) <0.4 ($\text{N}\beta\text{-C3,5}$)	463 463 463 463 463 463 463 463
	pyridine- d_5	2.7 ($\text{N}\beta\text{-C8'}$)	664
<i>Z</i> -isomer	DMSO-d_6	2.2 ($\text{N}\beta\text{-C8'}$)	664
<i>E</i> -isomer			
	CDCl_3	<0.3 ($\text{N}\beta\text{-3,5}$) 0.3 ($\text{N}\alpha\text{-C4}$)	466 466
	CDCl_3	<0.3 ($\text{N}\beta\text{-C3,5}$) 0.3 ($\text{N}\alpha\text{-C4}$)	466 466

TABLE 140

Some ^{15}N - ^{13}C couplings across five bonds (absolute values if sign not given)

Compound	Solvent	$^5J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
$\text{Me}_2\text{N}-\overset{(5)}{\text{CH}}=\overset{(4)}{\text{CH}}-\overset{(3)}{\text{CH}}=\overset{(2)}{\text{CH}}-\overset{(1)}{\text{CHO}}$	CDCl_3	0 (N-C1)	32
$\text{Me}_2\text{N}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CHO}$	CDCl_3	0 (N-C3)	32
	CDCl_3	0.6 (N α -C4')	379
<i>E</i> -isomer	CDCl_3	0.8 (N α -C4')	467
<i>E</i> -isomer	CDCl_3	0.9 (N α -C4')	468
$\text{Me}_2\text{N}-p\text{-C}_6\text{H}_4-\text{N}=\text{N}-\text{Ph}$	CDCl_3	0.6 (N α -C4')	379
$\text{HO}-p\text{-C}_6\text{H}_4-\text{N}=\text{N}-\text{Ph}$	DMSO	0.85 (N β -C4)	379
		0.7 (N α -C4')	379
$\text{Br}-p\text{-C}_6\text{H}_4-\text{N}=\text{N}-\text{Ph}$	CDCl_3	0.5 (N β -C4)	379
$\text{HO}-p\text{-C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4-p\text{-NO}_2$	DMSO	0.8 (N α -C4')	379
$\text{H}_2\text{N}-p\text{-C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4-p\text{-OH}$	DMSO	0.8 (N β -C4)	379
$\text{Me}_2\text{N}-p\text{-C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4-p\text{-NO}_2$	CDCl_3	0.8 (N α -C4')	379
	CDCl_3	0.8 (N β -C4)	467
	CDCl_3	1.0 (N β -C4)	468
	CDCl_3	<0.5 (N β -C4)	463
	CDCl_3	1.17 (N β -C4)	463
		0.73 (N α -C4')	463

TABLE 140—*cont.*

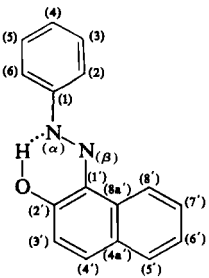
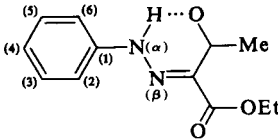
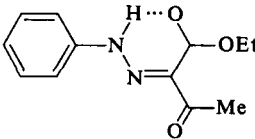
Compound	Solvent	$^5J(^{15}\text{N}-^{13}\text{C})$ (Hz)	Ref.
	CDCl_3	<0.4 ($\text{N}\alpha\text{-C4}'$) 0.4 ($\text{N}\alpha\text{-C5}'$) <0.4 ($\text{N}\alpha\text{-C7}'$) <0.4 ($\text{N}\beta\text{-C6}'$) <0.4 ($\text{N}\beta\text{-C4}$)	463 463 463 463 463
	CDCl_3	0.3 ($\text{N}\beta\text{-C4}$)	466
	CDCl_3	0.3 ($\text{N}\beta\text{-C4}$)	466

TABLE 141
Some ^{15}N - ^{15}N couplings across one bond (absolute values)

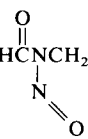
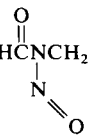
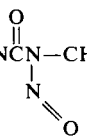
Compound	Solvent	$^1J(^{15}\text{N}-^{15}\text{N})$ (Hz)	Ref.
$[\text{MoBr}(\text{N}_2\text{Et})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$	THF	12.0	667
$[\text{WBr}(\text{N}_2\text{Et})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$	THF	11.9	667
$[\text{MoCl}(\text{N}_2\text{COMe})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$	THF	12.0	667
$[\text{WCl}(\text{N}_2\text{COMe})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$	THF	12.0	667
$[\text{ReCl}_2(\text{N}_2\text{COPh})(\text{EtN})(\text{PPh}_3)_2]$	toluene	15.0	667
$[\text{WH}(\text{N}_2)_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]\text{HCl}_2$	THF	4	394
<i>trans</i> - $[\text{ReClN}_2(\text{PMe}_2\text{Ph})_4]$	THF	4	394
	toluene (-40°C)	4	394
	CH_2Cl_2	3-5	394
<i>trans</i> - $[\text{FeHN}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]\text{BPh}_4$	THF	4	394
<i>mer</i> - $[\text{OsCl}_2\text{N}_2(\text{PMe}_2\text{Ph})_3]$	THF	4	394
<i>mer</i> - $[\text{OsHCIN}_2(\text{PMe}_2\text{Ph})_3]$	THF	4	394
<i>mer</i> - $[\text{OsBr}_2\text{N}_2(\text{PMe}_2\text{Ph})_3]$	THF	4.5	394
<i>mer</i> - $[\text{OsHBrN}_2(\text{PMe}_2\text{Ph})_3]$	THF	4	394
<i>mer</i> - $[\text{OsBr}_2\text{N}_2(\text{PEt}_2\text{Ph})_3]$	THF	4	394
<i>trans</i> - $[\text{RhClN}_2\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2]$	THF	5	394
<i>trans</i> - $[\text{WFN}_2\text{H}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$	THF	14	394
<i>trans</i> - $[\text{WBrN}_2\text{H}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$	THF (-40°C)	14	394
$\text{ClCH}_2\text{CH}_2\text{NHCNCH}_2\text{CH}_2\text{Cl}$ 	CDCl_3	21.0	429
	$\text{CF}_3\text{CH}_2\text{OH}$	22.5	429
	$\text{DMSO}-d_6$	22.5	429
	pyridine	21.9	429
	dioxane + phosphate buffer (pH = 5.0)	21.7	429
	dioxane + phosphate buffer (pH = 7.0)	21.7	429
$\text{C}_6\text{H}_{11}\text{NHCNCH}_2\text{CH}_2\text{Cl}$ 	CDCl_3	22.2	429
	dioxane + phosphate buffer (pH = 5.0)	22.3	429
	dioxane + phosphate buffer (pH = 7.2)	21.7	429
$\text{H}_2\text{NCN}-\text{CH}_2\text{CH}_2\text{F}$ 	CDCl_3	22.3	429
	$\text{DMSO}-d_6$	22.3	429
	pyridine- d_5	22.3	429

TABLE 141—*cont.*

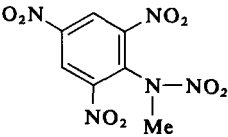
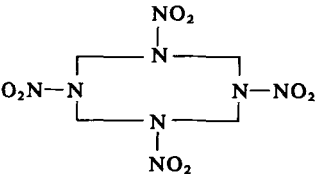
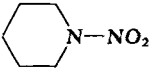
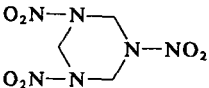
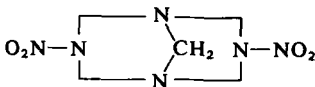
Compound	Solvent	$^1J(^{15}\text{N}-^{15}\text{N})$ (Hz)	Ref.
$\text{MeCH}_2\text{CH}_2\text{NC}(\text{S})\text{N}(\text{O})\text{CH}_2\text{CH}_2\text{Me}$	CHCl_3 acetone DMSO $\text{CF}_3\text{CH}_2\text{OH}$	22.2 22.4 22.3 21.8	430 430 430 430
$\text{MeCH}_2\text{NC}(\text{S})\text{N}(\text{O})\text{CH}_2\text{Me}$	CHCl_3 acetone	22.2 22.2	430 430
$\text{H}-\text{N}(\text{CH}_2)_2\text{N}(\text{O})=\text{S}$	acetone	21.1	430
MeNHNO_2 Me_2NNO_2	acetone- d_6 acetone- d_6	4.9 5.0	462 462
	acetone- d_6	4.9	462
	acetone- d_6	4.5	462
	acetone- d_6	7.3	462
	acetone- d_6	8.9	462
	DMSO- d_6	8.5	462

TABLE 141—*cont.*

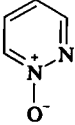
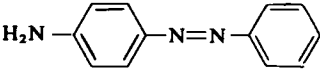
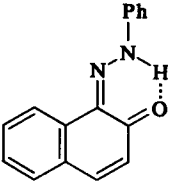
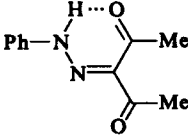
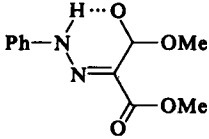
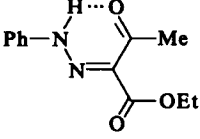
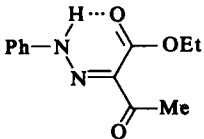
Compound	Solvent	$^1J(^{15}\text{N}-^{15}\text{N})$ (Hz)	Ref.
$\text{MeN}(\text{NO}_2)_2$	DMSO- d_6	12.2	462
	acetone- d_6	14.0	141
	DMSO- d_6	15.5	382
	DMSO- d_6 (20%)/HCl (10:1 v/v)	15.4	382
	CDCl_3 (230 K)	11.6	436
	(250 K)	11.7	436
	(270 K)	11.9	436
	(290 K)	11.9	436
	(310 K)	12.0	436
	(330 K)	12.2	436
	CDCl_3	11.04	436
	CDCl_3	10.70	436
	CDCl_3	11.10	436
	CDCl_3	10.80	436

