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Nitrogen Nuclear Magnetic Resonance Spectroscopy in Inorganic, Organometallic, and Bioinorganic Chemistry

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Joan Mason was born in London in 1923 and took her B.A., M.A., and Ph.D. degrees at the University of Cambridge (in fact "titles" to these degrees, as women were not officially members of the University). After war work on acrylics with I.C.I., her graduate work was on boron carbide (for the atomic energy authority) and then in fluorine chemistry, with H. J. Emeléus. She did postdoctoral work in boron chemistry with A. B. Burg at the University of Southern California (Fulbright scholar) and fluorine chemistry with A. L. Henne at Ohio State. After 5 years at University College London, she spent 8 years in Exeter, Devon, raising 3 children. She returned to chemistry at the University of East Anglia in 1964 and joined the Open University in 1970. Her current research interests are mainly in nitrogen chemistry and NMR spectroscopy (application and theory) and in women's contribution to science, actual and potential.

I. Introduction: ^{14}N and ^{15}N NMR

Nitrogen NMR spectroscopy is said to be approaching the stage that ^{13}C NMR reached a decade ago when FT (Fourier transform) techniques were bringing it within general reach. As well as the potential applications, nitrogen NMR parameters have an intrinsic interest since they can be interpreted by physical models[1] comparable to those the chemist has for other forms of spectroscopy, vibrational or electronic, for example. This is because nitrogen is chemically very versatile. It combines with almost all elements and has oxidation numbers from −3 to +5, coordination numbers from 1 to 6, and bond orders up to 3, the variety being reflected

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in its range of chemical shifts, 1100 ppm for diamagnetic compounds. This account of nitrogen shielding is designed to be evaluative and to complement earlier reviews.[2-6]

Interestingly, a nitrogen shift was the first to be observed in NMR spectroscopy, as "an annoying ambiguity" (a physicist's phrase[7a]) in the magnetic moment of nitrogen as measured in ^{14}N resonance in a solution of NH_4NO_3.[7b] In practice, nitrogen NMR spectroscopy has been bedevilled by technical problems, but these are slowly yielding to modern techniques. Earlier work[2-5] used the ^{14}N nucleus which is nearly 100% abundant but quadrupolar ($I = 1$); Herbison-Evans and Richards' 1964 paper[8] contains the seeds of much subsequent nitrogen work. In future, most will be done in high resolution with the rare ^{15}N nucleus ($I = {}^1/_2$, natural abundance 0.365%); but there will still be a place for ^{14}N NMR as detailed below. For convenient reference the literature citations in this review are labeled as to the nitrogen isotope with which the work is concerned.

^{14}N and ^{15}N both suffer from low magnetogyric ratios (γ), resulting in low NMR sensitivity and low working frequencies, small spin–spin coupling constants, and long relaxation times for ^{15}N. [$\gamma/10^7$ rad T^{-1} s^{-1} is 1.933 for ^{14}N and -2.711 for ^{15}N, compared with 26.752 for ^1H and 6.726 for ^{13}C. The *sensitivity* relative to ^1H is therefore 10^{-3} for ^{14}N or ^{15}N; cf. 10^{-2} for ^{13}C. The *receptivity* at natural abundance, relative to ^{13}C, is 5.7 for ^{14}N but 0.022 for ^{15}N.[9]] The Boltzmann exponent ($\gamma \hbar m B_0/kT$), the resonance frequency, and coupling constant J(NX) are all proportional to γ. J(NN) and the dipole–dipole relaxation rate are proportional to γ^2. The signal intensity[10] for n nuclei is proportional to $nB_0{}^2\gamma^3/T$, which clearly demonstrates the disadvantage of a low γ and advantages in working at higher field B_0, with larger samples, and possibly at lower temperatures T(K).

A further problem for ^{15}N is that the negative γ gives negative nuclear Overhauser enhancement (NOE) factors with proton decoupling when dipole–dipole relaxation by protons is important,[6] so that signals may be diminished, as discussed below.

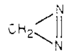
The use of ^{15}N NMR spectroscopy in organometallic and bioinorganic chemistry will increase with increasing availability of wide-bore high-field FT spectrometers, as developed in California by J. D. Roberts[11] for natural-abundance work with ^{15}N. "Wide bore" implies sample volumes of 20 cm^3 or more, and the new generation of superconducting spectrometers now uses fields up to 500 MHz for protons (11.7 T).

Sensitivity enhancement by transfer of nuclear polarization from protons (or fluorine or phosphorus) coupled to ^{15}N will become increasingly important, however. This is independent of the sign of γ, and means in effect that the difficult ^{15}N nucleus can be studied by way of the abundant nucleus, with high intrinsic sensitivity and efficient relaxation.[33-35]

II. ^{14}N Measurements

^{14}N NMR is dominated by quadrupolar relaxation, since the nuclear electric quadrupole is coupled to the nuclear spin. As the molecule tumbles, the change in the electric field gradient (q) around the ^{14}N nucleus relaxes the electric quadrupole, and this relaxes the spin also. The lower the local symmetry about nitrogen, the large is q, the faster the quadrupolar relaxation, and the broader the line, by the uncertainty principle. In principle, q becomes zero for spherical symmetry around nitrogen, but this is not attained in practice even for $NH_4{}^+$(aq) for which relaxation is wholly quadrupolar, as described below. (It will be interesting to see if conditions can be devised in which dipole–dipole relaxation can be observed for $NH_4{}^+$.) Even in the paramagnetic complexes [$K_3M(CN)_6$] (M = Cr, Mn, Fe) the ^{14}N line widths were found to be determined by quadrupolar relaxation, although the chemical shifts were determined by the contact interaction.[12]

Table I. ^{14}N Line Widths and Approximate Relaxation Times at Ambient Temperatures

		$\Delta\nu_{1/2}$/Hz[a]	T_1/ms[b]	ref
Me_4NBr (aq, 1 M)		v sh	10^4	13
N*N*O (*n*-hexane)		v sh	2960	25
*N*NO (*n*-hexane)			281	25
NH_4Cl (aq H^+, 1 M)		v sh	1600	13
CH_3NC (l)		0.26	1200	23
$NaNO_3$ (aq)		4	80	*c*
Pd-CNBu-*t*		4-12	80-30	14
NaNCO (aq, 1 M)		7	45	*c*
NH_3 (l)		8	38	13
 (ether)		10	32	*c*
KNCO (aq)		13	24	23
$MeNO_2$ (l)		16	20	*c*
MeN_3 (l)	β-N	17	19	23
	γ-N	19	17	23
N_2(l, -196 °C)		26	12	29
NaN_3 (aq)	α-N	73	4.4	23
	β-N	22	14.5	23
NaCN (aq, 5 M)		67	5	*c*
CH_3CN (l)		80	4	*c*
KNCS (aq, 5 M)		96	3.3	*c*
MeN_3 (l)	α-N	100	3.2	23
urea (aq)		110	2.9	*c*
HCONHMe (l)		120	2.6	*c*
$Ti(NMe_2)_4$ (l)[d]		135	2.4	*c*
pyridine (l)		200	1.6	*c*
$Si(NMe_2)_4$ (l)[d]		200	1.6	*c*
$NaNO_2$ (aq, 5 M)		240	1.3	*c*
$P(NMe_2)_3$ (l)[d]		300	1.1	*c*
$As(NMe_2)_3$ (l)[d]		400	0.8	*c*

[a] Line width at half-height. [b] $T_1 = T_q \simeq T_2 \simeq 1/\pi\Delta\nu_{1/2}$, where T_q is the quadrupolar relaxation time. [c] D. M. Kanjia and J. Mason, measured with a Bruker WP60 spectrometer at 4.33 MHz, with broad-band decoupling, where appropriate; typically with pulse width 20 μs. [d] Sample contains 10% (v/v) of deuterated solvent, which reduces the line width if the viscosity is reduced.

The ^{14}N quadrupole moment, however, is relatively small ($Q = 1.55 \times 10^{-26}$ cm^2, about 5 times the value for ^2H). The Sternheimer antishielding factor arising from distortion of the closed electron shells by external charges is relatively small also for an atom the size of nitrogen.[13] High-resolution work is therefore possible with ^{14}N, with measurement of small coupling constants, so long as the local symmetry is sufficiently high. Table I gives approximate line widths and relaxation times for a variety of nitrogen groupings. Relatively sharp lines are obtained for ammonium ions ($NR_4{}^+$) or immonium ($R_2C{=}NR_2{}^+$) ions, nitrates or nitro compounds, and also for linear groups such as R—N≡C,[14,15] M=NR,[16] or M—N≡CR,[17] where M is a metal. For these narrower ^{14}N lines, FT techniques with fast pulsing and accumulation can offset the low sensitivity of ^{14}N NMR.

Many interesting groups, however, are bent at nitrogen, which carries a lone pair; examples are amines, heterocycles, and azo or nitrito compounds. Small shifts and spin–spin splitting are then obscured, and for lines broader than a few hundred hertz there is an additional problem in FT NMR of magnetoacoustic effects, because of the low working frequency.[18] The pulse sets up eddy currents in the probe ("ringing") which decay at a rate comparable with that of the free induction decay. For the broader lines, therefore, continuous wave (wide line) techniques may be preferable to pulse work for ^{14}N. An alternative is the use of double resonance (INDOR) for ^{14}N coupled to ^{1}H (or ^{19}F, etc.); a precision of ±4 ppm was reported for $^{1}H\{^{14}N\}$ measurements of pyrimidines.[19]

The Relation between ^{14}N Line Width and Electronic Symmetry. The line widths and relaxation times given in Table I are approximate. They are sensitive to experimental conditions such as the viscosity of the sample (which is sensitive to temperature), and the spin–lattice relaxation time T_1 as determined from the line width is underestimated if part of the broadening is due to unresolved spin–spin coupling.

Unexpectedly, the quadrupolar mechanism is found to dominate the relaxation even for solutions of NH_4^+ and NR_4^+, in which we might expect the field gradient at nitrogen to be very small, and as mentioned above, the lines are sharp. All the same, aqueous NH_4^+ shows zero NOE, so dipole–dipole relaxation of nitrogen by protons must be insignificant.[2,13] The Brownian motion of the solvent dipoles provides the necessary fluctuations of the electric field gradient.[13] Thus T_1 ($\simeq T_2$) = T_q (T_q being the quadrupolar relaxation time), and the ^{14}N line width for aqueous ionic solutions is given by eq 1, where μ is the dipole moment of water, r_0 the

$$\Delta\nu_{1/2} = \frac{1}{\pi T_q} = \frac{6}{r_0^5}\left[\frac{\beta e Q \mu}{\hbar}\right]^2 c_{H_2O}\tau_s \qquad (1)$$

minimum distance of water from the ion, c_{H_2O} the concentration of water molecules, and τ_s the correlation time of the ion, assumed short on the NMR time scale.[10,13] β stands for $P(1 - \gamma_\infty)$, where P is the polarizability of the medium and γ_∞ the Sternheimer antishielding factor (equal to about −4 for NH_4^+ in ammonium alum[20]).

For molecular fluids, T_1 ($\simeq T_2$) = T_q as before, and the ^{14}N line width is given by[21-24] eq 2 (again, for τ much

$$\Delta\nu_{1/2} = \frac{1}{\pi T_q} \propto \left(1 + \frac{\eta^2}{3}\right)\left[\frac{e^2qQ}{\hbar}\right]^2 \tau_q \qquad (2)$$

smaller than the inverse of the Larmor frequency). The ^{14}N line width therefore increases as the square of the nuclear quadrupole coupling constant $e^2qQ/\hbar$, as demonstrated for the two nitrogens in N_2O,[25] and may be increased by increase in η, the asymmetry factor of the field gradient tensor q, where η lies between 0 and 1.

The line width is proportional also to the (effective) correlation time τ_q which the tumbling molecule takes to reorient in the magnetic field. The order of magnitude of τ_q is about 10^{-11} s for normal liquids, and this time increases with increase in molecular size and awkwardness of shape, although the effective τ_q may be reduced by internal rotation of a group such as azide or nitrite.

τ_q decreases with increase in temperature and is proportional to the viscosity of the medium, which decreases exponentially with increase in temperature. ^{14}N line widths are relatively small, therefore, if the molecule or ion is small and compact. For larger molecules, sharper lines are obtained by reduction in sample viscosity, as by the use of mobile solvents[22] or of higher temperatures.[22,26] The high mobility of perfluoro compounds, for example, is advantageous in ^{14}N work.