TABLE 141—*cont.*

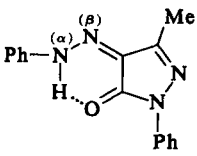
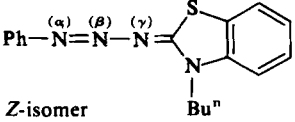
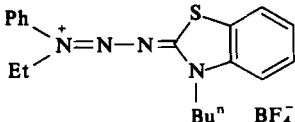
Compound	Solvent	$^1J(^{15}\text{N}-^{15}\text{N})$ (Hz)	Ref.
	CDCl_3	11.13 ($N\alpha-N\beta$)	436
	CH_2Cl_2	15.1	435
	CH_2Cl_2	15.0	435
	<i>Z</i> -isomer pyridine- d_5	19.0 ($N\alpha-N\beta$) 11.8 ($N\beta-N\gamma$)	380 380
<i>E</i> -isomer	pyridine- d_5	13.2 ($N\alpha-N\beta$) 14.8 ($N\beta-N\gamma$)	380 380
	DMSO- d_6	11.8 ($N\alpha-N\beta$) 12.2 ($N\beta-N\gamma$)	380 380
$\text{Ph}-\text{N}=\text{N}-\text{C}_6\text{H}_4-p-\text{NEt}_2$	CDCl_3	14.6	380
$\text{Na}^+[\text{N}=\text{N}=\text{N}]^-$	H_2O	11.5	376
	D_2O	11.3	316
$\text{PhCO}-\text{N}=\text{N}=\text{N}$ (α) (β) (γ)	Et_2O	16.0 ($N\alpha-N\beta$) 6.0 ($N\beta-N\gamma$)	376 376
MeN_3	benzene	14.4 ($N\alpha-N\beta$) 8.2 ($N\beta-N\gamma$)	316 316
HN_3	Et_2O	13.95 ($N\alpha-N\beta$) 7.2 ($N\beta-N\gamma$)	316 316

TABLE 141—*cont.*

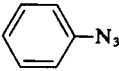
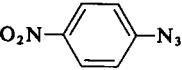
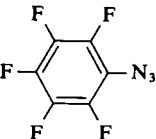
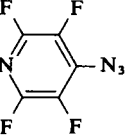
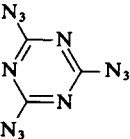
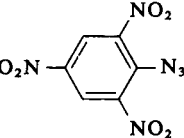
Compound	Solvent	$^1J(^{15}\text{N}-^{15}\text{N})$ (Hz)	Ref.
	acetone	13.4 ($N\alpha-N\beta$) 7.8 ($N\beta-N\gamma$)	316 316
	DMSO	13.8 ($N\alpha-N\beta$) 7.4 ($N\beta-N\gamma$)	316 316
	CDCl_3	14.3 ($N\alpha-N\beta$) 7.3 ($N\beta-N\gamma$)	316 316
	CDCl_3	8.8 ($N\beta-N\gamma$)	316
	CD_2Cl_2	16.1 ($N\alpha-N\beta$) 6.1 ($N\beta-N\gamma$)	316 316
	DMSO	14.0 ($N\alpha-N\beta$) 6.3 ($N\beta-N\gamma$)	316 316
$\text{N}\equiv\text{C}-\text{N}_3$	CD_3CN	16.0 ($N\alpha-N\beta$) 6.0 ($N\beta-N\gamma$)	316 316
ClN_3	CD_2Cl_2	24.0 ($N\alpha-N\beta$) 7.8 ($N\beta-N\gamma$)	316 316

TABLE 142

Some ^{15}N - ^{15}N couplings across two bonds (absolute values)

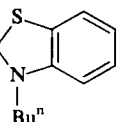
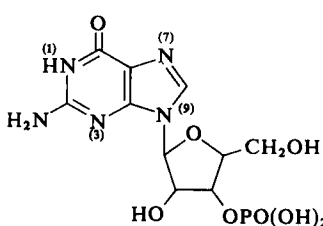
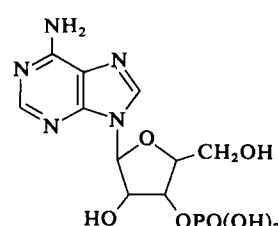
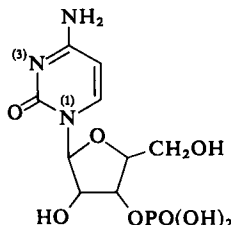
Compound	Solvent	$^2J(^{15}\text{N}-^{15}\text{N})$ (Hz)	Ref.
$\text{PhCO}-\overset{(\alpha)}{\text{N}}=\overset{(\beta)}{\text{N}}=\overset{(\gamma)}{\text{N}}$	Et_2O	1.5 ($\text{N}\alpha-\text{N}\gamma$)	376
S_4N_3^+	HNO_3	8.5	367
$\text{Ph}_3\text{As}=\text{N}-\text{S}_3\text{N}_3$	CHCl_3	2.2	367
 Z-isomer	pyridine- d_5	1.3 ($\text{N}\alpha-\text{N}\gamma$)	380
E-isomer	pyridine- d_5	10.9 ($\text{N}\alpha-\text{N}\gamma$)	380
 BF_4^-	DMSO- d_6	4.9 ($\text{N}\alpha-\text{N}\gamma$)	380
 (1) (7) (9) (3)	H_2O (pH = 3)	2.2 ($\text{N1}-\text{NH}_2$)	680
		6.0 ($\text{N3}-\text{NH}_2$)	680
		3.7 ($\text{N9}-\text{N3}$)	680
	(pH = 7)	2.2 ($\text{N1}-\text{NH}_2$)	680
		6.0 ($\text{N3}-\text{NH}_2$)	680
		3.7 ($\text{N9}-\text{N3}$)	680
	(pH = 10)	6.0 ($\text{N1}-\text{NH}_2$)	680
		6.0 ($\text{N3}-\text{NH}_2$)	680
 (1) (3) (9)	H_2O (pH = 3)	1.0 ($\text{N1}-\text{NH}_2$)	680
		1.5 ($\text{N3}-\text{N9}$)	680
	(pH = 7)	5.2 ($\text{N1}-\text{NH}_2$)	680
		2.2 ($\text{N3}-\text{N9}$)	680
 (3) (1)	H_2O (pH = 3)	1.5 ($\text{N3}-\text{NH}_2$)	680
	(pH = 7)	5.8 ($\text{N3}-\text{NH}_2$)	680

TABLE 142—*cont.*

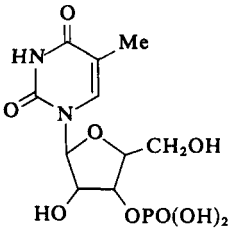
Compound	Solvent	$^2J(^{15}\text{N}-^{15}\text{N})$ (Hz)	Ref.
	H ₂ O (pH = 3)	2.2 (N1-N3)	680
	(pH = 7)	2.2 (N1-N3)	680

TABLE 143

Some ^{15}N - ^{15}N couplings across three bonds (absolute values)

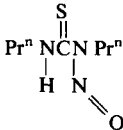
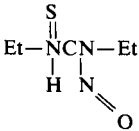
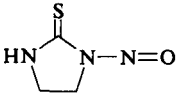
Compound	Solvent	$^3J(^{15}\text{N}-^{15}\text{N})$ (Hz)	Ref.
	CHCl ₃	3.8 (NH-NO)	430
	acetone	3.2 (NH-NO)	430
	DMSO	2.5 (NH-NO)	430
	CF ₃ CH ₂ OH	3.5 (NH-NO)	430
	CHCl ₃	2.7 (NH-NO)	430
	acetone	2.2 (NH-NO)	430
	acetone	3.9 (NH-NO)	430
[PtCl ₂ (Bu ¹ N=CH-CH=NBu ¹)(η^2 -styrene)]	acetone-d ₆ (-80 °C)	5	410
<i>trans</i> -[{PtCl ₂ (PBu ₃) ₂] ₂ (Bu ¹ N=CH-CH=NBu ¹)]	CDCl ₂	2.4	410

TABLE 144

Some ^{19}F - ^{15}N couplings across one bond (absolute values)

Compound	Solvent	$^1J(^{19}\text{F}-^{15}\text{N})$ (Hz)	Ref.
$\text{FN}=\text{NF}$ <i>cis</i>	CFCl_3	203.4 ^a	99
<i>trans</i>	CFCl_3	190.7 ^c	99
$\text{NH}_3\text{F}^+ \text{O}_3\text{SCF}_3^-$	$\text{CF}_3\text{SO}_2\text{H}$	47.6 ^a	99
NOF_3	neat	188.0 ^a	99
$\text{NF}_4^+ \text{BF}_4^-$	HF	323.3 ^a	99
$\text{NF}_4^+ \text{AsF}_6^-$	HF	323.3 ^a	99
$\text{FN}\equiv\text{NAsF}_6^-$	HF	475.5 ^a	99
$\text{NOF}_2^+ \text{AsF}_6^-$	HF	356.3 ^a	99
NO_2F	neat	152.9 ^a	99
$\text{F}_2\text{N}(\alpha)=\text{N}(\beta)\text{F}^+ \text{AsF}_6^-$	HF	273.5 ^a (N β)	99
<i>trans</i> - $\text{WFN}_2\text{H}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$	THF	~ 60	394

(a) Recalculated from ^{19}F - ^{14}N couplings.

TABLE 145

Some ^{19}F - ^{15}N couplings across two bonds (absolute values)

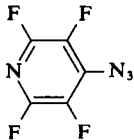
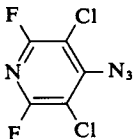
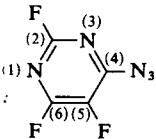
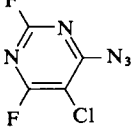
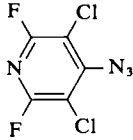
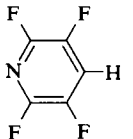
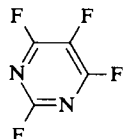
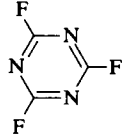
Compound	Solvent	$^2J(^{19}\text{F}-^{15}\text{N})$ (Hz)	Ref.
$\text{FN}=\text{NF}$ <i>cis</i>	CFCl_3	51.9 ^a	99
<i>trans</i>	CFCl_3	102.4 ^a	99
$\text{FXeN}(\text{SO}_2\text{F})_2$	BrF_5	39.2 (N-Xe-F)	292
$\text{HN}(\text{SO}_2\text{F})_2$	BrF_5	7.2 (N-S-F)	292
	CDCl_3	50	316
	CDCl_3	52	316
	CDCl_3	50.6 (N1)	316
		59.5 (N3)	316
	CDCl_3	51 (N1)	657

TABLE 145—*cont.*

Compound	Solvent	$^2J(^{19}\text{F}-^{15}\text{N})$ (Hz)	Ref.
	CDCl_3	52.1 (N1)	316
		53.6 (N3)	316
	CDCl_3	52 (N1)	657
		54 (N3)	657
	CDCl_3	52	657
	CDCl_3	50.4	657
	CDCl_3	52	657
	CDCl_3	52	657
	CDCl_3	52	657

(a) Recalculated from ^{19}F - ^{14}N couplings.

TABLE 146

Some ^{31}P - ^{15}N couplings across one bond (absolute values if sign not given)

Compound	Solvent	$^1J(^{31}\text{P}\text{--}^{15}\text{N})$ (Hz)	Ref.
$\begin{array}{c} \text{Cl} \quad \text{Me} \\ \diagdown \quad / \\ \text{P} \text{---} \text{N} \\ / \quad \diagdown \\ \text{Ph} \quad \text{CH}_2\text{Ph} \end{array}$	CHCl_3	77.6	36
$\text{Cl}_2\text{P}\text{--}\text{NMe}_2$	CHCl_3	89.4	36
$\text{Cl}_2\text{P}\text{--}\text{NPh}_2$	CHCl_3	92.3	36
$\text{Cl}_2\text{P}\text{--}\text{NPr}^i_2$	CHCl_3	95.2	36
$\text{Cl}_2\text{P}\text{--}\text{NBu}^s_2$	CHCl_3	96.7	36
$\begin{array}{c} \text{Me} \\ / \\ \text{Cl}_2\text{P}\text{---}\text{N} \\ \diagdown \\ \text{CH}_2\text{Ph} \end{array}$	CHCl_3	90.8	36
$\begin{array}{c} \text{Cl} \\ \diagdown \\ \text{P}\text{---}\text{NMe}_2 \\ / \\ \text{Ph} \end{array}$	CHCl_3	76.2	36
$\begin{array}{c} \text{Cl} \\ \diagdown \\ \text{P}\text{---}\text{NEt}_2 \\ / \\ \text{Ph} \end{array}$	CHCl_3	79.1	36
$\begin{array}{c} \text{Cl} \\ \diagdown \\ \text{P}\text{---}\text{NPr}^n_2 \\ / \\ \text{Ph} \end{array}$	CHCl_3	80.6	36
$\begin{array}{c} \text{Cl} \\ \diagdown \\ \text{P}\text{---}\text{P}\text{---}\text{NPr}^i_2 \\ / \\ \text{Ph} \end{array}$	CHCl_3	82.0	36
$\begin{array}{c} \text{Cl} \\ \diagdown \\ \text{P}\text{---}\text{NBu}^n_2 \\ / \\ \text{Ph} \end{array}$	CHCl_3	80.6	36
$\begin{array}{c} \text{Cl} \\ \diagdown \\ \text{P}\text{---}\text{NBu}^s_2 \\ / \\ \text{Ph} \end{array}$	CHCl_3	82.0	36
$\begin{array}{c} \text{Cl} \\ \diagdown \\ \text{P}\text{---}\text{N}(\text{CH}_2\text{Ph})_2 \\ / \\ \text{Ph} \end{array}$	CHCl_3	82.0	36
$(\text{Et}_2\text{N})_2\text{P}\text{--}\text{NPr}^i_2$	CHCl_3	83.6 ($\text{P}\text{--}\text{NPr}^i_2$)	36

TABLE 146—*cont.*

Compound	Solvent	$^1J(^{31}\text{P}-^{15}\text{N})$ (Hz)	Ref.
$\begin{array}{c} \text{Pr}^n_2\text{N} \\ \diagdown \\ \text{P}-\text{NPr}^i_2 \\ \diagup \\ \text{Cl} \end{array}$	CHCl_3	86.4 (P-NPr ⁱ ₂)	36
$\begin{array}{c} \text{Me}_2\text{N} \\ \diagdown \\ \text{P}-\text{NMe}_2 \\ \diagup \\ \text{Cl} \end{array}$	CHCl_3	77.6	36
$(\text{Me}_2\text{N})_2\text{P}-\text{NMe}_2$	CHCl_3	60.1	36
$\begin{array}{c} \text{Me}_2\text{N} \\ \diagdown \\ \text{P}-\text{NMe}_2 \\ \diagup \\ \text{Et}_2\text{N} \end{array}$	CHCl_3	54.4 (P-NMe ₂)	36
$\begin{array}{c} \text{Me}_2\text{N} \\ \diagdown \\ \text{P}-\text{NMe}_2 \\ \diagup \\ \text{Pr}^i_2\text{N} \end{array}$	CHCl_3	51.5 (P-NMe ₂)	36
$\begin{array}{c} \text{Me}_2\text{N} \\ \diagdown \\ \text{P}-\text{NMe}_2 \\ \diagup \\ \text{EtO} \end{array}$	CHCl_3	69.0 (P-NMe ₂)	36
$\begin{array}{c} \text{Et}_2\text{N} \\ \diagdown \\ \text{P}-\text{NMe}_2 \\ \diagup \\ \text{Cl} \end{array}$	CHCl_3	79.5 (P-NMe ₂)	36
$(\text{Et}_2\text{N})_2\text{P}-\text{NMe}_2$	CHCl_3	50.0 (P-NMe ₂)	36
$\begin{array}{c} \text{Et}_2\text{N} \\ \diagdown \\ \text{P}-\text{NMe}_2 \\ \diagup \\ \text{Pr}^i_2\text{N} \end{array}$	CHCl_3	52.9 (P-NMe ₂)	36
$\text{Me}_2\text{P}-\text{NMe}_2$	CHCl_3	39.0	36
$\text{Ph}_2\text{P}-\text{NMe}_2$	CHCl_3	61.8	36
$\begin{array}{c} \text{Cl} \\ \diagdown \\ \text{P}-\text{NMe}_2 \\ \diagup \\ \text{Me} \end{array}$	CHCl_3	75.0	36
$\begin{array}{c} \text{Cl} \\ \diagdown \\ \text{P}-\text{NMe}_2 \\ \diagup \\ \text{Ph} \end{array}$	CHCl_3	76.2	36
$\text{Cl}_2\text{P}-\text{NMe}_2$	CHCl_3	89.4	36
$\begin{array}{c} \text{Me}_2\text{N} \\ \diagdown \\ \text{P}-\text{NMe}_2 \\ \diagup \\ \text{Ph} \end{array}$	CHCl_3	75.7	36

TABLE 146—*cont.*

Compound	Solvent	$^1J(^{31}\text{P}-^{15}\text{N})$ (Hz)	Ref.
$\begin{array}{c} \text{Pr}_2^i\text{N} \\ \diagdown \\ \text{P}-\text{NMe}_2 \\ \diagup \\ \text{Cl} \end{array}$	CHCl_3	80.9 (P-NMe ₂)	36
(EtO) ₂ P-NMe ₂	CHCl_3	75.0	36
$\begin{array}{c} \text{Cl} \\ \diagdown \\ \text{P}-\text{NEt}_2 \\ \diagup \\ \text{Ph} \end{array}$	CHCl_3	79.1	36
$\text{Cl}_2\text{P}-\text{NEt}_2$	CHCl_3	92.3	36
$\begin{array}{c} \text{Me}_2\text{N} \\ \diagdown \\ \text{P}-\text{NEt}_2 \\ \diagup \\ \text{Cl} \end{array}$	CHCl_3	79.4 (P-NEt ₂)	36
(Me ₂ N) ₂ P-NEt ₂	CHCl_3	72.1 (P-NEt ₂)	36
$\begin{array}{c} \text{Me}_2\text{N} \\ \diagdown \\ \text{P}-\text{NEt}_2 \\ \diagup \\ \text{Et}_2\text{N} \end{array}$	CHCl_3	66.2 (P-NEt ₂)	36
$\begin{array}{c} \text{Me}_2\text{N} \\ \diagdown \\ \text{P}-\text{NEt}_2 \\ \diagup \\ \text{Pr}_2^i\text{N} \end{array}$	CHCl_3	49.8 (P-NEt ₂)	36
$\begin{array}{c} \text{Et}_2\text{N} \\ \diagdown \\ \text{P}-\text{NEt}_2 \\ \diagup \\ \text{Cl} \end{array}$	CHCl_3	80.9	36
(Et ₂ N) ₂ P-NEt ₂	CHCl_3	61.5	36
$\begin{array}{c} \text{Et}_2\text{N} \\ \diagdown \\ \text{P}-\text{NEt}_2 \\ \diagup \\ \text{Pr}_2^i\text{N} \end{array}$	CHCl_3	52.9 (P-NEt ₂)	36
$\begin{array}{c} \text{Pr}_2^i\text{N} \\ \diagdown \\ \text{P}-\text{NEt}_2 \\ \diagup \\ \text{Cl} \end{array}$	CHCl_3	79.1 (P-NEt ₂)	36
$\begin{array}{c} \text{Cl} \\ \diagdown \\ \text{P}-\text{NPr}_2^i \\ \diagup \\ \text{Ph} \end{array}$	CHCl_3	82.0	36
$\text{Cl}_2\text{P}-\text{NPr}_2^i$	CHCl_3	95.2	36
$\begin{array}{c} \text{Me}_2\text{N} \\ \diagdown \\ \text{P}-\text{NPr}_2^i \\ \diagup \\ \text{Cl} \end{array}$	CHCl_3	83.0 (P-NPr ₂ ⁱ)	36