III. ^{15}N Measurements

^{15}N spectroscopy has the intrinsic advantage of high resolution (spin $^1/_2$), but natural abundance work may need the use of a (widebore) superconducting spectrometer for adequate sensitivity, as mentioned above. Enrichment is, of course, necessary for the observation of NN spin–spin coupling, and spectroscopy with 95% of ^{15}N is several times more sensitive than with ^{13}C in natural abundance. In contrast to ^{14}N, however, work with ^{15}N suffers from *long* relaxation times,[6] and a relaxation reagent is usually necessary for reasonable acquisition times for nitrogen without nearby hydrogen, as described below.

A. Relaxation of ^{15}N

Relaxation processes are similar for ^{15}N and ^{13}C in comparable groups (such as NH_2 and CH_2), but the relative contributions differ. Dipole–dipole (dd) relaxation by protons, which is dominant for organic ^{13}C, is about four times slower for ^{15}N. The dd relaxation rate is given by eq 3, where n_H is the number of hy-

$$\frac{1}{T_{1dd}} = \frac{n_H \hbar^2 \gamma_N^2 \gamma_H^2}{r^6}\tau_c \qquad (3)$$

drogens at distance r. The γ^2 dependence gives a 6-fold increase in the dd relaxation rate for ^{13}C relative to ^{15}N which is offset to some extent by the inverse r^6 term, bond distances to nitrogen being somewhat shorter. (The dependence on r^{-6} and on γ^2 for the neighbor magnetic nucleus means that dd relaxation by other nuclei than protons is much less efficient, but is favored by multiple bonding.) Note that the dependence of the dd rate on the relevant correlation time τ_c now gives the advantage (in contrast to ^{14}N work) to larger molecules, since the longer correlation time decreases overlong relaxation times.[11]

^{15}N coupled to ^{14}N, as in NN groups with natural abundance of ^{15}N, experiences also Abragam's "scalar relaxation of the second kind", when the quadrupolar relaxation time for the ^{14}N is short compared with the reciprocal of the $^{14}N^{15}N$ coupling constant J(NN). This form of relaxation is comparable to that produced by chemical exchange.[24]

The low value of γ for ^{15}N means that relaxation mechanisms that do not depend on γ, such as the spin–rotation (sr) interaction, become evident. This mechanism becomes more favorable as the temperature increases. Relaxation by spin-*internal* rotation of ^{15}N is observed in n-butyl nitrite.[27] sr relaxation is dominant for nitromethane,[28] $^{15}N_2$,[29] and aqueous $^{15}NO_3^-$ and $^{15}NO_2^-$ above room temperature.[30] At lower temperatures intermolecular dd interactions (which are disfavored in D_2O since $\gamma_D < \gamma_H$) and the "otherwise elusive"

Table II. ^{15}N Spin-Lattice Relaxation Times at Ambient Temperatures

	T_1/s	T_1/s with relaxation agent	ref
PhCN (l)	~500		28
ND_3 (l)	413		*a*
$Ca(NO_3)_2$ (1:1 w/w in D_2O)	300		30
NH_3 (l)	186		*a*
$Ca(NO_3)_2$ (0.6:1 w/w in H_2O)	180		30
$PhNO_2$ (l)	170		*b*
$NH_4\mathit{NO}_3$ (1:1 w/w in H_2O)	140		30
CH_3CN (l)	90	53, 5×10^{-4} M $[Gd(dpm)_3]$	31
pyridine (l)	85	3.7, 0.05 M $[Cr(acac)_3]$	31
trans-PhNNPh (2.7 M in $CDCl_3$)	56		27
NH_4NO_3 (1:1 w/w in H_2O)	37		30
$NaNO_2$ (0.6:1 w/w in D_2O)	27		30
$(Me_2N)_3PO$ (l)	25		*c*
n-BuONO (l)	24		27
KCN (0.4 M in H_2O)	24		30
$NaNO_2$ (0.6:1 w/w in H_2O)	23		30
$HCONH_2$ (with 10% $(CD_3)_2SO$)	14.5		32
$PhNH_2$ (l)	13	3.0, 0.05 M $[Cr(acac)_3]$	31
N_2 (l, -196 °C)	12		29
$TPPH_2^{2+}$ ($CHCl_3$, CF_3COOH)[d]	1.9		155a

[a] W. M. Litchman and M. Alei, *J. Chem. Phys.*, 56, 5818 (1972). [b] D. Schweitzer and H. W. Spiess, *J. Magn. Reson.*, 16, 243 (1974). [c] W. von Philipsborn. [d] *meso*-Tetraphenylphorphyrin dication (see section VIII D).

shielding anisotropy (sa) mechanism take over.

Multiply bonded nitrogen groupings may be strongly anisotropic, as, for example, triply bonded nitrogen with $\Delta\sigma$ ($= \sigma_{\parallel} - \sigma_{\perp}$) ca. 500–600 ppm (discussed in sections VD and XII). For these groups sa relaxation is favored, since the rate is proportional to the square of the shielding anisotropy $\Delta\sigma$. The rate is proportional also to B_0^2, so sa relaxation becomes more important in higher-field work.

Table II shows some ^{15}N relaxation times observed for purified materials. In practice faster relaxation is observed, due to traces of paramagnetic impurities (such as transition metal ions) to which (basic) nitrogen may be particularly sensitive. A relaxation reagent is usually necessary for nitrogen without attached hydrogen, in smallish molecules, and in the absence of interaction with a protic solvent; $[Cr(acac)_3]$ is commonly used in nonpolar solvents, as it does not cause line broadening.[31] Shift differentials are observed, however, if different concentrations of $[Cr(acac)_3]$ are used in the sample and in a reference material (such as nitromethane) in a coaxial tube. A shift of −1 ppm (i.e., upfield) is observed if the concentration of $[Cr(acac)_3]$ in such reference material is 36 mmol/L greater than in the sample.[44]

B. Spin Polarization Effects in ^{15}N NMR: *Nuclear Overhauser Enhancement*

For ^{15}N wholly relaxed by dd interaction with protons, the maximum signal-to-noise gain (NOE) on proton decoupling is $G_{max} = 1 + \gamma_H/2\gamma_N = -3.93$. This negative enhancement (the signal being inverted) is often achieved for nitrogen with attached hydrogen. Negative signals are sometimes obtained (with proton decoupling) even for nitrogen without directly bonded hydrogen, as noted in sections VIIIB and VIIID. But as G values commonly range between −3.9 and +1, depending on relaxation mechanisms and correlation times, signals may be diminished or nulled. This is a significant hazard in ^{15}N NMR spectroscopy. Larger molecules, because of their longer correlation times, may have a favorably short T_{1dd}, but a correspondingly unfavorable NOE factor.[11] If required, the NOE may be minimized by the use of a relaxation reagent (such as $[Cr(acac)_3]$) or by gated decoupling.[32] On the other hand, the NOE can have useful diagnostic value, as in assigning resonances.

For ^{15}N nuclei spin–spin coupled to protons, special pulse techniques may be used to enhance sensitivity, e.g., INEPT,[33] SPT,[34] cross-polarization.[35] For such nuclei, also, ^{15}N NMR parameters can be measured by pulsed proton NMR spectroscopy by indirect (pseudo-Indor) techniques. The free induction decay is subtracted from the one obtained with irradiation of ^{15}N transitions to give the ^{15}N satellites, off-resonance decoupling yielding the nitrogen shifts.[36]

IV. Scales of Nitrogen Shifts

A common scale is used for ^{14}N and ^{15}N chemical shifts, since isotope effects are relatively small, as discussed below, and many ^{14}N resonances are relatively broad.

A. ^{14}N and ^{15}N Isotope Effects

Detailed studies of primary ("no-bond") isotope effects as between ^{14}N and ^{15}N chemical shifts are lacking, but the differences appear to be negligible for practical purposes,[37] and are expected to be small.[38] Secondary (one-bond) isotope effects are readily observed, however, as in low-abundance ^{15}N studies of molecules with N–N bonds. Because of vibrational anharmonicity, the heavier molecule sits lower in the potential well, so that the average bond length is shorter.[38] This generally corresponds to a stronger bond and to higher shielding, perhaps by a few tenths of 1 ppm,[38,39] as observed for end nitrogen in NNO[40] and nitroso nitrogen in N_2O_3,[41] which has the $ONNO_2$ structure.[42,43] Isotope effects are much smaller for the more symmetrically placed atoms, N*N*O and ON*N*O$_2$. The isotope shift is proportional to the number of ligand atoms isotopically substituted, as observed for ^{15}N in deuterated ammonias. (The coupling constants were unaffected by the isotope substitution.)[45]

B. Nitrogen Referencing; Solvent Effects

Nitrogen may be very susceptible to solvent effects, notably when basic. Downfield shifts of a few ppm are observed for solvents which hydrogen bond to nitrogen (relative to nonpolar solvents) and upfield nitrogen shifts for solvents which hydrogen bond to hydrogen attached to nitrogen.[2,4–6,46] Reproducibility is best served, therefore, by an external standard in a narrow coaxial tube, which may also contain the deuterated locking substance. Susceptibility corrections are usually less than 0.5 ppm. Because of the common scale, a

Table III: Nitrogen Shielding Tensors and Anisotropies[a]

compd	method[b]	σ	σ_{av}	$\sigma_{\parallel}$	$\sigma_{\perp}$	$\Delta\sigma$	ref
NH_3	sr	(264.5)	264.5	237.7	278.0	−40.3	50b
*N*NO	sr	96 (CCl_4)	104	349	−18	367 (36)	189
	sr		105	349	−18	367 (18)	190
	lc			349	−18	367 (10)	106
N*N*O	sr	12 (CCl_4)	20	359	−149	508 (47)	189
	sr		5	364	−174	538 (22)	190
	lc		−37	364	−144	508 (10)	106
ClCN	sr	8 (l)[d]	−306	350[g]	−635	985 (20)	191
CH_3CN	s, dr	−9 (g)	21	346 (8)	−142 (5)	488 (8)	53a
	lc					452 (10)	192
HCN	sr	−8 (l)[e]	−27	348[g]	−215	563 (10)	187
N_2	sr	−60 (g)[f]	−101	335	−319	654 (20)	186
				338[g]			
	s					603 (28)	198
pyridine	s	−74 (l)	−53	−168	395, −387	672 (20)	195
CH_3NC	lc	−118 (l)	130	370	10	360 (73)	193
$PhNO_2$	s	−126 (l)	−134	30	−32, −399	−398	196, 197
NH_4*N*O_3	s, dr	−131 (aq)	−131	9	−188, −214	210 (5)	194
PN	sr		−349	350[g]	−698	1047 (20)	188

[a] The shielding terms are explained in the text. All values are in ppm. [b] sr = spin-rotation (isolated molecule), lc = liquid crystal, s = solid, dr = double resonance. [c] Error limits are those of the original authors. [d] Reference 59. [e] Reference 50a. [f] Reference 141. [g] Reference 185.

nitrogen standard must give a sharp ^{14}N resonance.

Nitrogen referencing is a vexed question, for there is no agreement on a reference standard, or even on sign convention. Many workers use aqueous ammonium[2,14] or nitrate[15,16,46,47] ion, or both together.[32,48] Roberts and co-workers[46] use 1 M $D^{15}NO_3$ in D_2O (at higher nitric acid concentrations NO_3^- exchanges with HNO_3 and NO_2^+ in the equilibrium $HNO_3 + H^+ = H_2O + NO_2^+$). Randall and co-workers[32,48] use 5 M $^{15}NH_4{}^{15}NO_3$ (in 2 M HNO_3) which serves also for phase referencing, with the nitrate signal upright and the ammonium signal inverted by the NOE with proton decoupling. (The acid suppresses exchange between NH_4^+ and H_2O or D_2O.)

The use of liquid nitromethane[4-6] avoids problems of pH and concentration dependence, but many shifts are then negative on the δ sign convention (positive downfield) now adopted for ^1H and ^{13}C. Liquid ammonia has been advocated as high-field standard,[6] but is impractical, not least because the shifts are highly sensitive to impurities and to the nature of the hydrogen bonding, and therefore to temperature, which is seldom known accurately. Me_4N^+ and Et_4N^+ as high-field standards[49] are less subject to medium effects than is NH_4^+, but have not been widely used. Cross-referencing to the proton frequency in Me_4Si finds some support,[2,19,49] as does the use of a deuterium-locking frequency. The δ sign convention is gaining ground, but is not used by Roberts and co-workers[46] or by Witanowski and Webb.[4,5]

Not wishing to raise the height of this tower of Babel, we tabulate nitrogen shifts positive downfield of aqueous NH_4^+ (in 5 M NH_4NO_3/2 M HNO_3) as high-field standard and refer also to liquid $MeNO_2$ (which has δ 358,[6] 359,[5] or 361[46] on this scale; Roberts' nitric acid reference has δ 355[46]). The rationale is the comparison with carbon or oxygen. For carbon, the δ scale gives the shifts positive downfield of Me_4Si, which resonates in the region of CH_4 (δ −13.2), which is the carbon analogue of NH_4^+ in shielding terms. Similarly, ^{17}O shifts are referred to H_2O as high-field standard.