TABLE 146—*cont.*

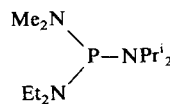
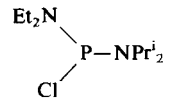
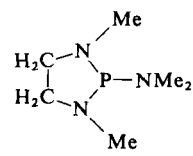
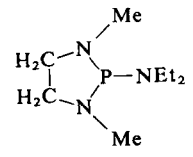
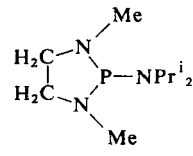
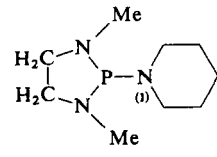
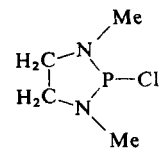
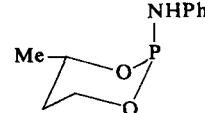
Compound	Solvent	$^1J(^{31}\text{P}-^{15}\text{N})$ (Hz)	Ref.
$(\text{Me}_2\text{N})_2\text{P}-\text{NPr}^i_2$	CHCl_3	80.9 (P-NPr $^i_2$)	36
	CHCl_3	81.0 (P-NPr $^i_2$)	36
	CHCl_3	86.4 (P-NPr $^i_2$)	36
	CHCl_3	51.5 (P-NMe) 91.2 (P-NMe $_2$)	479
	CHCl_3	51.5 (P-NMe) 92.6 (P-NEt $_2$)	479 479
	CHCl_3	50 (P-NMe) 96 (P-NPr $^i_2$)	479 479
	CHCl_3	51.5 (P-NMe) 92.7 (P-N1)	479 479
	CHCl_3	63.2	479
	acetone/ CHCl_3 (1:3 v/v)	35.4	476

TABLE 146—*cont.*

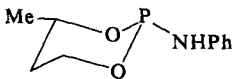
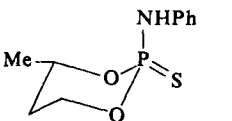
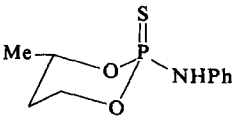
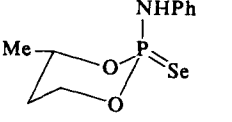
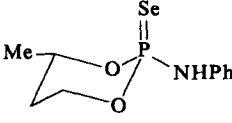
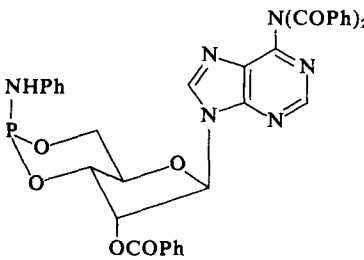
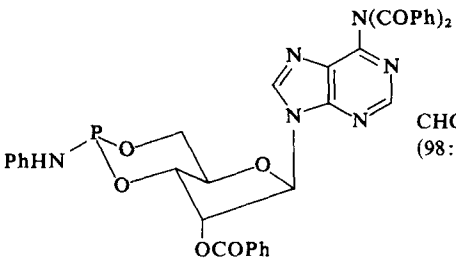
Compound	Solvent	$^1J(^{31}\text{P}-^{15}\text{N})$ (Hz)	Ref.
	acetone/ CHCl_3 (1:3 v/v)	49.6	476
	benzene	10.8	476
	benzene	24.5	476
	benzene	0.8	476
	benzene	12.6	476
	$\text{CHCl}_3 + \text{EtOH}$ (98:2 v/v)	37.6	476
	$\text{CHCl}_3 + \text{EtOH}$ (98:2 v/v)	49.5	476

TABLE 146—*cont.*

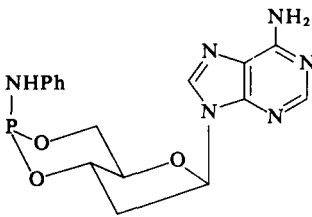
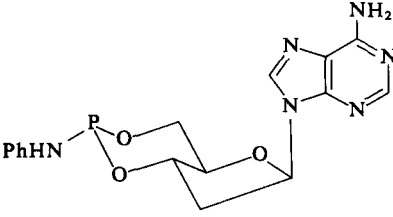
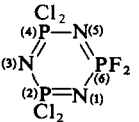
Compound	Solvent	$^1J(^{31}\text{P}-^{15}\text{N})$ (Hz)	Ref.
	$\text{CHCl}_3 + \text{MeOH}$ (3:2 v/v)	37.0	476
	$\text{CHCl}_3 + \text{MeOH}$ (3:2 v/v)	48.0	476
Cyclophosphazines; see Table 105 for structures			
$(\text{NPMe}_2)_3$	CDCl_3	26.1 (ring P-N)	660
$[\text{NP}(\text{NHMe})_2]_3$	CDCl_3	7.7	660
$[\text{NP}(\text{NMe}_2)_2]_3$	CDCl_3	7.5	660
$[\text{NP}(\text{NHEt})_2]_3$	CDCl_3	7.8	660
$[\text{NP}(\text{Net}_2)_2]_3$	CDCl_3	6.1	660
$[\text{NP}(\text{NHPh})_2]_3$	CDCl_3	6.6	660
$[\text{NP}(\text{OEt})_2]_3$	CDCl_3	6.4	660
$[\text{NP}(\text{SEt})_2]_3$	CDCl_3	51.0	660
$[\text{NP}(\text{SPh})_2]_3$	CDCl_3	53.3	660
$(\text{NPF}_2)_3$	CDCl_3	24.9	660
$(\text{NPCl}_2)_3$	CDCl_3	31.7	660
$(\text{NPBr}_2)_3$	CDCl_3	55.8	660
	CDCl_3	-30.7 (P2,4-N3)	474
		-21.0 (P2-N1) or (P4-N5)	474
		+13.4 (P6-N1,5)	474
$\text{N}_3\text{P}_3\text{Cl}_4(\text{NH}_2)_2$	CDCl_3	-35.8 (P2,4-N3)	474
		-33.0 (P2-N1) or (P4-N5)	474
		-7.4 (P6-N1,5)	474
$\text{N}_3\text{P}_3\text{Cl}_4(\text{SEt})_2$	CDCl_3	-34.1 (P2,4-N3)	474
		-38.8 (P2-N1) or (P4-N5)	474
		-48.1 (P6-N1,5)	474

TABLE 146—*cont.*

Compound	Solvent	$^1J(^{31}\text{P}-^{15}\text{N})$ (Hz)	Ref.
(NPM e_2) $_3$	CDCl_3	-26.1	49, 105
[NP(NMe $_2$) $_2$] $_3$	CDCl_3	-7.5	49, 105
[NP(NHEt) $_2$] $_3$	CDCl_3	-7.8	49, 105
[NP(OMe) $_2$] $_3$	CDCl_3	7.5	49, 105
[NP(OPh) $_2$] $_3$	CDCl_3	7.1	49, 105
[NP(SET) $_2$] $_3$	CDCl_3	-51.0	49, 105
(NPF $_2$) $_3$	CDCl_3	24.9	49, 105
(NPCl $_2$) $_3$	CDCl_3	-31.7	49, 105
(NPBr $_2$) $_3$	CDCl_3	-55.8	49, 105
[NP(NH $_2$) $_2$] $_3$	CDCl_3	-7.8	49, 105
[NP(OH) $_2$] $_3$	CDCl_3	6.4	49, 105
(NPM e_2) $_4$	CDCl_3	-23.8	49, 105
[NP(NMe $_2$) $_2$] $_4$	CDCl_3	14.2	49, 105
[NP(NHEt) $_2$] $_4$	CDCl_3	5.5	49, 105
[NP(OMe) $_2$] $_4$	CDCl_3	32.7	49, 105
[NP(OPh) $_2$] $_4$	CDCl_3	37.5	49, 105
[NP(SET) $_2$] $_4$	CDCl_3	-34.0	49, 105
(NPF $_2$) $_4$	CDCl_3	68.8	49, 105
(NPCl $_2$) $_4$	CDCl_3	-6.9	49, 105
(NPBr $_2$) $_4$	CDCl_3	-35.3	49, 105
[NP(NMe $_2$) $_2$] $_5$	CDCl_3	19.4	49, 105
[NP(OMe) $_2$] $_5$	CDCl_3	39.0	49, 105
(NPF $_2$) $_5$	CDCl_3	71.8	49, 105
(NPCl $_2$) $_5$	CDCl_3	-3.0	49, 105
[NP(NMe $_2$) $_2$] $_6$	CDCl_3	29.3	49, 105
[NP(OMe) $_2$] $_6$	CDCl_3	41.5	49, 105
(NPCl $_2$) $_6$	CDCl_3	-2.0	49, 105
N $_3$ P $_3$ Cl $_6$	CDCl_3	31.7	622
	CDCl_3	32.2 (P2,4-N3)	622
		30.4 (P2-N1) or (P4-N5)	622
		17.9 (P6-N1,5)	622
		36.1 (P6-N7)	622
		5.8 (P6-N1,5)	622
N $_3$ P $_3$ Cl $_4$ (NHPh) $_2$	CDCl_3	34.4 (P2,4-N3)	622
		32.2 (P2-N1)	622
		(P4-N5)	
		38.9 (P6-N7)	622
		6.6	622
N $_3$ P $_3$ (NHPh) $_6$	CDCl_3		622
N $_3$ P $_3$ Cl $_5$ NH $_2$	CDCl_3	33.5 (P6-N7)	622
<i>gem</i> -N $_3$ P $_3$ Cl $_4$ (NH $_2$) $_2$	EtOH + benzene- d_6	33.6 (P6-N7)	622
N $_3$ P $_3$ Cl $_5$ NHMe	CDCl_3	33.8 (P6-N7)	622
<i>gem</i> -N $_3$ P $_3$ Cl $_4$ (NHMe) $_2$	CDCl_3	36.3 (P6-N7)	622
<i>trans</i> -N $_3$ P $_3$ Cl $_4$ (NHMe) $_2$	CDCl_3	32.1 (P6-N7)	622
<i>cis</i> -N $_3$ P $_3$ Cl $_4$ (NHMe) $_2$	CDCl_3	33.0 (P6-N7)	622
N $_3$ P $_3$ Cl $_5$ NMe $_2$	CDCl_3	25.7 (P6-N7)	622

TABLE 146—*cont.*

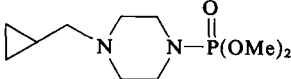
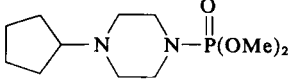
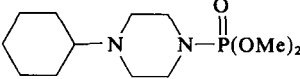
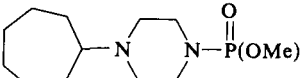
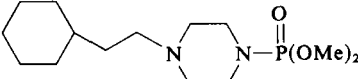
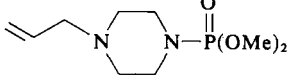
Compound	Solvent	$^1J(^{31}\text{P}-^{15}\text{N})$ (Hz)	Ref.
<i>trans</i> -N ₃ P ₃ Cl ₄ (NMe ₂) ₂	CDCl ₃	25.3 (P6–N7)	622
<i>cis</i> -N ₃ P ₃ Cl ₄ (NMe ₂) ₂	CDCl ₃	26.0 (P6–N7)	622
[NMePO(OMe)] ₄	CDCl ₃	28.6	473
[NP(OMe) ₂] ₄	CDCl ₃	32.7	473
HN $\left[\begin{array}{c} \text{O} \\ \parallel \\ -\text{P}(\text{OH})_2 \end{array}\right]_2$	CDCl ₃	33.6	626
Pr ⁱ –N $\begin{array}{c} \text{O} \\ \parallel \\ \text{P}(\text{OMe})_2 \end{array}$	CDCl ₃	41	626
Bu ⁱ –N $\begin{array}{c} \text{O} \\ \parallel \\ \text{P}(\text{OMe})_2 \end{array}$	CDCl ₃	40.2	626
 N $\begin{array}{c} \text{O} \\ \parallel \\ \text{P}(\text{OMe})_2 \end{array}$	CDCl ₃	40.5	626
 N $\begin{array}{c} \text{O} \\ \parallel \\ \text{P}(\text{OMe})_2 \end{array}$	CDCl ₃	40.1	626
 N $\begin{array}{c} \text{O} \\ \parallel \\ \text{P}(\text{OMe})_2 \end{array}$	CDCl ₃	40.3	626
 N $\begin{array}{c} \text{O} \\ \parallel \\ \text{P}(\text{OMe})_2 \end{array}$	CDCl ₃	40.9	626
 N $\begin{array}{c} \text{O} \\ \parallel \\ \text{P}(\text{OMe})_2 \end{array}$	CDCl ₃	40.0	626
 N $\begin{array}{c} \text{O} \\ \parallel \\ \text{P}(\text{OMe})_2 \end{array}$	CDCl ₃	39.9	626
Ph–N $\begin{array}{c} \text{O} \\ \parallel \\ \text{P}(\text{OMe})_2 \end{array}$	CDCl ₃	40.7	626
PhCH ₂ –N $\begin{array}{c} \text{O} \\ \parallel \\ \text{P}(\text{OMe})_2 \end{array}$	CDCl ₃	39.5	626

TABLE 146—*cont.*

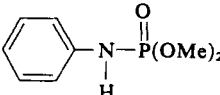
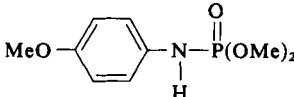
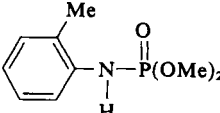
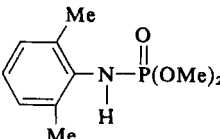
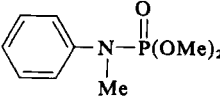
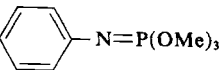
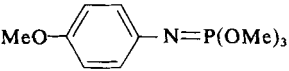
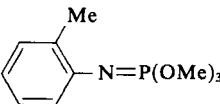
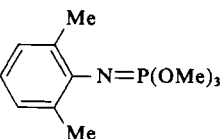
Compound	Solvent	$^1J(^{31}\text{P}-^{15}\text{N})$ (Hz)	Ref.
	CDCl_3 (1.5 M)	42.6	665
	CDCl_3 (1.5 M)	42.9	665
	CDCl_3 (1.5 M)	44.3	665
	CDCl_3 (1.5 M)	43.2	665
	aniline/ CHCl_3 (3:1 v/v)	42.8	665
	aniline/ CDCl_3 (3:1 v/v)	42.5	665
	aniline/ CDCl_3 (3:1 v/v)	42.6	665
	aniline/ CDCl_3 (3:1 v/v)	42.9	665
	aniline/ CDCl_3 (3:1 v/v)	44.1	665
2'-Deoxyadenosine cyclic 3',5'-(Sp)-phosphoranilidate	pyridine	47.7	478
2'-Deoxyadenosine cyclic 3',5'-(Rp)-phosphoranilidate	pyridine	36.7	478

TABLE 146—*cont.*

Compound	Solvent	$^1J(^{31}\text{P}-^{15}\text{N})$ (Hz)	Ref.
$(\text{MeO})_3\text{P}=\text{N}-\text{Et}$	CHCl_3	6.8	681
$(\text{MeO})_3\text{P}=\text{N}-\text{Ph}$	CHCl_3	11.4	681
$(\text{Me}_2\text{N})_3\text{P}=\text{N}-\text{Et}$	CHCl_3	29.05 (P=N)	681
		32.7 (P-NMe ₂)	681
$(\text{Me}_2\text{N})_3\text{P}=\text{N}-\text{Ph}$	CHCl_3	24.5 (P=N)	681
		24.4 (P-NMe ₂)	
$(\text{Me}_2\text{N})_3\text{P}=\text{N}-\text{tosyl}$	CHCl_3	30.1 (P-NMe ₂)	681
	CHCl_3	11.0 (P=N)	681
		34.8 (P-NMe ₂)	681
		15.9 (P-NMe)	681
	CHCl_3	4.5	681
$(\text{Me}_2\text{N})_3\text{P}-\text{N}_3-\text{tosyl}$	CHCl_3	<i>ca.</i> 6 (P-N ₃)	681
		29.8 (P-NMe ₂)	
4-MeOC ₆ F ₄ N=PCl ₃	benzene	22.5	623
4-MeC ₆ F ₄ N=PCl ₃	benzene	21.4	623
4Cl-C ₆ F ₄ N=PCl ₃	benzene	20.1	623
PhN=PCl ₃	benzene	20.1	623
4-CF ₃ C ₆ F ₄ N=PCl ₃	benzene	16.3	623
4-CN-C ₆ F ₄ N=PCl ₃	benzene	16.4	623
4-NO ₂ -C ₆ F ₄ N=PCl ₃	benzene	16.3	623
2-NO ₂ -C ₆ F ₄ N=PCl ₃	benzene	12.6	623
2-NO ₂ -5-CF ₃ -C ₆ F ₃ N=PCl ₃	benzene	11.3	623
	benzene	17.6	623
	benzene	15.1	623
$\text{Ph}_3\text{P}=\text{NS}_3\text{N}_3$	CHCl_3	48.9	367
$\text{Ph}_3\text{P}=\text{NSNSS}$	CHCl_3	58.0	367
1,5-(Ph ₃ P=N) ₂ S ₄ N ₄	CHCl_3	43.9?	367
		47.6?	367

TABLE 146—cont.

Compound	Solvent	$^1J(^{31}\text{P}-^{15}\text{N})$ (Hz)	Ref.
	CD ₂ Cl ₂	55.6 (P-NPri ⁱ ₂)	480
		98.9 (P-NMe)	480

TABLE 147

Some $^{31}\text{P}-^{15}\text{N}$ couplings across two bonds (absolute values)

Compound	Solvent	$^2J(^{31}\text{P}-^{15}\text{N})$ (Hz)	Ref.
<i>trans</i> -[ReClN ₂ (PMe ₂ Ph) ₄]	THF	5	394
<i>trans</i> -[FeHN ₂ (Ph ₂ PCH ₂ CH ₂ PPh ₂) ₂ BPh ₄]	THF	2	394
<i>mer</i> -[OsBrN ₂ (PMe ₂ Ph) ₃]	THF	2	394
<i>mer</i> -[OsCl ₂ N ₂ (PEt ₂ Ph) ₃]	THF	1	394
<i>mer</i> -[OsBr ₂ N ₂ (PEt ₂ Ph) ₃]	THF	1.5	394
<i>trans</i> -[RhClN ₂ {P(C ₆ H ₁₁) ₃ }] ₂	CH ₂ Cl ₂	4	394
	DMSO-d ₆	1.0	297
	acetone-d ₆	1.5	297
	CDCl ₃	52.5	297
		35.4 <1	297

Table 148

Some ^{31}P - ^{15}N couplings across three bonds (absolute values)

Compound	Solvent	$^3J(^{31}\text{P}-^{15}\text{N})$ in Hz	Ref
$\text{N}_3\text{P}_3\text{ClNH}_2$	CDCl_3	4.4 (P-NH ₂)	622
<u>gem</u> - $\text{N}_3\text{P}_3\text{Cl}_4(\text{NH}_2)_2$	EtOH + benzene	4.0 (P-NH ₂)	622
$\text{N}_3\text{P}_3\text{Cl}_5\text{NHMe}$	CDCl_3	4.2 (P-NHMe)	622
<u>gem</u> - $\text{N}_3\text{P}_3\text{Cl}_4(\text{NHMe})_2$	CDCl_3	4.0 (P-NHMe)	622
<u>trans</u> - $\text{N}_3\text{P}_3\text{Cl}_4(\text{NHMe})_2$	CDCl_3	4.3/2.5 (P-NHMe)	622
<u>cis</u> - $\text{N}_3\text{P}_3\text{Cl}_4(\text{NHMe})_2$	CDCl_3	4.5/4.5 (P-NHMe)	622
$\text{N}_3\text{P}_3\text{Cl}_5\text{NMe}_2$	CDCl_3	3.6 (P-NMe ₂)	622
<u>trans</u> - $\text{N}_3\text{P}_3\text{Cl}_4(\text{NMe}_2)_2$	CDCl_3	3.1/1.8 (P-NMe ₂)	622
<u>cis</u> - $\text{N}_3\text{P}_3\text{Cl}_4(\text{NMe}_2)_2$	CECl_3	3.5/3.5 (P-NMe ₂)	622
$\text{N}_3\text{P}_3\text{Cl}_5\text{NHPh}$	CDCl_3	4.1 (P-NHPh)	622
		<1 (P-N)	622