C. Absolute Scale of Nitrogen Shielding

Nitrogen shielding can now be referred to an absolute scale[50a,61] based on the NH_3 sr constants obtained by Kukolich by very high resolution beam maser measurements, which give $\sigma_{av}(N) = 264.5$ ppm for the isolated molecule.[50b] The absolute shielding σ' for nitrogen in other molecules can be derived from its chemical shift (δ) relative to liquid NH_3 at 25 °C by $\sigma' = 246.2 - \delta$, or relative to liquid $MeNO_2$ at 25–30 °C by $\sigma' = -135.8 - \delta$ (etc.).[50a] It is important to specify the state of the molecule, for temperature corrections may be significant, and medium or gas-to-liquid shifts for nitrogen (in contrast to fluorine, for example) may be large and of either sign, dependent on the manner of the hydrogen bonding:[46] thus $\delta(\text{liq}) - \delta(\text{gas}) \simeq 20$ ppm for NH_3 and −12 for HCN.[50a] Such medium effects account for the discrepancies noted[59] between sr values of nuclear shielding and chemical shifts measured in the liquid phase for NH_3 and HCN. (sr values have been reported for N_2 and N_2O also but have larger error limits.)[50a]

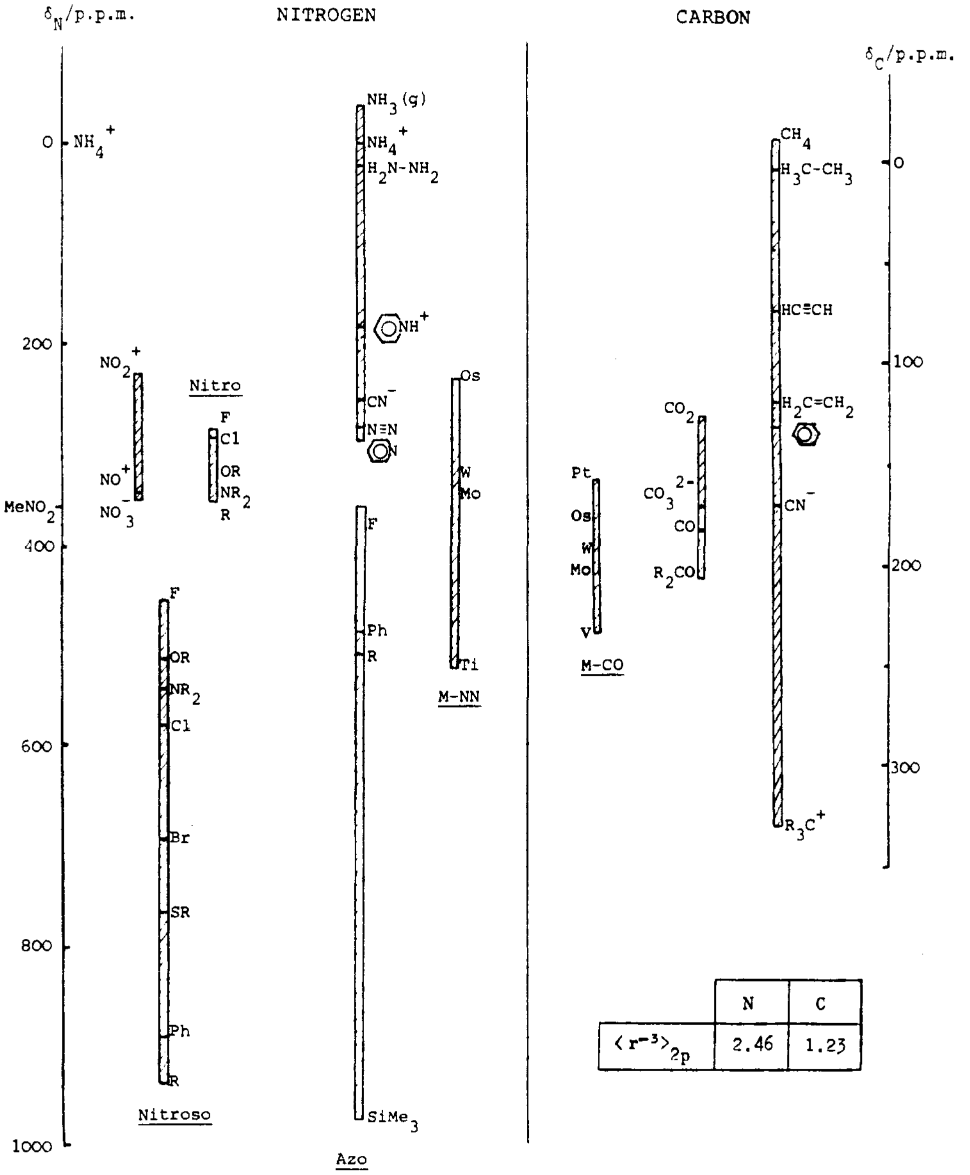
Absolute shieldings so obtained by experiment are of value for comparison with those obtained by quantum mechanical calculations and also for "back-of-envelope" estimates of shifts to be expected from the variation of one or other of the factors which influence the chemical shift. In the "local term" theory the absolute shielding is given approximately by the algebraic sum of the (local) diamagnetic term $\sigma_d{}^A$ ($\simeq$ 325 ppm for nitrogen)[50c] and the paramagnetic term $\sigma_p{}^A$ which is sensitive to electronic structure, as discussed in section V.

V. Patterns of Nitrogen Chemical Shifts

Nuclear magnetic shielding is a periodic phenomenon,[1] and it is useful to compare nitrogen shifts with those of its carbon neighbor, since these are better known. There are strong similarities, and the differences are well accounted for by qualitative shielding theory.

A. Parallelisms of Carbon and Nitrogen Shifts

Figure 1 is a comparison chart. The resonances of NH_4^+ and CH_4 appear at high field, and moving downfield we find H_2NNH_2 and CH_3CH_3, then $N{\equiv}N$ and $HC{\equiv}CH$, azo $-N{=}N-$ and $>C{=}C<$, nitroso $-N{=}O$ and keto $>C{=}O$, and so on; we return to this sequence below. Note the parallelism also between



	N	C
$\langle r^{-3}\rangle_{2p}$	2.46	1.23

Figure 1. Comparison of nitrogen and carbon chemical shifts.

pyridine and benzene and between M–NN and M–CO (dinitrogen and carbonyl ligands). Systematic differences between the two patterns are in the larger range for nitrogen (1100 ppm) than for carbon (400 ppm) for diamagnetic compounds, and the greater deshielding of nitrogen carrying a lone pair.

We mentioned initially that a particular interest of nitrogen chemical shifts compared with those of protons or carbon is that they clearly illustrate a physical model for nuclear magnetic shielding. This is because nitrogen can carry a lone pair, and the strongest deshielding is observed for groups such as azo, nitroso, bent diazenido M–*N*NR (etc.), which have a low-lying n → π* state. The paramagnetic term which dominates chemical shifts in fact expresses the deshielding due to circulations of electrons in the magnetic field between the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied MOs (LUMOs), and the n → π* circulation can be taken as archetype.

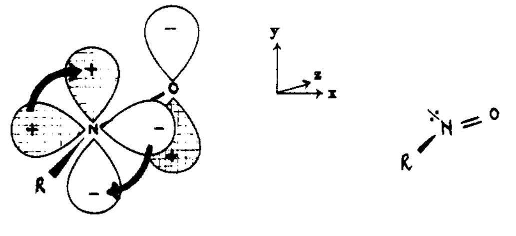


Figure 2. Rotation of charge in an $n_N \rightarrow \pi^*$ excitation, as in the nitroso group. The nitrogen 2s and $2p_x$ electrons have lone-pair character. The nitrogen $2p_x$ orbital (which lies in the RNO plane) is shown horizontal in the diagram, and the NO π_y^* orbital (perpendicular to the RNO plane) is shown as vertical. The arrows show that the n → π* excitation involves rotation of charge ($2p_x \rightarrow 2p_y$). The $2p_x$ electrons also have some σ-bonding character, so the excitation can be written n(σ) → π*.

B. Paramagnetic Circulations

Figure 2 shows that the n → π* excitation, in a nitroso group for example, has $p_x \rightarrow p_y$ character, which means that it involves rotation of charge, a local current around nitrogen. Such virtual excitations are made possible by the polarization of the electrons in the magnetic field. As shown by second-order perturbation theory, the field mixes in with the ground-state excited states in which charge circulates, notably σ ↔ π, which include n → π* states, since nitrogen lone-pair orbitals are normally part of the σ framework. For carbon in delocalized systems the HOMOs commonly have π symmetry, and the excited states important in nuclear magnetic shielding are $\pi \rightarrow \sigma^*$,[50d] as is also the case for metals in complexes, for which the important excited states are d → d (in fact $d\pi \rightarrow d\sigma^*$). Other possibilities for nitrogen are $\pi \rightarrow \pi'^*$ states involving in-plane and out-of-plane π orbitals, as in covalent azides,[50e] or in the absence of π bonds, $n \rightarrow \sigma^*$ states in amines R_3N, or $\sigma \rightarrow \sigma^*$ for four-coordinate nitrogen (R_4N^+), so long as charge circulates from an n or σ orbital into a σ^* orbital pointing in another direction ($\sigma_x \rightarrow \sigma_y^*$).

These excitations are magnetic dipole allowed, but electric dipole forbidden, and therefore optically forbidden. They are observed in electronic spectra if there is vibronic interaction or if there is an associated electric-dipole-allowed excitation, such as the s → p component of an $n_N \rightarrow \pi^*$ transition. (The more familiar $\sigma_x \rightarrow \sigma_x^*$ or $\pi_x \rightarrow \pi_x^*$ excitations, in which charge moves only in linear paths, are electric dipole allowed, giving strong electronic absorption, but are magnetically inactive.[1])

Although our discussion is of diamagnetic compounds, these circulations are "paramagnetic" since their effect is normally to reinforce the applied field. The nitrogen line moves farther downfield the smaller is the (virtual) excitation energy ΔE, which can be envisaged as a frontier orbital separation ΔE(HOMO–LUMO) for rotation of charge in the magnetic field.

C. Qualitative Theory of Nuclear Magnetic Shielding

The approximate ("local term", or "atom in a molecule") theory[51] gives the shielding as the algebraic sum of a diamagnetic (σ_d^A) and a paramagnetic (σ_p^A) term arising from electronic circulations on the observed atom A, plus a third term $\sum \sigma^{AB}$ summing the contributions from the other atoms B. The variation in the diamagnetic term is small for a given element,[50d] and $\sum \sigma^{AB}$ is expected to be small as the "distant" contributions tend to cancel, so the main contributor to the chemical shift is the variation in the paramagnetic term σ_p^A (cf. section IVC). For a second-row element this is given by eq 4, where μ_0 is the permeability of free space,

$$\sigma_p^A = \frac{-\mu_0 \mu_B^2 \langle r^{-3} \rangle_{2p} \sum Q}{2\pi \Delta E} \qquad (4)$$

$\mu_B = e\hbar/2m$ is the Bohr magneton, $\langle r^{-3} \rangle_{2p}$ is the mean inverse cube of the 2p electron radius, the Q terms (obtained from the charge density–bond order matrix) express the imbalance of charge in the valence shell of A, and ΔE is an effective excitation energy. This a a rather drastic approximation of a more rigorous formulation which sums over all excited states with orbital angular momentum but is still confined to currents on the atom A. The (rather inadequate) neighbor anisotropy approximation is used to estimate the shielding contributions from all the other atoms in the molecule.[51] The most rigorous theory, due to Ramsey, uses molecular shielding terms which can only be calculated for very small molecules. In circumstances in which the "atom-in-a-molecule" approach is inadequate (e.g., for heavy atom ligands), an "atom-plus-ligand" approximation has been suggested.[1]

D. Factors Influencing the Chemical Shift

Our present interest is in the physical picture underlying the three terms in the above expression for σ_p^A as they influence the chemical shift. The downfield shift δ is the larger the closer the paramagnetic circulation is to the nucleus (the larger is the radial factor $\langle r^{-3} \rangle_{2p}$), the greater the asymmetry of the valence electrons (the larger is $\sum Q$), and the easier the excitation (the smaller is ΔE); but these three factors are not independent.