<u>gem</u> -N ₃ P ₃ Cl ₄ (NHPPh) ₂	CDCl ₃	3.4 (P-NHPPh)	622
		<1 (P-N)	622
N ₃ P ₃ Cl ₆	CDCl ₃	<1 (P-N)	622
N ₃ P ₃ (NHPPh) ₆	CDCl ₃	<1 (P-N)	622
<u>trans</u> -[RhClN ₂ {P(C ₆ H ₁₁) ₃ } ₂]	CH ₂ Cl ₂	0.8	622
Ph ₃ P=N-S ₃ N ₃	CHCl ₃	4.3	367
1,5-(Ph ₃ P=N) ₂ S ₄ N ₄	CHCl ₃	4.3	367

Table 149
Some $^{195}\text{Pt}-^{15}\text{N}$ couplings across one bond (absolute values)

Compound	Solvent	$^1J(^{195}\text{Pt}-^{15}\text{N})$ in Hz	Ref
$[\text{Pt}(\text{NO}_2)\text{Cl}_5]^{2-}$	D_2O	394 (<u>trans</u> to Cl^-)	413
<u>trans</u> $[\text{Pt}(\text{NO}_2)\text{Cl}_4\text{Br}]^{2-}$	D_2O	393 (<u>trans</u> to Cl^-)	413
<u>cis</u> $[\text{Pt}(\text{NO}_2)\text{Cl}_4\text{Br}]^{2-}$	D_2O	366 (<u>trans</u> to Br^-)	413
<u>mer,trans</u> $[\text{Pt}(\text{NO}_2)\text{Cl}_3\text{Br}_2]^{2-}$	D_2O	400 (<u>trans</u> to Cl^-)	413
<u>fac,cis</u> $[\text{Pt}(\text{NO}_2)\text{Cl}_3\text{Br}_2]^{2-}$	D_2O	400 (<u>trans</u> to Cl^-)	413
<u>mer,cis</u> $[\text{Pt}(\text{NO}_2)\text{Cl}_3\text{Br}_2]^{2-}$	D_2O	367 (<u>trans</u> to Br^-)	413
<u>cis,mer</u> $[\text{Pt}(\text{NO}_2)\text{Cl}_2\text{Br}_3]^{2-}$	D_2O	403 (<u>trans</u> to Cl^-)	413
<u>cis,fac</u> $[\text{Pt}(\text{NO}_2)\text{Cl}_2\text{Br}_3]^{2-}$	D_2O	366 (<u>trans</u> to Br^-)	413
<u>trans,mer</u> $[\text{Pt}(\text{NO}_2)\text{Cl}_2\text{Br}_3]^{2-}$	D_2O	360 (<u>trans</u> to Br^-)	413
<u>trans</u> $[\text{Pt}(\text{NO}_2)\text{ClBr}_4]^{2-}$	D_2O	403 (<u>trans</u> to Cl^-)	413
<u>cis</u> $[\text{Pt}(\text{NO}_2)\text{ClBr}_4]^{2-}$	D_2O	372 (<u>trans</u> to Br^-)	413
$[\text{Pt}(\text{NO}_2)\text{Br}_5]^{2-}$	D_2O	372 (<u>trans</u> to Br^-)	413

<u>trans</u> [Pt(NO ₂) ₂ Cl ₄] ²⁻	D ₂ O	336 (<u>trans</u> to NO ₂ ⁻)	413
<u>trans</u> [Pt(NO ₂) ₂ Br ₄] ²⁻	D ₂ O	342 (<u>trans</u> to NO ₂ ⁻)	413
		405 (<u>trans</u> to Br ⁻)	413
<u>cis</u> [Pt(NO ₂) ₂ Cl ₄] ²⁻	D ₂ O	424 (<u>trans</u> to Cl ⁻)	413
<u>cis</u> [Pt(NO ₂) ₂ Cl ₃ Br] ²⁻	D ₂ O	430 (<u>trans</u> to Cl ⁻)	413
		399 (<u>trans</u> to Br ⁻)	413
<u>cis</u> [Pt(NO ₂) ₂ ClBr ₃] ²⁻	D ₂ O	433 (<u>trans</u> to Cl ⁻)	413
		397 (<u>trans</u> to Br ⁻)	413
<u>cis</u> [Pt(NO ₂) ₂ ClBr ₃] ²⁻	D ₂ O	433 (<u>trans</u> to Cl ⁻)	413
		397 (<u>trans</u> to Br ⁻)	413
		342 (<u>trans</u> to NO ₂ ⁻)	413
<u>mer</u> [Pt(NO ₂) ₃ Cl ₃] ²⁻	D ₂ O	446 (<u>trans</u> to Cl ⁻)	413
		360 (<u>trans</u> to NO ₂ ⁻)	413

Table 149 (continued)

<u>mer</u> [Pt(NO ₂) ₃ ClBr ₂] ²⁻	D ₂ O	415(<u>trans</u> to Br ⁻)	413
		363(<u>trans</u> to NO ₂ ⁻)	413
		467(<u>trans</u> to Cl ⁻)	413
<u>mer</u> [Pt(NO ₂) ₃ Br ₃] ²⁻	D ₂ O	421(<u>trans</u> to Br ⁻)	413
		369(<u>trans</u> to NO ₂ ⁻)	413
<u>fac</u> [Pt(NO ₂) ₃ Cl ₃] ²⁻	D ₂ O	460(<u>trans</u> to Cl ⁻)	413
<u>fac</u> [Pt(NO ₂) ₃ Cl ₂ Br] ²⁻	D ₂ O	466(<u>trans</u> to Cl ⁻)	413
<u>trans</u> [Pt(NO ₂) ₄ Cl ₂] ²⁻	D ₂ O	488(<u>trans</u> to Cl ⁻)	413
		391(<u>trans</u> to NO ₂ ⁻)	413
<u>cis</u> [Pt(NO ₂) ₄ ClBr] ²⁻	D ₂ O	486(<u>trans</u> to Cl ⁻)	413
		459(<u>trans</u> to Br ⁻)	413
		394(<u>trans</u> to NO ₂ ⁻)	413
<u>cis</u> [Pt(NO ₂) ₄ Br ₂] ²⁻	D ₂ O	455(<u>trans</u> to Br ⁻)	413
		394(<u>trans</u> to NO ₂ ⁻)	413

$[\text{Pt}(\text{NO}_2)_5\text{Cl}]^{2-}$	D_2O	518 (<u>trans</u> to Cl^-)	413
		415 (<u>trans</u> to NO_2^-)	413
$[\text{Pt}(\text{NO}_2)_5\text{Br}]^{2-}$	D_2O	482 (<u>trans</u> to Br^-)	413
		415 (<u>trans</u> to NO_2^-)	413
$[\text{Pt}(\text{NO}_2)\text{Cl}_3]^{2-}$	D_2O	589 (<u>trans</u> to Cl^-)	413
<u>trans</u> $[\text{Pt}(\text{NO}_2)\text{Cl}_2\text{Br}]^{2-}$	D_2O	570 (<u>trans</u> to Br^-)	413
<u>cis</u> $[\text{Pt}(\text{NO}_2)\text{Cl}_2\text{Br}]^{2-}$	D_2O	580 (<u>trans</u> to Cl^-)	413
<u>cis</u> $[\text{Pt}(\text{NO}_2)\text{ClBr}_2]^{2-}$	D_2O	568 (<u>trans</u> to Br^-)	413
<u>trans</u> $[\text{Pt}(\text{NO}_2)\text{ClBr}_2]^{2-}$	D_2O	570 (<u>trans</u> to Cl^-)	413
$[\text{Pt}(\text{NO}_2)\text{Br}_3]^{2-}$	D_2O	562 (<u>trans</u> to Br^-)	413
<u>trans</u> $[\text{Pt}(\text{NO}_2)_2\text{Cl}_2]^{2-}$	D_2O	470 (<u>trans</u> to NO_2^-)	413
<u>trans</u> $[\text{Pt}(\text{NO}_2)_2\text{ClBr}]^{2-}$	D_2O	459 (<u>trans</u> to NO_2^-)	413
<u>trans</u> $[\text{Pt}(\text{NO}_2)_2\text{Br}_2]^{2-}$	D_2O	452 (<u>trans</u> to NO_2^-)	413
<u>cis</u> $[\text{Pt}(\text{NO}_2)_2\text{Cl}_2]^{2-}$	D_2O	679 (<u>trans</u> to Cl^-)	413

Table 149 (continued)

<u>cis</u> [Pt(NO ₂) ₂ ClBr] ²⁻	D ₂ O	665(<u>trans</u> to Cl ⁻)	413
		665(<u>trans</u> to Br ⁻)	413
<u>cis</u> [Pt(NO ₂) ₂ Br ₂] ²⁻	D ₂ O	651(<u>trans</u> to Br ⁻)	413
[Pt(NO ₂) ₃ Cl] ²⁻	D ₂ O	757(<u>trans</u> to Cl ⁻)	413
		535(<u>trans</u> to NO ₂ ⁻)	413
[Pt(NO ₂) ₃ Br] ²⁻	D ₂ O	665(<u>trans</u> to Cl ⁻)	413
		745(<u>trans</u> to Br ⁻)	413
		522(<u>trans</u> to NO ₂ ⁻)	413
[Pt(NO ₂) ₄] ²⁻	D ₂ O	592(<u>trans</u> to NO ₂ ⁻)	413
[Pt(NH ₃) ₄] ²⁺	H ₂ O	281.4	412
	D ₂ O	283	407
	H ₂ O	286	276
[<u>cis</u> Pt(NH ₃) ₂ (H ₂ O) ₂] ²⁺	H ₂ O	378	412
	D ₂ O	383 ^a	407
		390	407

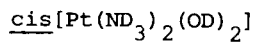
	H ₂ O	387	415
	H ₂ O	388	276
[<u>cis</u> Pt(Me ₂ CHNH ₂) ₂ (OH) ₂ Cl ₂]	DMSO	266	412
[Pt(NH ₃) ₂ OH ₂] ²⁺	D ₂ O	342 ^a	407
		342	407
	H ₂ O	342	415
[Pt(NH ₃) ₂ OH ₃] ³⁺	H ₂ O	339	415
	D ₂ O	342	407
[<u>cis</u> PtCl(H ₂ O)(NH ₃) ₂] ⁺	D ₂ O	356 ^a	407
	H ₂ O	343(<u>trans</u> to Cl ⁻)	276
		368(<u>trans</u> to H ₂ O)	276
[<u>cis</u> PtCl ₂ (NH ₃) ₂]	D ₂ O	303	407
	DMF	302	415
	H ₂ O	325	276
[Pt(NH ₃) ₂ (OH) ₂]	D ₂ O	293	407

Table 149 (continued)

$[\text{PtOH}(\text{H}_2\text{O})(\text{NH}_3)_2]^+$	D_2O	330	407
$[\text{PtCl}(\text{H}_2\text{O})(\text{NH}_3)_2]^+$	D_2O	342(<u>trans</u> to Cl^-)	407
		361(<u>trans</u> to H_2O)	407
$[\text{PtCl}(\text{OH})(\text{NH}_3)_2]$	D_2O	347(<u>trans</u> to Cl^-)	407
		288(<u>trans</u> to OH^-)	407
<u>cis</u> $[\text{Pt}(\text{Pr}^{\text{n}}\text{NH}_2)_2(\text{OH})_4]$	D_2O	249	415
<u>cis, cis, trans</u> $[\text{Pt}(\text{Pr}^{\text{n}}\text{NH}_2)_2\text{Cl}_2(\text{OH})_2]$	D_2O	266	415
<u>cis, cis, trans</u> $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2(\text{OH})_2]$	$\text{H}_2\text{O}/\text{H}_2\text{O}$	275	415
<u>cis</u> $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$	H_2O	247	415
$[\text{Pt}(\text{NH}_3)_2(\text{ethyl malonate})]$	H_2O	366	415
$[\text{Pt}(\text{NH}_3)_2(\text{cyclobutanedicarboxylate})]$	H_2O	360	415
$[\text{Pt}(\text{ethylenediamine})]$	H_2O	411	415
$[\text{Pt}(\text{NH}_3)\text{Cl}_3]^-$	H_2O	324	276
$[\text{Pt}(\text{NH}_3)(\text{H}_2\text{O})_3]^{2+}$	H_2O	387	276

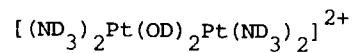
$[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$	H_2O	329 (<u>trans</u> to Cl)	276
		282 (<u>trans</u> to NH_3)	276
<u>cis</u> $[\text{Pt}(\text{NH}_3)_2\text{pyCl}]^+$	H_2O	343 (<u>trans</u> to Cl)	276
		273 (<u>trans</u> to py)	276
<u>cis</u> $[\text{Pt}(\text{NH}_3)_2\text{py}(\text{H}_2\text{O})]^{2+}$	H_2O	290 (<u>trans</u> to py)	276
		384 (<u>trans</u> to H_2O)	276
<u>cis</u> $[\text{Pt}(\text{NH}_3)_2(\text{py})_2]^{2+}$	H_2O	288 (<u>trans</u> to py)	276
$[\text{Pt}(\text{NH}_3)_3(\text{py})]^{2+}$	H_2O	302 (Pt- NH_3)	276
$[\text{Pt}(\text{NH}_3)_3\text{py}]^{2+}$	H_2O	295 (NH_3 <u>trans</u> to py)	276
		277 (Pt-py)	276
<u>cis</u> $[\text{Pt}(\text{NH}_3)_2\text{anCl}]^+$	H_2O	351 (<u>trans</u> to Cl)	276
		287 (<u>trans</u> to an)	276
<u>cis</u> $[\text{Pt}(\text{NH}_3)_2(\text{an})_2]^{2+}$	H_2O	307 (Pt- NH_3)	276
<u>cis</u> $[\text{Pt}(\text{ND}_3)_2(\text{D}_2\text{O})_2]^{2+}$	D_2O	410	411
<u>cis</u> $[\text{Pt}(\text{ND}_3)_2(\text{D}_2\text{O})(\text{OD})]$	D_2O	360	411

Table 149 (continued)



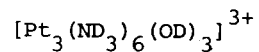
300

411



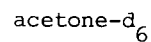
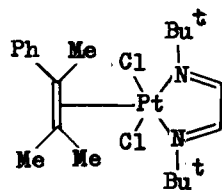
360

411



340

411



156

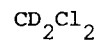
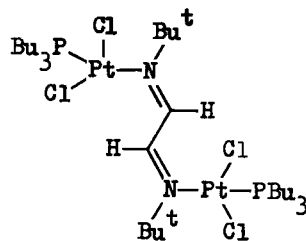
410

135(-80°)

410

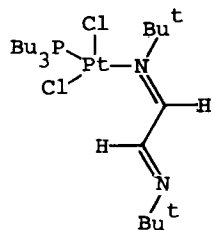
178(-80°)

410



211

410



CDCl_2 (-50°)

217

410

trans $[\text{PtCl}_2(\text{hexylamine}) \text{PBu}_3^n]$

CDCl_3

138

410

trans $[\text{PtCl}_2(\text{Bu}^+\text{NH}_2) \text{PBu}_3^n]$

CDCl_3

159

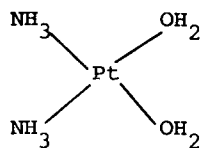
410

trans $[\text{PtCl}_2 \text{ an}(\text{PBu}_3^n)]$

CDCl_3

103

410



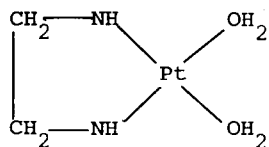
H_2O

386 (from ^{15}N NMR)

408

387 (from ^{195}Pt NMR)

408



H_2O

426 (from ^{15}N NMR)

408

421 (from ^{195}Pt NMR)

408

Table 149 (continued)

	H_2O	414 (from ^{15}N NMR)	408
		421 (from ^{195}N NMR)	408
	CDCl_3	301.7	297
	acetone- d_6	304.7	297

L =

$\text{P}^{\text{n}}\text{Bu}_3$	CDCl_3	294.1	409
$\text{P}(\text{OEt})_3$	CDCl_3	303.0	409
$\text{P}(\text{p-MeC}_6\text{H}_4)_3$	CDCl_3	323.6	409
$\text{As}^{\text{n}}\text{Bu}_3$	CDCl_3	366.2	409
$\text{C}=\text{N}-\text{Ph}$	CDCl_3	397.1	409
$\text{As}(\text{p-MeC}_6\text{H}_4)_3$	CDCl_3	413.3	409
	DMSO	416.2	409
DMSO	CDCl_3	431.0(broad)	409
	DMSO	422.1	409
piperidine	CDCl_3	464.7	409
$\text{NH}_2(\text{CH}_2)_5\text{Me}$	CDCl_3	478.0	409
pyridine	CDCl_3	494.2	409

(a) Recalculated from $^{195}\text{Pt}-^{14}\text{N}$ Couplings.

Table 150

Some ^{195}Pt - ^{15}N couplings across two and three bonds (absolute values)

Compound	Solvent	$2-3 J(^{195}\text{Pt}-^{15}\text{N})$ in Hz	Ref
$\text{Pt}(\text{CN})_4$	D_2O	(^2J) 61.2	399
$[\text{cis-Pt}(\text{NH}_3)(\text{N-Me-imidazole})_2]^{2+}$	H_2O	(^3J) 26.1 (N-Me)	1
$[\text{Pt}(\text{H}_2\text{O})(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)(\text{N-Me-imidazole})]^{2+}$	H_2O	(^3J) 24.7 (N-Me)	1
$[\text{Pt}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)(\text{N-Me-imidazole})_2]^{2+}$	H_2O	(^3J) 25.5 (N-Me)	1
$\text{trans-PtCl}_2(\text{CH}_2\text{CH}_2\text{N}^+\text{HMe}_2)(\text{NHMe}_2)$	CDCl_3	(^3J) 51	1