The radial factor has been used as a rough scaling factor for the charts in Figure 1. The free atom value of $\langle r^{-3} \rangle_{2p}$ for nitrogen (2.46 au) is double the carbon value (1.23 au),[52] so the scales are plotted in 1:2 ratio. For atoms in molecules various estimates are possible. $\langle r^{-3} \rangle_{2p}$ can be obtained from the atomic charge, as calculated or measured by X-ray photoelectron spectroscopy; with electronegative substituents nitrogen becomes more positive, r decreases, and $\langle r^{-3} \rangle$ and the deshielding increase.

A comparison of the radial factors for similarly bonded carbon and nitrogen, as in the cyano group $-C{\equiv}N$, can be obtained from the shielding anisotropy $\Delta\sigma$ measured for each of the two nuclei. Waugh and co-workers[53a] have determined the values of $\Delta\sigma$ ($= \sigma_\parallel - \sigma_\perp$) for ^{15}N and ^{13}C in solid $CH_3{}^{13}C^{15}N$ as 488 (±3) and 204 (±3) ppm, respectively. As a first approximation we may equate the ΔE and $\sum Q$ terms for the triply bonded atoms, obtaining a ratio of 2.4 for the ^{15}N and ^{13}C radial factors in this molecule. A similar value of $\Delta\sigma$ has been obtained for solid $^{15}N_2$, 500 (±20) ppm. as averaged by zero point motion, or ca. 600 ppm for the static or the gaseous molecule.[53b] Inductive and conjugative effects of the substituents of course affect the energy term also, and this normally dominates, as we shall see in discussions of the "perfluoro effect".

The variation in the $\sum Q$ term accounts in part for the unexpected sequence of the N–N and C–C bond orders, single then triple then double, in Figure 1. The order is that of increasing asymmetry of the nitrogen charge. The value is smallest ($\sum Q \simeq 2$) for nitrogen when saturated (NH_4^+, NH_3, N_2H_4) or triply bonded (N_2, CN^-, XCN, NO^+); cf. the sharper line obtained in ^{14}N resonance for these more "symmetrical" groups. $\sum Q$ increases to ca. 2.5 for doubly bonded nitrogen (C=N, N=N, N=O) and to ca. 2.8 for NO_3^- and XNO_2. These values parallel those demonstrated by Pople for carbon.[51] However, the $\sum Q$ and ΔE terms, also, are closely related. In a (spherical) free atom $\sum Q$ and ΔE and the paramagnetic term vanish (leaving only the diamagnetic shielding term). The ΔE separation tends to decrease as the asymmetry increases, so the $\sum Q$ and $(\Delta E)^{-1}$ terms tend to act in the same direction. Thus qualitative arguments are often based on changes in ΔE, the frontier orbital separation for rotation of charge in the magnetic field.

E. The ΔE Factor in Chemical Shifts: δ/λ Correlations

The patterns of chemical shifts in Figure 1 are well interpreted by variations in effective excitation energy. NH_4^+ resonates at high field in nitrogen resonance (σ_p small) because of the high local symmetry *and* because ΔE is large between the σ and σ^* orbitals; NH_4^+ (like CH_4) absorbs only in the vacuum uv region. There are similar parallels between N_2H_4 and C_2H_6, N_2 and C_2H_2, NO_3^- and CO_3^{2-}, and pyridine and benzene, as discussed below. But there is a larger downfield shift for nitrogen bearing a lone pair. Nitrate ion resonates at medium field (cf. carbonate) because $\sum Q$ and $\langle r^{-3} \rangle$ are large, but azo or nitroso compounds resonate at very low field because $\sum Q$ is large and ΔE is very small, as shown by the colors of these compounds. The major contribution to the chemical shift comes from the deshielding of nitrogen by the ($n \rightarrow \pi^*$) circulation of lone pair electrons in π^* orbitals of the N=N or N=O groups.

Figure 1 shows, indeed, that the nitrogen line moves downfield for nitroso or nitrosyl compounds X—N=O as the $n \rightarrow \pi^*$ band moves to longer wavelength (λ):[43] NOF is colorless, nitrosamines and nitrites are pale yellow, thionitrites red, and *C*-nitroso compounds deep blue. This sequence illustrates the balance of the factors determining the shielding. The NOF line is at highest field, despite the inductive effective of the fluoro substituent which tends to pull in the p electrons, increasing the radial factor and the shift (δ). This inductive effect stabilizes σ *and* π orbitals on nitrogen, but the interaction with π electrons on fluorine destabilizes the NO π^* orbital. Therefore the σ system (which includes the lone-pair orbital) in NOF is stabilized relative to the π^* orbitals, increasing ΔE (relative to RNO, say, where R is alkyl). This is analogous to the "perfluoro effect" observed in electronic and electron spectroscopy for π-bonded systems.[54] Thus the NOF nitrogen line is at relatively high field because ΔE is large, outweighing the increase in the radial term. For the XNO compounds a range of 600 ppm in chemical shift (δ) corresponds to a range of 400 nm in $\lambda(n \rightarrow \pi^*)$, representing $(\Delta E)^{-1}$.

A similar δ/λ correlation is shown by azo compounds (diazenes) XN=NX,[47,55] with FN=NF at highest field: a range of 500 ppm in nitrogen shift corresponds to 400 nm in $\lambda(n \rightarrow \pi^*)$. The shifts also correlate inversely with the lone-pair orbital ionization energy I, determined by photoelectron spectroscopy (PES).[47] In some compounds the lone-pair (n_N) orbital of the resonant nitrogen is not the HOMO for the group, this being a π orbital containing nonbonding electrons on a neighboring atom (in tetrazenes, *N*-nitrosamines, or nitrites, for example). But the lone-pair orbital is nevertheless the frontier orbital for the nitrogen which bears it, since an atom's own electrons are the most important in the shielding.

If we compare groups with $n \rightarrow \pi^*$ states we find that δ and λ both increase in the order (N=C) < (N=N) < (N=O) as the increasing electronegativity of the element doubly bonded to nitrogen lowers the π^* relative to the n_N orbital.[56] Substituent conjugative effects (−R) increase δ and λ when the substituent extends (stabilizes) the π^* orbital. They reduce δ and λ when the substituent (such as N, O, or F) carries lone-pair electrons, raising the π^* orbital (+R). Overall the ΔE term overcomes the radial factor, the constitutive terms being much the same for double-bonded nitrogen.

At very low field are the nitrogen lines for Me_3CNO[56] and $Me_3SiN{=}NSiMe_3$[47] which are deep blue, and $(Me_2SONO)^+$, which is green.[57]

F. Protonation Shifts

It has long been known[8,58] that protonation of π-bonded nitrogen gives a sizeable upfield shift, as shown in Figure 1 for pyridine. This is attributed largely to the increase in ΔE when the n_N electrons are stabilized by forming a σ bond to nitrogen; cf. the disappearance of the $n \rightarrow \pi^*$ band from the UV spectrum. There are similarly large upfield shifts from HCN[59] to $HCNH^+$,[60] and from MeCN to $MeCNH^+$ or MeCNMe.[60] Commonly the protonation shift is the larger the more deshielded the nitrogen.

Protonation of ammonia or saturated amines usually leads to a downfield shift of up to 20 ppm[46] (despite the increase in local symmetry) which may be related to the increase in the radial factor as the molecule becomes positively charged.

These protonation shifts are simple examples of the coordination shifts discussed in section VIII.

VI. Inorganic Azines and Azenes

This section compares inorganic azines, in which nitrogen is nominally singly bonded to a nonmetallic heteroelement, with those in which π bonding is explicit in the formulation, as in $—N{=}PX_3$ or —N=S= azenes. The nominally singly bonded compounds show varying degrees of delocalization of n_N electrons into substituent π orbitals, pπ for boron or carbon, pπ or dπ for silicon, phosphorus, and sulfur. This shading into double-bond character makes it difficult to classify various compounds as azanes or azenes, and we shall confine the latter term to formally doubly bonded groups such as $—PX_2{=}N—$ or $R_2S{=}N—$. Figure 3 shows the ranges of shifts observed for nominally single bonds; the dotted lines continue the range as π delocalization increases, deshielding nitrogen.

A. Periodic Trends

Chemical shifts of all nuclei show a marked periodicity with the substituent, for analogous compounds.[61] Figure 3 shows that the ranges of nitrogen shifts follow the trends that are observed for other nuclei when singly bonded, downfield across the row and upfield down the group of the substituent. Deshielding correlates with increasing electronegativity of the substituent, since this brings down the σ^* HOMO relative to the n_N electrons, reducing $\Delta E(n_N \rightarrow \sigma^*)$. The inductive effect also increases the radial factor, reinforcing the trend. Down the group, with decrease in electronegativity of the substituent and more diffuse orbitals, ΔE tends to increase and the radial factor to decrease, and the line goes upfield. This can (loosely) be called an inductive pattern, although other (periodic) effects are present also when elements from different rows are being compared.[61] Note that for fluorine attached to *saturated* nitrogen the "perfluoro effect" is to *de*shield, in contrast to the effect when nitrogen is multiply bonded (as in NOF, when the combination of (−I) inductive effect and (+R) conjugative effect increases $\Delta E(n \rightarrow \pi^*)$, decreasing δ and λ).

B. Boron–Nitrogen Compounds

A wide range of boron–nitrogen compounds has been studied by Nöth and Wrackmeyer and co-workers in ^{11}B and ^{14}N resonance.[62-69] The highest nitrogen shielding is found in amine–boranes, $R_3N{\cdot}BR'_3$ (R, R′ = H, alkyl),[62] and there is a clear analogy between the coordination shifts from amine to amine–borane and the

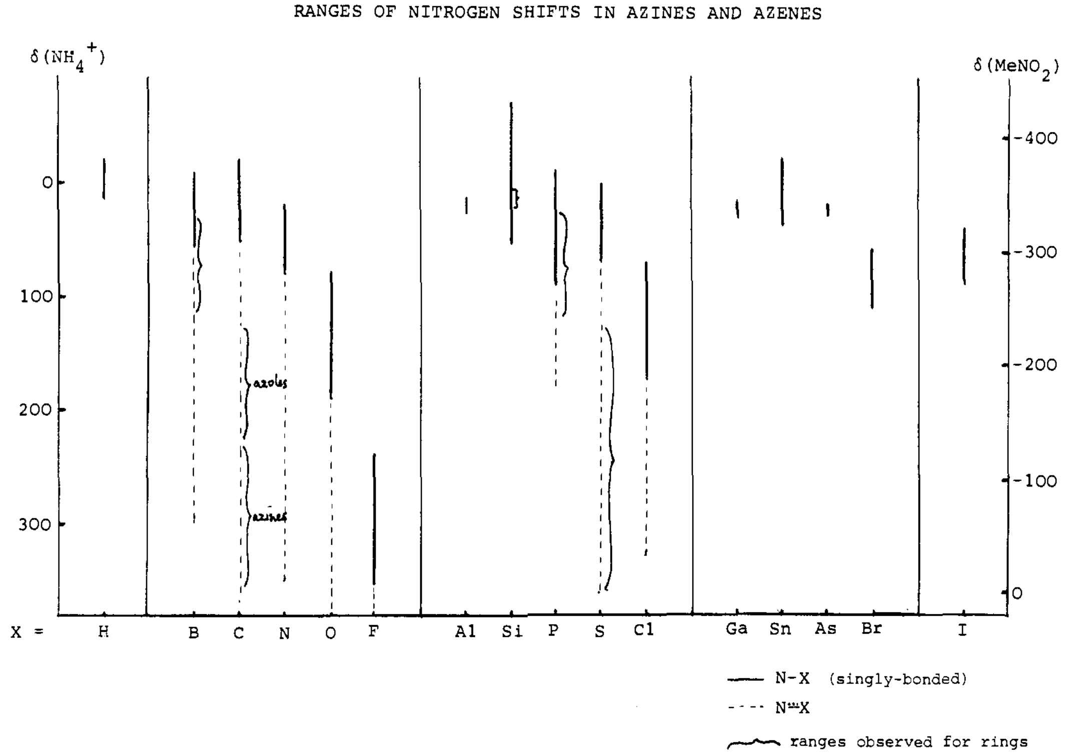


Figure 3. Ranges of nitrogen shifts in azines and some azenes.

protonation shifts discussed above. At lower field, pyridine–borane ^{14}N resonances[65,70] lie between those of pyridine and pyH^+. Nitrile resonances in *p*-$XC_6H_4CN{\cdot}BCl_3$ compounds lie between those of PhCN and $PhCNH^+$,[71] the nitrogen shielding decreasing in the order X = Cl > Me ≳ Br > MeO > H.

In accord with Figure 1, the amine–boranes $R_3N{\cdot}BR'_3$ and the isoelectronic and isosteric alkanes $R_3C{\cdot}CR'_3$ show nearly linear relationships between $\delta(^{14}N)$ or $\delta(^{11}B)$ and the corresponding $\delta(^{13}C)$.[62,63] Similar correlations are found for aminoboranes in which boron and nitrogen are 3-coordinate, and between the nitrogen shifts and those of the isosteric ureas, carbamates, amides, and related compounds.[64,65]

The aminoboranes or borylamines are alkene analogues, to the extent of their $>\bar{B}{=}N^+<$ character. For the fully methylated compounds the nitrogen shielding decreases with increase in the number of borons onto which its non-σ-bonding electrons can delocalize, i.e., $BN_3 > BN_2 > BN > B_2N > B_3N$, from $B(NMe_2)_3$ to $(Me_2B)_3N$, covering a range of 180 ppm.[62,63] This trend to lower field with increase in double-bond character of the nitrogen is a ($-R$) conjugative effect reducing ΔE, opposing the inductive effect (cf. Figure 3) of increased shielding as the substituents become more electronegative.

In the borylamines Me_2NBRX the nitrogen shielding decreases in the order X = NMe_2 ≫ Cl ≳ Me > SMe > Br over a range of 60 ppm, although the substituent is on boron. In the borylhydrazines XRBNMeNMeBRX the nitrogen shielding decreases in the order X = F > Cl ~ Br (a difference of 25 ppm). The nitrogen shift is a useful criterion of planarity, as in the hydrazine derivatives.[66] ^{14}N shifts have been used as a probe of back-bonding from C≡C to boron in $(R_2N)_2BC{\equiv}C$ compounds.[67]

For the cycloborazines $(XBNR)_3$ the nitrogen resonance is in the same region as that of diborylamines such as $(Me_2B)_2NMe$. Very many [^{14}N]borazines have been studied, with substituents R = H, alkyl, Ph, Bz; X = H, alkyl, Ph, C_6F_5, NMe_2, OMe, SMe, halogen, NCO, NCS, and CN. The boron and nitrogen shielding increases with increase in the calculated π-electron density (q_π).[68,72] The X substituents with strong (+R) conjugative effect to raise ΔE (N, O, F) increase the nitrogen shielding (relative to that for X = H, Me, Cl).[68] That the significant variable is ΔE is shown by the upfield shift (47 ppm for ^{14}N) of the ^{11}B and ^{14}N lines of the borazine $(MeBNMe)_3$ when it forms a hexahapto complex with $[Cr(CO)_3]$.[73]

C. Silicon- (and Tin-) Nitrogen Compounds

A large number of silicon–nitrogen compounds have been examined in nitrogen resonance.[74-80] Valiant attempts have been made to disentangle inductive and conjugative ($p\pi$–$d\pi$) effects of a variety of substituents, but such interpretations are difficult because of the complexity of the factors.

For unsubstituted or methylated aminosilanes we again have a balance of substituent effects: the periodic trend of increased nitrogen shielding when silyl replaces H or Me, opposed by the deshielding consequent on n_N delocalization (which is relatively small when only $d\pi$ orbitals are available). The nitrogen is still pyramidal when there is only one silyl substituent, but becomes planar when there are two or three.

In the aminosilanes $Me_{4-n}Si(NMe_2)_n$ the differences in nitrogen shift are small,[74] and the trend is opposite to that for the aminoboranes. Nitrogen shielding increases with silylation, $SiN > SiN_2 > SiN_3 > SiN_4$, over a range of only 8 ppm. The silylamines $(H_3Si)_nNH_{3-n}$ also show this (inductive) trend ($Si_3N > Si_2N > NH_3$), with a range of 30 ppm, as do the silylamino–PF_2 compounds.[77] However the aminoborane pattern is observed for $(Me_3Si)_nNH_{3-n}$, suggesting that the effects of n_N delocalization now dominate: the shielding decreases in the NH series, $NH_3 > SiN > Si_2N > Si_3N$, over a range of 30 ppm, and also in the NMe series, although Me_3N is out of line.[76] In Si–N ring compounds[75] nitrogen is deshielded (by 10–40 ppm) relative to the corresponding Si–N "monomer", but not relative to extended $(Si–N)_n$ chains.

Because of the wide range of $(Me_3Si)_2NX$ compounds (with X = various metals, halogens, etc.)[76] it is likely that an interesting periodicity of the nitrogen shift with substituent X will be observed, if comparable species can be obtained in solution.

Nitrogen in alkyl stannylamines is more shielded than in the silylamines, as shown in Figure 3.[76]

In the tricyclic boratrane,[79] silatrane,[79,80] and stannatrane[81] compounds the transannular bonds from nitrogen to boron, silicon, or tin are usefully studied by nitrogen NMR. Indeed, the ^{15}N shifts are reported to be more sensitive to the coordinative Si←N interaction than the ^{29}Si shifts in silatranes $X\overline{Si(OCH_2CH_2)_3N}$.[80a] With variation of the X substituent on silicon, the nitrogen shielding decreases in the order X = Me > vinyl > Ph > CH_2I > H > CH_2Cl > OEt > $CHCl_2$ > $CH_2NEt_3^+$ > Cl > Br as the coordinative interaction increases (with some steric interaction of larger X substituents with oxygen, strengthening the Si–N bond). In a parallel study the ^{15}N shifts in several of these silatranes were found to correlate with the Taft σ^* constants of the X substituent.[80b] The nitrogen studies clearly confirm that the boron is 4-coordinate and the silicon 5-coordinate, whereas in the stannatranes the tin can become 6-coordinate by trimerization, and intramolecular dynamic processes are observed.[81]

D. Phosphorus–Nitrogen Compounds

Methylated aminophosphines, like the aminosilanes, show mixed patterns.[82] The nitrogen shielding decreases slightly with increasing substitution by phosphorus in the conjugative sequence $PN_3 > PN_2 > P_2N$, but Me_2PNMe_2 is out of order. Halogen substitution of phosphorus deshields both phosphorus and nitrogen, the shielding decreasing as Me > F > Cl > Br in the X_2PNMe_2 compounds.[82,77] In $N(PF_2)_3$ the nitrogen (which is planar) is more strongly deshielded (relative to the (methylamino)phosphines) than the phosphorus is.[83]

In the cyclophosphazenes $(N{=}PX_2)_n$,[84] also, the ranges of nitrogen and phosphorus shifts are comparable for a variety of X substituents (on phosphorus). The ring ^{14}N shielding decreases as X = NMe_2 > OMe ~ F > Cl > Br, which is reminiscent of the sequence for XNO compounds but with conjugative effects accentuated relative to inductive effects of the substituents, which are now one atom removed.[84] ^{15}N measurements on cyclic chloro- and mercaptophosphazenes[85] show that the nitrogen shielding decreases OR > SR > Cl and also that the effects of ring size are small. The nitrogen resonances in $(NPCl_2)_{3-5}$ agree within 11 ppm and vary irregularly. The variation of $^1J(PN)$ from 32 Hz (n = 3) to 2 Hz (n = 5) shows that the conformation (or ring puckering) is variable, as expected from those found in the solids. Indeed, the nitrogen resonances in the cyclophosphazenes lie in the same region as do those of the corresponding open-chain compounds.[82,84]

A series of heterocyclic phosphoramidates $(CH_2)_nN–PO(OMe)_2$ (n = 2–8) has been measured in ^{15}N resonance.[86] The phosphorus is exocyclic, and the main interest in the nitrogen shifts is the high-field resonance typical of 3-membered rings for the aziridine (n = 2) in which the nitrogen is pyramidal, and the downfield shift with ring enlargement as the nitrogen becomes planar (sp^2) with concomitant increase in coupling constant $J(PN)$, a correlation noted again in section VIIIC.

Can the nitrogen chemical shifts contribute to the perennial discussion of how "aromatic" are the inorganic heterocycles? This is an interesting question, since each physical method probes aromaticity in its own way. Clearly, nitrogen is deshielded with increasing opportunity for π delocalization of n_N electrons onto a boron, silicon, or phosphorus ligand, and this conjugative effect (lowering ΔE) can be distinguished from opposing conjugative effects (of nitrogen, oxygen, or fluorine substituents raising ΔE) and from inductive effects whether the substituents are attached to nitrogen or to the ligand. Again, there are parallel changes in the one-bond coupling constant as the nitrogen lone pair electrons are increasingly used in π bonding.

Delocalization, though necessary, is not a sufficient criterion for aromaticity. Nitrogen shielding in cycloborazines, -silazanes, and -phosphazenes is similar to that in the corresponding open-chain compounds, but this is not an argument against calling the ring compounds aromatic, since the ^{13}C shielding in benzene (which is determined by the σ–π HOMO–LUMO separations) closely resembles that observed for doubly bonded carbon in cyclohexene!

For nitrogen bearing a lone pair, a reasonable comparison, as a criterion of aromaticity, is with the aromatic heterocycle *sym*-triazine (δ 263),[87] in which nitrogen is deshielded by $n \rightarrow \pi^*$ circulations using the aromatic π^* orbitals, due allowance being made for inductive (and conjugative) effects on the other ring atoms. The rather high shielding observed for nitrogen in phosphazenes or silazanes does not match this criterion of aromaticity. This conclusion accords with other physical evidence against classifying these compounds as aromatic, such as the absence of lower energy $n_N \rightarrow \pi^*$ absorption. In the phosphazenes, this lack is attributed to stabilization of the n_N electrons relative to the π^* orbital by in-plane $p\pi$–$d\pi$ delocalization and by the electronegative substituents in the ring and on phosphorus (the relatively large ΔE being consistent with the relatively high-field nitrogen resonance).[84]

E. Sulfur–Nitrogen Compounds

There is a great variety of thiazenes, and some are clearly aromatic.[88] The comparison is facilitated by the similarity in electronegativity of sulfur and carbon, the Pauling scale showing 2.5 for each, as against 3.0 for nitrogen. The nitrogen resonances cover a range of 500 ppm,[89–98] or 800 ppm if thionitrites XSNO are included.[43] Characteristic regions are observed for singly bonded S–N compounds at high field and for open-chain and cyclic thiazenes at medium field, with higher bond orders in between (Figure 3). Singly bonded compounds include sulfenamides ($R_2N–S–X$),[89] sulfonamides,[91] and cyclic sulfurimides (S–NMe–S, etc.).[92] For doubly bonded nitrogen the shielding decreases

$XN{=}SX_2 \sim XN{=}CX_2 > XN{=}NX$, with increasing electronegativity of the atom doubly bonded to nitrogen decreasing $\Delta E(n_N \rightarrow \pi^*)$. Within the thiazene series $XN{=}SX_2$ the nitrogen shielding increases as the ligands on sulfur become more electronegative, increasing the polarity of the SN bond and the delocalization of n_N electrons onto the SX_2 group; thus $XN{=}SF_2$ nitrogen lines are at fairly high field, just below the single-bond region, because of the $XN^+{\equiv}SF_2$ character. Increased nitrogen shielding may then run parallel with shortening of the SN bond and widening of the XNS angle.[91]

Overall, the nitrogen shielding in SN groups resembles that in corresponding CN groups, but not (of course) if the shape at nitrogen is different. Thus sulfinylamines C–NSO[89,90] and diimides $XS{=}N{=}SX$[91,93] resonate at medium field, well downfield of cyanates XNCO and carbodiimides $RN{=}C{=}NR$, since the sulfur compounds are bent at nitrogen.

We mentioned above the comparison with the nitrogen shift in *s*-triazine as a criterion of aromaticity for inorganic heterocycles. Indeed, many cyclothiazenes resonate downfield of *s*-triazine, including isothiazole, 2,1,3-thiadiazoles[91,93] and the ring cation $S_4N_3^+$. As shown in the first inorganic application of ^{15}N NMR,[94] $S_4N_3^+$ resonates 100 ppm downfield of *s*-triazine. The $S_4N_3^+$ ring is flat, and aromatic by other criteria, being a 10π-electron system.[68] Nitrogen in the cage molecule S_4N_4 is more shielded by 250 ppm,[95] although deshielded relative to singly bonded S–N. Other ring, cage, and open-chain thiazenes have nitrogen shifts between these extremes,[96-98] and with the variety of S–N species now being characterized it is likely that interesting correlations will emerge.