Table 151
Some ^{15}N - ^{11}B couplings across one bond

Compound	Solvent	$^1J(^{15}\text{N}-^{11}\text{B})$ in Hz	Ref
$\text{B}(\text{NHMe})_3$	benzene- d_6 (1:1 v/v) ⁶	-45.0	126
$\text{Me}_3\text{N} \rightarrow \text{BF}_3$	CH_2Cl_2	-18.70	124
$\text{Me}_3\text{N} \rightarrow \text{BF}_2\text{Cl}$	CH_2Cl_2	-18.61	124
$\text{Me}_3\text{N} \rightarrow \text{BF}_2\text{Br}$	CH_2Cl_2	-18.47	124
$\text{Me}_3\text{N} \rightarrow \text{BFCl}_2$	CH_2Cl_2	-17.52	124
$\text{Me}_3\text{N} \rightarrow \text{BFBr}_2$	CH_2Cl_2	-17.44	124
$\text{Me}_3\text{N} \rightarrow \text{BCl}_3$	CH_2Cl_2	-16.5	124
$\text{Me}_3\text{N} \rightarrow \text{BFI}_2$	CH_2Cl_2	-14.3	124
$\text{Me}_3\text{N} \rightarrow \text{BCl}_2\text{Br}$	CH_2Cl_2	-16.13	124
$\text{Me}_3\text{N} \rightarrow \text{BCl}_2\text{I}$	CH_2Cl_2	-15.4	124
$\text{Me}_3\text{N} \rightarrow \text{BClBr}_2$	CH_2Cl_2	-15.72	124
$\text{Me}_3\text{N} \rightarrow \text{BClBrI}$	CH_2Cl_2	-14.66	124
$\text{Me}_3\text{N} \rightarrow \text{BBr}_3$	CH_2Cl_2	-15.23	124
$\text{Me}_3\text{N} \rightarrow \text{BClI}_2$	CH_2Cl_2	-13.93	124
$\text{Me}_3\text{N} \rightarrow \text{BBr}_2\text{I}$	CH_2Cl_2	-14.3	124
$\text{Me}_3\text{N} \rightarrow \text{BBrI}_2$	CH_2Cl_2	-13.2	124
$\text{Me}_3\text{N} \rightarrow \text{BI}_3$	CH_2Cl_2	-12.09	124

Table 152

Some ^{27}Al - ^{15}N couplings across one bond (absolute values)

Compound	Solvent	$^1J(^{27}\text{Al}-^{15}\text{N})$ in Hz	Ref.
$\text{AlCl}_3(\text{NCS})^-$	MeCN	56	1115
$\text{AlCl}_3(\text{NCO})^-$	MeCN	56	1115
$\text{AlCl}_2(\text{NCS})_2^-$	MeCN	63	1115

Data recalculated from ^{14}N couplings

Table 153

Some ^{57}Fe - ^{15}N couplings across one bond (absolute values)

Compound	Solvent	$^1J(^{57}\text{Fe}-^{15}\text{N})$ in Hz	Ref
Fe(II) low-spin complexes with meso- tetraphenylporphyrin (TPP)			1
Fe(TPP)(pyridine) $_2$	pyridine/D $_2$ O	7.8 (N-porphyrin)	1
Fe(TPP)(morpholine) $_2$	CDCl $_3$	8.0 (N-porphyrin)	1
Fe(TPP)(pyrrolidine) $_2$	CDCl $_3$	7.5 (N-porphyrin)	1

TABLE 154

Some ^{59}Co - ^{15}N couplings across one bond (absolute values)

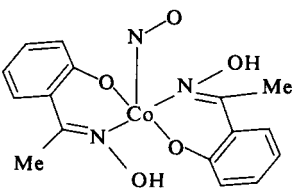
Compound	Solvent	$^1J(^{59}\text{Co}-^{15}\text{N})$ (Hz)	Ref.
$\text{Co}^{3+}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)$	D_2O	63.8	1
$\text{Co}^{3+}(\text{NH}_3)_6$	D_2O	62.5	1
	DMSO	9 (Co-NO)	397

Table 155

Some ^{71}Ga - ^{15}N couplings across one bond (absolute values)

Compound	Solvent	$^1J(^{71}\text{Ga}-^{15}\text{N})$ in Hz	Ref
$\text{GaCl}_3(\text{NCS})^-$	MeCN	133	481
$\text{GaCl}_2(\text{NCS})_2^-$	MeCN	161	481

Data recalculated from ^{14}N couplings.

Table 156

Some ^{95}Mo - ^{15}N couplings across one bond (absolute values)

Compound	Solvent	$^1J(^{95}\text{Mo}-^{15}\text{N})$ in Hz	Ref
$(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{NO})$	CH_3CN (293 K)	64.4	398
$(\eta^5\text{-C}_5\text{Me}_5)\text{Mo}(\text{CO})_2(\text{NO})$	CH_3CN (343 K)	64.4	398
$\text{HB}(3,5\text{-Me}_2\text{-pyrazolyl})_3\text{Mo}(\text{CO})_2(\text{NO})$	DMF (423 K)	61.6 (Mo-NO)	398

Data recalculated from ^{14}N couplings.

Table 157

Some ^{103}Rh - ^{15}N couplings across one bond (absolute values)

Compound	Solvent	$^1J(^{103}\text{Rh}-^{15}\text{N})$ in Hz	Ref
<u>trans</u> - $\text{RhCl}(\text{CO})(\text{NO})(\text{PPr}_3^i)_2(\text{ClO}_4)$	CH_2Cl_2	4.5	397
$\text{RhCl}(\text{PPr}_e^i)_2(\text{p-Me-C}_6\text{H}_4\text{-NSO})$	DMSO	15.5	1
<u>trans</u> - $\text{RhCl}[(\text{N}_2)\text{P}(\text{C}_6\text{H}_{11})_3]_2$	CH_2Cl_2	30	394

TABLE 158

Some ^{113}Cd - ^{15}N couplings across one bond (absolute values if sign not given)

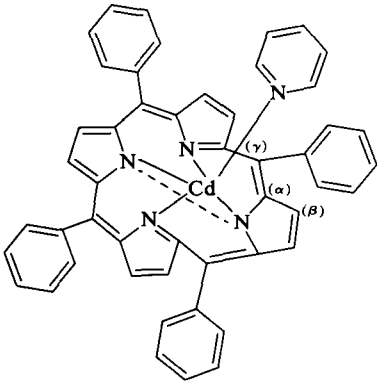
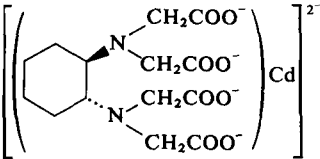
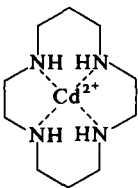
Compound	Solvent	$^1J(^{113}\text{Cd}-^{15}\text{N})$ (Hz)	Ref.
	CDCl_3	+150.1 (30 °C) (Cd-TPP) +150.3 (33 °C) (Cd-TPP)	401 401
	H_2O (10% D_2O)	80.9 (^{15}N - ^{111}Cd) 83.8 (^{15}N - ^{113}Cd)	273 273
	H_2O (10% D_2O) $(\text{NO}_3^-)_2$	75.0 (N axial) 125.0 (N equatorial) 110 (<i>trans</i> -III isomer)	273 273 273
Cd^{II} -Gly $^+$	H_2O (-40 °C)	170	682
Cd^{II} -Gly $_2$	as emulsions)	165	682
Cd^{II} -Gly $_3$		140	682

Table 159

Some ^{119}Sn - ^{15}N couplings across one bond

Compound	Solvent	$^1J(^{119}\text{Sn}-^{15}\text{N})$ in Hz	Ref
Me_3SnNHPH	benzene	-26.3	627
$[\text{Me}_3\text{Sn}]_2\text{NPh}$	benzene	-41.4	627
$\text{Me}_3\text{SnNMePh}$	benzene	+2.2	627
$\text{Me}_2\text{Sn}[\text{NMePh}]_2$	benzene	+24.0	627
$\text{MeSn}[\text{NMePh}]_3$	benzene	+87.0	627
$\text{Sn}[\text{NMePh}]_4$	benzene	+175.0	627
$\text{Me}_3\text{SnN}[\text{PMe}_2]\text{Ph}$	benzene	+9.5	627
$\text{Me}_3\text{SnN}[\text{P}(\text{S})\text{Me}_2]\text{Ph}$	benzene	-21.0	627

Table 160

Some ^{129}Xe - ^{15}N couplings across one bond (absolute values)

Compound	Solvent	$^1J(^{129}\text{Xe}-^{15}\text{N})$ in Hz	Ref
$\text{Xe}[\text{N}(\text{SO}_2\text{F})_2]_2$	SO_2ClF	259 (-40°C)	291
$\text{FXeN}(\text{SO}_2\text{F})_2$	SO_2ClF	307 (-40°C)	291
	BrF_5	307.4	292

TABLE 161
Some ^{199}Hg - ^{15}N couplings across one bond

Compound	Solvent	$^1J(^{199}\text{Hg}-^{15}\text{N})$ (Hz)	Ref.
	H_2O (10% D_2O)	317.7	273
cydta =			
$[\text{Hg}(\text{cydta})]^{2-}$	H_2O (10% D_2O)	365.7	273
$[\text{Hg}(\text{H cydta})(\text{OH})]^{2-}$	H_2O (10% D_2O)	395.5	273
$[\text{Hg}(\text{H cydta})\text{Cl}]^{2-}$	H_2O (10% D_2O)	388.7	273

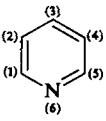
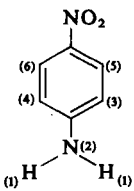
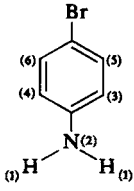
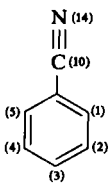
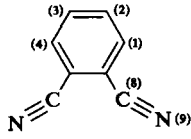
TABLE 162
Some ^{207}Pb - ^{15}N couplings across one bond (absolute values)

Compound	Solvent	$^1J(^{207}\text{Pb}-^{15}\text{N})$ (Hz)	Ref.
	H_2O (10% D_2O)	187.5	273
	DMSO	207.5 (N equatorial) 19.8 (N axial)	1 1
$\text{MePbN}[\text{SnMe}]_2$	benzene	238 ^a	629
and $[\text{MePb}]_2\text{NSnMe}_3$ (mixture)		238 ^a	629

(a) Recalculated from ^{14}N - ^{207}Pb couplings.

TABLE 163

Some direct dipolar couplings with ^{15}N

Compound	D_{ij} (Hz)	Ref.
	-105.44 (1, 6) -12.46 (2, 6) -2.80 (3, 6)	683 683 683
	-198.6 (1, 2) 29.4 (2, 3) 28.6 (2, 5)	172 172 172
	-456.6 (1, 2) 9.7 (2, 3) 16.3 (2, 5)	172 172 172
	-35.55 (1, 11+2, 11) -7.45 (3, 11)	675 675
	83.88 (1, 9+4, 9) 13.53 (3, 9+4, 9)	144 144

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