In contrast to the simple chromophores (such as XNO) described above and in common with organic polyaza heterocycles, the thiazenes do not show clear δ/λ relationships. In the thiazenes, this is because prominent bands in the UV–visible spectra are due to excitations that are not relevant to the nitrogen shielding either because they are magnetic dipole forbidden (e.g., $\pi \rightarrow \pi^*$) or because the charge circulation is closer to sulfur than to nitrogen, using sulfur electrons *or* LUMOs mainly on sulfur.

F. N–N, N–O, and N–Halogen Compounds

Nitrogen in hydrazines ($R_2N{-}NR_2$, R = H, alkyl) resonates at rather high field,[99,100] as shown in Figure 4. In hydrazine derivatives with R = Ph, F, etc., the deshielding follows the order observed in ammonia derivatives, $NH_3 > MeNH_2 > PhNH_2 > NF_3$.[101-104] As expected, hydrazine derivatives with planar nitrogen, such as borylhydrazines,[66] or the hydrazido(2–) ligand in metal complexes (section VIIC) resonate at lower field than hydrazines ($R_2N{-}NH_2$) in which nitrogen is pyramidal.

Figure 3 shows the range of nitrogen shifts, slightly downfield of ammonia and amines, for singly bonded N–O as in hydroxylamines or amine oxides, R_3NO. π-bonded nitrogen, however, becomes more shielded on N-oxidation (as on protonation), as from N_2 to N_2O,[105,106] azo to azoxy to bisnitroso (azodioxy),[56] nitrile to nitrile oxide[107] or fulminate,[108] pyridine to the *N*-oxide,[8] NO^+ to NO_2^+,[43,57,109] NO_2^- to NO_3^-, RONO to $RONO_2$,[109] N_2O_3 to N_2O_4 (and to N_2O_5),[41,43,103] hyponitrile($^-ONNO^-$) to nitrohydroxamate ($^-ONNO_2^-$),[41,55] and also NF_3 to ONF_3.[101-104] In NF_3 both HOMO and LUMO are combinations of "lone-pair" orbitals. (ONF_3 is a rather unusual "amine oxide", with a very strong NO bond.) In these compounds (in contrast to the amine oxides) the increase in ΔE and in the local symmetry with N-oxidation, which increases the shielding, outweighs the effect of the increase in radial factor as the nitrogen becomes more positive.

N-halogen bonds are rather uncommon, and few nitrogen shifts have been published.[76] Monochloramines R_2NCl resonate at high field,[4] then (slightly downfield) $RNCl_2$,[44,76] with quinonoid chlorimine compounds ($>C{=}NCl$) at medium field.[44] In each category the tendency is for the nitrogen shielding to increase down the group of the halogen substituent, although there are exceptions to this as in $(Me_3Si)_2NX$ compounds (X = Cl, Br, I)[76] with a minimum at X = Br, and similarly for the *N*-halosuccinimides.[44] NF_3 is close to NO_3^- in chemical shift,[101-104] slightly upfield of $FN{=}NF$ (cis and trans)[102] and downfield of $C{=}NCl$ compounds.

VII. Ranges of Nitrogen Shifts in Functional Groups

In section VIII we shall be comparing nitrogen shifts in coordinated ligands with those in corresponding functional groups in organic and organometallic compounds. Figure 4 is a bar chart for such functional groups. The horizontal lines span the resonances so far observed, and the asterisks mark those of related inorganic species; note that the differences between them are small.

The correlation with ΔE(HOMO–LUMO) is again evident. The highest shielding is found in the amines, for which the radial factor is small, the local symmetry fairly high, and ΔE large. The n_N HOMO is stable since the "lone-pair" electrons have σ-bonding character, and the σ^*(NH) LUMO is relatively high in energy. The lowest energy electronic absorption ($n(\sigma) \rightarrow \sigma^*$) is in the far-ultraviolet region.[110] As described above, protonation or N-oxidation commonly shifts the line downfield somewhat.

Ambidentate Groups. Nitrogen shows fairly high shielding in the linear groups with cumulated double bonds, $N{=}C{=}N$,[111] $N{=}C{=}O$,[90,112] etc.; in this as in other respects they resemble triply bonded groups such as $C{\equiv}N$.[105] In the ambidentate groups cyanate NCO[90,112] and thiocyanate NCS[90,113,114] the nitrogen shielding in the anion increases with N-alkylation[90,112-114] (stabilizing the n_N electrons relative to the π^* orbital) and decreases with O- or S-alkylation[112-114] (stabilizing the π^* relative to the n_N orbital); the nitrogen shifts are well-known as a criterion of the mode of linkage.[112-114]

Nitrogen in cyanides RCN and isocyanides RNC is shielded relative to the free anion CN^-, and is further shielded on protonation of the cyanide to $RCNH^+$,[61] or on N-oxidation to RCNO,[107] as mentioned above. Müller's measurements of azides[115-117] with triple enrichment of ^{15}N has shown that NNN resembles NCO and NCS as ambidentate groups, since the resonance of the terminal nitrogen in azide ion generally moves upfield for N_α in RN_3 (R = H, alkyl, aryl . . .)[50e,115] but downfield for N_γ. The central nitrogen (N_β) resonance stays in much the same place. The shielding usually

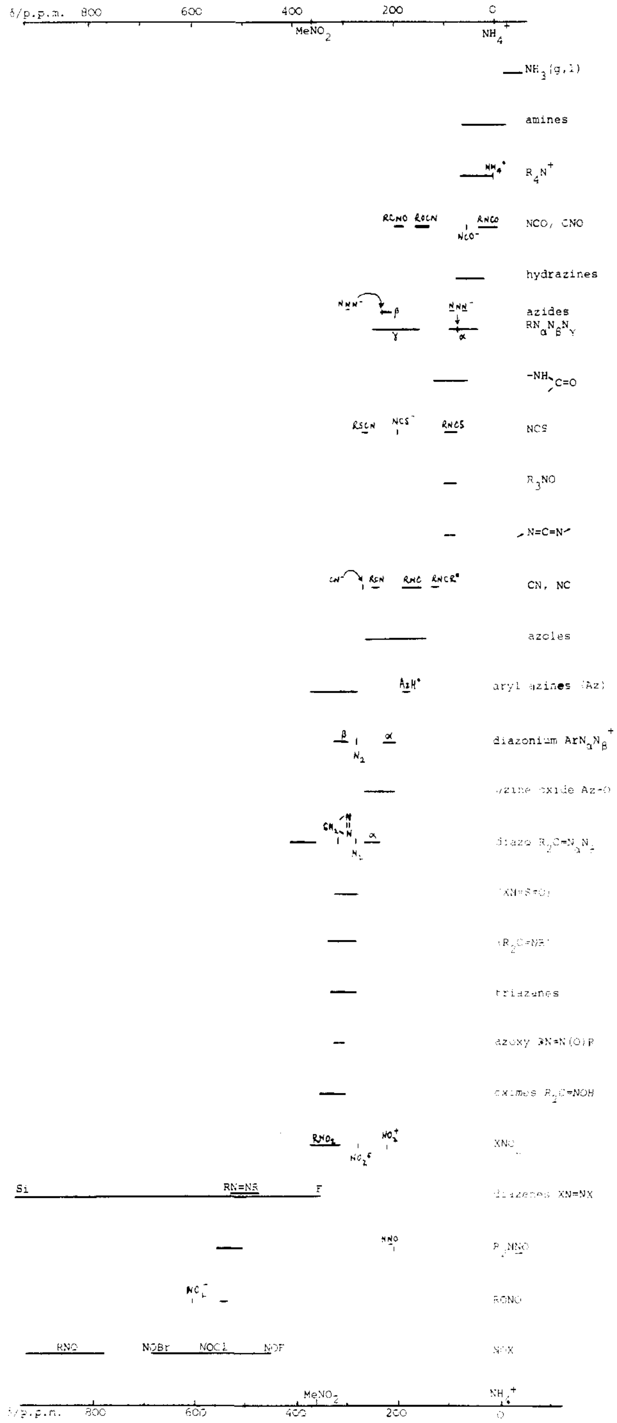


Figure 4. Ranges of nitrogen shifts in functional groups.

decreases $N_\alpha > N_\gamma > N_\beta$, but the β and γ lines are often close together, and they just cross over for azides XN_3 with X = Cl,[117] CN, *sym*-trinitrophenyl,[115] *p*-toluenesulfonyl (Ts),[118] or halopyridyl.[50e] Remarkably, diazonium compounds ($ArNN^+$)[118a,119] follow the ambidentate pattern, with N_α more shielded and N_β less shielded than in the free N_2 molecule,[120,141] and even the diazo group $R_2C{=}NN$ largely does so.[118a-d]

Dramatic deshielding by about 250 ppm is observed for N_α and N_β in the triazene anion $TsNNNTs^-$ compared with azide ion;[121a] cf. other triazenes.[121] This is no doubt associated with bending at each conjugated nitrogen. We shall see many more examples of the remarkable electronic lability of NNN and NN groups in organometallic and complex compounds.

NO_2 is an ambidentate group with a large difference in nitrogen shift consequent on geometrical differences for the two modes of linkage. Nitro compounds RNO_2 resonate at medium field (with NO_3^-), and nitrites RONO with bent 2-coordinate nitrogen some 200 ppm downfield. Olah and co-workers report that ^{15}N in $(Me_2SONO)^+$ is deshielded by 360 ppm compared with $(Me_2SNO_2)^+$.[57]

VIII. Coordination Shifts in Metal Complexes

A. General Principles

A coordination shift is the difference in chemical shift for a ligand atom in a coordination complex and in the free ligand. (A protonation shift is thus a special case.) The coordination shift is not necessarily larger or largest for the ligating atom, as can be seen in Figure 5, which is a bar chart for nitrogen-containing ligands. The horizontal lines span the shifts in simple complexes of the metals cited, whereas the asterisks mark the nitrogen shift for the free ligand or related species.

Experimentally, coordination shifts (of any ligating atom) are found to correlate with the symmetry of the complex, with trans influences, and with properties of the metal such as the d electron configuration, oxidation number, and periodicity. Comonly the shielding increases across the row and down the group of a transition metal. In the discussion which follows we shall try to isolate the contributing factors as far as possible, with the protonation (or alkylation) shift as point of reference.[1]

As mentioned earlier, the largest deshielding contribution comes from electric circulations that are largely on the resonant atom. Currents partly on a neighbor make a smaller contribution, for example, circulations on a ligating atom which use unoccupied d orbitals on the metal. Such contributions increase with decrease in the ligand field splitting. Circulations largely on a neighbor atom, such as $d\pi^* \rightarrow d\sigma^*$ circulations on the metal, make a smaller contribution, which falls off with distance as R^{-3}, and may shield or deshield a ligand atom. Circulations in d orbitals are possible also for transition or post-transition metals with d^{10} configurations, with s–d orbital mixing making room in the d shell. For $d^{10}s^2$ configurations, s–p mixing may allow p_x–p_y circulations, and so on.[1]

An interesting generalization from Figure 5 is that most coordination shifts are relatively small, a few tens of ppm. This can be understood in terms of fairly weak bonds being formed, and by the stabilization on coordination of both HOMO and LUMO for the resonant atom, so that the effective ΔE is not greatly changed. There are strong parallelisms therefore between the shielding sequence of ligands in Figure 5 and that of the corresponding functional groups in Figure 4, this sequence being related to inductive and conjugative effects as they influence ΔE. As discussed in the following sections, highest nitrogen shielding is observed for ammine and amine ligands, followed by nitrogen singly bonded to the metal in linear groups (NCO^-, N_3^-, NCS^-, NCR) or triply bonded to carbon (RCN and RNC). Fairly high shielding is shown also by hetaryl ligands and porphines, and unexpectedly by "interstitial" nitrogen in cobalt and rhodium carbonyl clusters. Hydrazido (2−) $M{=}N{-}NR_2$, "linear" diazenido $M{-}N{=}$

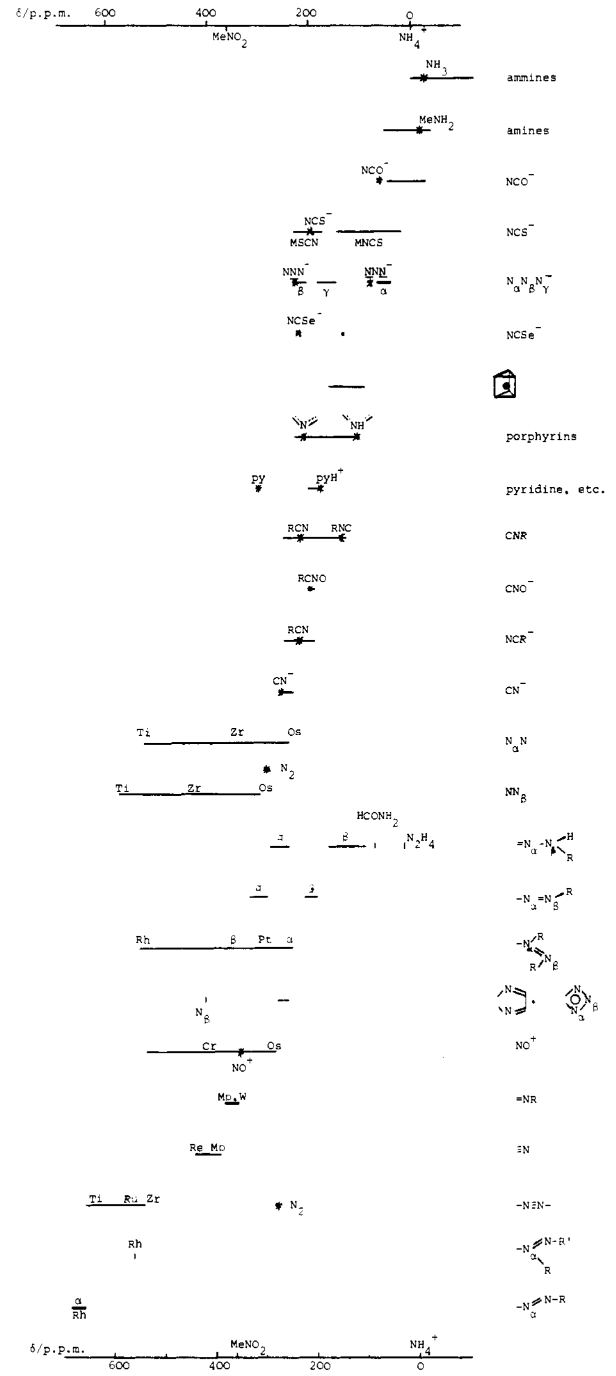


Figure 5. Nitrogen coordination shifts in metal complexes.

NR, M—N=O, M=NMe, and M≡N groups resonate at medium field, but dinitrogen M—NN groups resonate over a remarkably large range from medium to low field. At lowest field are bridging dinitrogen and α-bent diazenido ligands. A dramatic downfield shift of about 350 ppm accompanies bending at N_α in the diazenido ligand (with introduction of a low-lying $n \rightarrow \pi^*$ state), so the nitrogen shift is a useful criterion of the geometry of this and related groups.

B. Ammine and Amine Complexes

Although the protonation shift for ammonia is downfield (section VF), upfield coordination shifts have been observed for the (rather few) ammine complexes studied so far. This ligand is a good σ donor and poor $d\pi$ acceptor; Chatt, Ducanson, and Venanzi have suggested that there may be some degree of intramolecular hydrogen bonding, or negative hyperconjugation, in ammine complexes, with $N-H^{\delta+}$ (σ^*) as acceptor of $d\pi$ electronic charge.[122]

^{14}N shifts have been reported for d^6 ammine complexes of Co(III),[8,123] Ru(II), and Rh(III),[123] and ^{15}N shifts for Co(III)[124,125] and Pt(II) d^8.[126] Coordination shifts are 20–60 ppm upfield of the gaseous ligand, which resonates some 20 ppm upfield of aqueous or liquid NH_3.[127,128] (The large gas-to-liquid shift is related to the increase in hydrogen bonding.) Trans influences of up to 30 ppm are observed for cobalt hexaammine relative to pentaammines $[CoX(NH_3)_5]^{n+}$, the shielding of nitrogen trans to the X-ligand decreasing in the sequence $HSO_4^- \sim NO_3^- \sim H_2O > Cl^- > Br^- > NH_3 > NO_2^-$.[124,125] The sequence is consistent with nitrogen being deshielded when a weaker trans ligand is replaced by a stronger, weakening the metal-ammine bond (cf. section IVA). The effects of cis substitution are relatively small.[124,125] In cis-diammine platinum(II) complexes the coordination shifts are 45–65 ppm upfield of the gaseous ligand, and again there is a trans influence of about +20 ppm on substitution of trans H_2O by amine nitrogen.[126]

For the amine complexes measured so far the coordination shifts are largely downfield (positive) for closed-shell metal ions and upfield (negative) for d^6 and d^8 metal ions. The protonation shifts of the amines are usually downfield.[46,127,128] Nitrogen shifts have been reported for edta^{4-},[129] cydta^{4-} (*trans*-1,2-diaminocyclohexane-*N*,*N*,*N'N'*-tetraacetate),[130] and cyclam[130] (1,4,8,11-tetraazacyclotetradecane) complexes of closed shell metal ions and for complexes of Co(III),[131,132] Rh(III),[133] Pd(II),[134] and Pt(II).[126,134] For the first and second protonation of edta^{4-} the nitrogen line goes downfield by 5 and 17 ppm, and the coordination shifts are comparable to this: small and upfield for Li and Na, small and downfield for the metals of groups 2A and 2B. Interestingly, the line goes downfield down the group of the closed-shell metal ions, upfield across the row for the lighter metals, but downfield across the row for the heavier metals (Ba(II) to Hg(II)).[129] This behavior is matched by the complexes of cydta^{4-} with Ag(I), Cd(II), Hg(II), and Pb(II), the line going downfield (by a few ppm) down the group and across the row; similar results were obtained for cyclam complexes of Cd(II), Hg(II), and Pb(II).[130] As we shall see, opposite periodic trends are observed for transition-metal complexes. An unexpected observation on the cydta complexes is of a near-maximal nuclear Overhauser enhancement of the ^{15}N resonance, despite the absence of protons directly bound to nitrogen.[130]

Upfield coordination shifts of 0–45 ppm are reported for amine complexes of transition metals, all of which come from the right of the transition series: −30 to −40 ppm for tris(glycinato) complexes of Co(III) relative to the free glycinate anion, compared with protonation shifts of about −10 ppm.[131] Similarly, coordination shifts of −25 to −40 ppm are observed for tris(alkyldiamine) complexes of Rh(III),[133] and 0 to −33 ppm for the *n*-hexylamine ligand (NH_2R) in square-planar Pd(II) and Pt(II) complexes *trans*-$[MCl_2(NH_2R)L]$.[134] A trans influence of the ligand L is evident, the nitrogen shielding decreasing in the order L = $NH_2R \gg AsR_3 > PR_3$ for M = Pd, and L = $NH_2R > Cl \gg AsR_3 > C_2H_4 > PR_3$ for M = Pt. There is a linear relation between the nitrogen shifts for corresponding compounds of the two metals, but no upfield or downfield trend down the group (from Pd to Pt), just an expansion of the range. There is some correlation between the ^{15}N and ^{195}Pt shifts.[134] Similar coordination shifts (−30 to −45 ppm) are observed for $[Pt(en)L_2]^{2+}$ complexes, the replacement of H_2O as trans ligand by the stronger ligand 1-methylimidazole producing a downfield shift of 15 ppm.[126]

C. Linear Nitrogen Ligands

Linear triatomic ligands such as NCO^-, NCS^-, NNN^-, and CNO^- were discussed as ambidentate functional groups in section VIIA. They show similar shielding relationships in metal complexes, as a comparison of Figures 4 and 5 demonstrates. The nitrogen shielding is relatively high in the free anionic ligand and increases for ligating nitrogen, but coordination shifts for central or terminal nitrogen are relatively small and of either sign. ^{14}N shifts have been reported for cyanate N-bonded to Ag, Zn, Hg, Si, Ge, Sn, and P,[112] for thiocyanate N-bonded to Ru, Ni, Pt, Zn, and Cd[113] and Zn, Cd, and Sn,[114] for thiocyanate S-bonded to Rh, Ir, Pd, and Pt[113] and Hg,[113,114] and for selenocyanate Se-bonded to Sn.[114] ^{15}N shifts are now reported for thiocyanate N-bonded to Pt, Zn, and Cd, and S-bonded to Pd, Pt, and Hg,[135a] and contact shifts have been studied for thiocyanate complexes of a range of trivalent lanthanide ions.[135b]

Müller has measured ^{15}N shifts for azide bonded to metals and semimetals. Those of silicon[115] and phosphorus[116] resemble the organic azides discussed above. Although bent at the α nitrogen, the conjugated group (the NNN chromophore) is linear. The N_α resonance is at relatively high field, in contrast to that of bent conjugated nitrogen in diazenes and related compounds. The compounds of arsenic, Me_2AsN_3,[136] and tin, Me_3SnH_3,[137] exchange azido groups in solution, as do the trimeric azides of aluminium and gallium, $(Me_2MN_3)_3$,[136] via azide bridges. The trimers are aza heterocycles, with N_α of the azido groups bridging two Al or Ga to form six-membered rings.[136]

Terminal nitrogen in groups such as –SCN, –SeCN, or –NNN resonates slightly upfield of the region observed for cyano groups, for which coordination shifts of +(15–40) ppm have been observed in a variety of complexes: linear $[Au(CN)_2]^-$ and $[Hg(CN)_2]$, $[M(CN)_4]^{2-}$ both square planar (M = Ni, Pd, Pt) and tetrahedral (M = Zn, Cd), octahedral $[Os(CN)_6]^{4-}$ and $[Co(CN)_6]^{3-}$,[123] and $[Fe(CN)_6]^{4-}$, $[Co(CN)_6]^{3-}$, and $[Cr(CN)_5NO]^{2-}$;[8] cf. also ref 12. Similar ^{14}N shielding has been reported for the central nitrogen in the fulminato group –CNO (bound to Ni, Pd, Ag, Hg).[108]

As mentioned in section II, high-resolution ^{14}N work is possible with linear groups such as M—C≡N—R, M—N≡C—R, or imido M═N—R (R = H, alkyl), with measurement of small $^2J(NH)$ coupling contants, because the electronic symmetry around nitrogen is high, apparently, and the lines sharp. As Figure 5 shows, the nitrogen shielding in RNC and RCN ligands resembles that for M–CN, as reported for MCNR with R = *t*-Bu and M = Pd,[14] R = Me and M = Pd, Pt, Au,[15] R = H, Me, *n*-Hex, aryl, and M = Cr, Mo, W, Mn, Fe, Co, Ni, Cu, Au,[17] and for MNCR with R = Me, Ph, C_6F_5 and M = Cr, Mn, Pd, Pt.[17]

Imido-nitrogen resonances are down at medium field. For the W(VI) alkylimido complexes *trans*-$[WF_4({=}NMe)L]^{n-}$, small coupling constants ($^2J(NH) \sim 3$ Hz) have been resolved in spin-tickling experiments, and a trans influence has been observed, the ^{14}N shielding decreasing in the order $L = OMe^- > F^- \gg P(OMe)_3 > EtOAc \gtrsim (MeO)_2SO \gg MeCN$, over a range of 26 ppm. (Doubly bonded oxygen is the ligating atom in $(MeO)_2MeP{=}O$ and $(MeO)_2S{=}O$.) The electric field gradient around nitrogen in the W═NR group increases in the order R = Me < Et < *n*-Bu, and with replacement of trans fluoride by OMe^- in *trans*-$[WF_4(NMe)L]$.[16] A few ppm downfield of the (alkylimido)tungsten fluoride range is the (^{15}N) resonance of the imido complex *trans*-$[MoCl(NH)dppe_2]$ Cl (dppe = $Ph_2PCH_2CH_2PPh_2$), and just downfield of this, a range of about 50 ppm spanned by nitrido complexes (M≡N) of molybdenum and rhenium.[138,142]

The hydrazido(2−) ligand[139] has a linear M═N—N skeleton, and the range of N_α shifts is slightly upfield of the M═NR range (Figure 5) for the octahedral complexes of molybdenum and tungsten so far studied: highly ^{15}N-enriched *trans*-$[MF(NNH_2)dppe_2]BF_4$, $[MCl(NNH_2)(C_5H_5N)(PMe_2Ph)_3]Cl$, and $[M(NNH_2)(8\text{-quin})(PMe_2Ph)_3]Cl$ (8-quin = quinolin-8-olate). The N–H spin–spin splitting identifies the N_β resonance, which is at relatively high field; it is somewhat downfield of the region observed for hydrazines with pyramidal nitrogen,[99] no doubt because the NH_2 group is near-planar in M═N—NH_2, as in amides, and indeed the chemical shifts and coupling constants observed for β nitrogen in the hydrazido ligand resemble those for amides rather than those for organic hydrazines. The planarity allows deshielding (as also of carbon in amides) by $\pi \leftrightarrow \sigma$ circulations which are of lower energy than the $n(\sigma) \rightarrow \sigma^*$ circulations in pyramidal hydrazine groups. Replacement of hydrogen by alkyl on N_β leads to fairly small downfield shifts, as in organic molecules.

A remarkable range of absorption, of 300 ppm from medium to low field, has been reported for the dinitrogen ligand (the MNN group being linear). This range may be attributed to the electronic lability of the MNN group and also to the extent to which the transition-metal series have been covered, from Ti and Zr to Re, Fe, Os, and Rh (and perhaps to the range of coligands). Bercaw and co-workers[140] have used ^{15}N NMR to study binuclear complexes $[\{(\eta^5\text{-}C_5Me_5)_2MN_2\}_2N_2]$ (M = Ti, Zr), with a linear dinitrogen bridge M—N≡N—M giving a low-field singlet, and a terminal dinitrogen group $MN_\alpha N_\beta$ on each M giving two doublets. The chemical shifts are incorporated in Figure 5, with the provisional assignment of N_α as more shielded than N_β. The complexes are fluxional in solution, as shown by ^1H and ^{15}N variable-temperature studies, with site exchange of the $(C_5Me_5)^-$ ligands, coupled with a faster exchange of the terminal N_2 ligands with free dissolved N_2. Activation parameters E_a = 11 kcal mol^{-1} and $\Delta S^\ddagger = +10$ eu derived from the ^{15}N measurements seem to be related to the dissociation of a terminal N_2 ligand as rate-determining step in the fluxional process.[140]

The measurement of highly ^{15}N-enriched complexes $[M(N_2)_2L_4]$ of molybdenum and tungsten with mono- or bis(tertiary phosphine) ligands (L or L_2, respectively) has enabled tentative assignments of the N_α and N_β

resonances to be made.[141] The higher field signal is provisionally assigned to N_α by comparison of the observed coupling constants with those for related compounds (such as carbonyl complexes or organic diazo compounds) and on the basis of the expected diminution of the P–N spin-spin coupling constants with increase in the number of intervening bonds. (The well-known contraexamples in organic compounds, of which pyridine is the most notorious, appear to have special explanations which do not apply to the M–NN group.)[141]

Evidence which may perhaps support the assignment of the N_α and N_β resonances has now been obtained from observations on $AlMe_3$ adducts such as *trans*-$[ReCl(NNAlMe_3)(PMe_2Ph)_4]$.[142] On coordination of $AlMe_3$ to N_β of the dinitrogen ligand the N_α resonance shifts very slightly downfield, but the N_β resonance moves upfield by ca. 70 ppm, as expected for stabilization of the "lone-pair" electrons in forming a bond to aluminum. The inductive effect is likely to lower the LUMO also, but to a lesser extent, for N_β. The N_β shifts in the $AlMe_3$ adduct are comparable to those in the quasi-linear diazenido ligands described in the next section.

Recent work has extended the series to (mainly octahedral) dinitrogen complexes of rhenium, iron, and osmium, and (square planar) rhodium, in which the nitrogen is more shielded than in the complexes of molybdenum and tungsten.[119a,134,142] Indeed, the N_α resonance tends to move upfield across the row of the transition series and down the group,[142] and similarly for the hydrazido(2–) nitrogen and for ^{19}F and ^{31}P resonances, in analogous complexes.[139] A similar periodicity is observed in ^{13}C resonance for the carbonyl ligand,[143] which is isoelectronic with dinitrogen. By analysis of the ^{13}C shielding tensor in CO, $[Fe(CO)_5]$, and $[Ni(CO)]_4$, the upfield shift of the ^{13}C resonance across the row has been related to the decrease in π-back-bonding (through the reduction in the perpendicular component of the paramagnetic term, estimated from *sr* constants derived from *sr* and *sa* relaxation times).[144]

Some trans influences can be discerned. For the dinitrogen ligand the N_α and N_β shielding decreases, for a trans ligand L, in the order L = Br > Cl and L = N_2 > tertiary phosphine. This is consistent with reduced π back-bonding when there is a stronger trans ligand: the M–N bond weakens, but the N–N bond strengthens with reduced delocalization into the π^* orbital. This correlates with an observed increase in stretching frequency $\nu(NN)$; in general it is found that $\nu(NN)$ and the deshielding of N_α increase together. For the hydrazido(2–) ligand the N_α shielding decreases, for a *trans*-ligating atom L, in the order L = F > Cl > O.[139]

The square-planar complex $[RhCl(N_2)(P\text{-}i\text{-}Pr_3)_2]$ was measured in ^{15}N resonance to confirm that the N_2 ligand is bound end-on (η^1) in solution as in the solid[145] and correct an earlier claim that the N_2 ligand is coordinated side-on (η^2) to the transition metal.[146a] As yet this geometry has been demonstrated only in compounds in which there is also some "end-on" interaction of the dinitrogen with alkali metals.[146b]

Curiously, for the 15 or so dinitrogen complexes so far measured, as the N_α shielding decreases, so the ^1J(NN) coupling constant tends to increase in absolute magnitude, and the color changes from white to yellow to orange to red to blue-purple. (For spin–spin coupling the relevant ΔE refers to s orbitals and triplet states, whereas for nuclear magnetic shielding ΔE refers to p, d, f, ... orbitals and singlet states.)

Bridging dinitrogen has been measured in ^{15}N resonance for the titanium and zirconium complexes described above[140] and also for $[\{Ru(NH_3)_5\}_2N_2]^{4+}$.[142] This nitrogen resonates at very low field, for a linear group (as shown in Figure 5), consistent with extensive delocalization.

Reduction of the dinitrogen ligand is of considerable interest to studies of nitrogen fixation, as discussed in section X.

D. Bent Nitrogen Ligands

The diazenido ligand ($-N_\alpha{=}N_\beta-R$) may be singly bent (at N_β)[147] or doubly bent (at N_α and N_β).[148] Nitrogen NMR is a useful criterion of the geometry because of the dramatic downfield shift of about 350 ppm that is associated with bending at N_α.[149]

In highly ^{15}N-enriched complexes *trans*-$[MX(NNR)dppe_2]$ (M = Mo, W; X = Br, Cl; R = Et, COMe) in which the diazenido ligand is linear at N_α, the N_α and N_β resonances are somewhat downfield of the corresponding reasonances in the alkylhydrazido(2–) groups M=N—NHR (M = Mo, W, and R = Et) that were mentioned in the previous section;[138] cf. Figure 5. Indeed the alkylhydrazido(2–) ligand is the N_β-protonated form of the "singly bent" diazenido ligand, which might thus be termed "quasi-linear" since the conjugated group, or chromophore, is linear.

As expected, there is an upfield protonation shift from MNNEt to MNNHEt, of about 65 ppm,[149] which may be compared with the –150 ppm observed for the protonation of azobenzene.[150]

When the diazenido ligand is bent at N_α, as in the 5-coordinate complexes $[RhCl_2(NNC_6H_4\text{-}R\text{-}4)(PPh_3)_2]$ (R = H, NO_2), the N_α resonance is 350 ppm downfield of that in the quasi-linear ligand and 180 ppm downfield of that of azobenzene. There is an upfield "protonation" shift of 127 ppm from $[RhCl_2(NNC_6H_4NO_2\text{-}4)(PPh_3)_2]$ to $[RhCl_3(NHNC_6H_4NO_2\text{-}4)(PPh_3)_2]$.[149]

Reflecting our observation in section VIIIA that "coordination shifts are relatively small", if we take aryldiazonium compounds[118] $ArNN^+$ to represent the free quasi-linear diazenido ligand, we find that the terminal nitrogen resonates in the same region as diazenido N_α (or a few ppm upfield) and the nitrogen bonded to carbon resonates in the same region as the diazenido N_β.

The diazenido complexes illustrate the electronic versatility of the -NN- group, for the resonances so far measured cover a range of 500 ppm (which becomes 600 ppm if hydrazido complexes are included); cf. 600 ppm for diazenes from FN=NF to $Me_3SiN{=}NSiMe_3$.

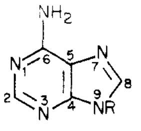
As noted above for complexes of cydta^{4-},[130] the β-nitrogen resonance in the quasi-linear diazenido complexes unexpectedly shows a sizeable NOE, although this nitrogen carries no directly bonded protons.[149] The bidentate diazabutadiene ligand (dab) in the complex $[Mo(CO)_4dab]$ shows a ^{15}N resonance slightly upfield of that for quasi-linear Mo—N=NR, as expected on replacement of N_β by the less electronegative carbon.[151]

A similar chemical shift is observed for chelating nitrogen in the phenylmercury derivative of diphenyltriazene, PhNHN=NPh (for which the coordination shift is -100 ppm). The bent central nitrogen resonates 166 ppm downfield.[121c] It will be interesting to compare these values for a four-membered ring with those for analogous five-membered rings when more results are available.

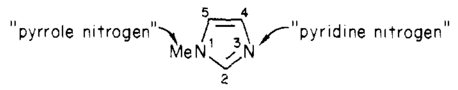
E. Azaaromatic Ligands and Porphyrins

The rather few studies by nitrogen NMR spectroscopy of azaheterocycles bound to metals have been prompted by the biological interest.

Early experiments with 70% ^{15}N-enrichment demonstrated that Mg^{2+} does not complex with nitrogen in adenosine triphosphate (ATP), although Zn^{2+} does.[152]



adenine ring in ATP



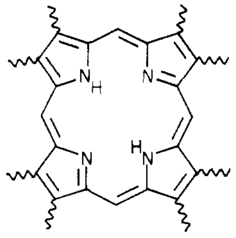
1-methylimidazole (MeIm)

The five nitrogen resonances were found to be little changed by the addition of equimolar $MgCl_2$ at pH 9.5, but substitution of $ZnCl_2$ produced small low-field shifts in the N-9 and 6-NH_2 resonances (of 1.5 and 2.6 ppm, respectively) and a shift of 3 ppm to higher field at N-7. These shifts suggest chelation of Zn^{2+} to NH_2 and N-7, analogous to the chelation of Mg^{2+} by glycine.[152a]

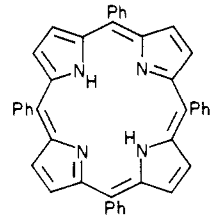
More recently the interaction of fully ^{15}N-labeled imidazole (Im) with aqueous Zn^{2+} has been examined,[152b] with reference to Zn(II) enzymes in which the metal is held by imidazole groups in histidine residues. The ^{15}N shifts were interpreted by equilibria involving $[ZnIm_m(H_2O)_n]^{2+}$ species with $m = 1$–4, and possibly $m = 5$ or 6 at higher ratios of imidazole to zinc, probably with $m + n \simeq 6$. Coordination to zinc is accompanied by upfield shifts of 10–20 ppm relative to neutral aqueous imidazole (for which a single nitrogen resonance is observed because of rapid exchange, self-association being small); cf. +30 ppm shifts for protonation at N-3 in acid and -20 ppm shifts for deprotonation at N-1 in alkaline solution. A similar study with aqueous Cd^{2+} showed smaller coordination shifts (8–12 ppm) and no evidence for $m > 4$.[152c] The authors estimated that a proton with a molecular weight of 50 000, containing fully ^{15}N-labeled histidine, could be studied in the same way with a widebore high-field spectrometer.[152b]

Interest in *cis*-diammineplatinum(II) complexes[126] arises from the antitumor activity of *cis*-dichlorodiammineplatinum(II) (DPP). This is known to inhibit DNA synthesis, perhaps by diffusing through the cell membrane as a neutral molecule and then exchanging H_2O for Cl^- to form a dication which attacks basic nitrogen sites of purine or pyrimidine bases in the nucleic acid chain. Nitrogen NMR (with 100% ^{15}N labeling) was found to be a sensitive probe of interactions between *cis*-diammineplatinum(II)(2+) species and 1-methylimidazole (MeIm) nitrogen, coordination shifts of -90 to -120 ppm being observed.[126] The shifts for the NH_3 and en ligands were described in section VIIIB and trans influences noted. For the MeIm ligand, similar relationships were observed. The resonance of the pyridine-type nitrogen goes downfield with increase in ligand field strength of the trans ligand L in the order $L = H_2O > NH_3 \gtrsim$ en over a range of 30 ppm, consistent with weakening of the Pt-imidazole bond by the stronger trans ligand. Parallel changes are observed in the ^{15}N–^{195}Pt coupling constants.

Beginning with the work of Boxer, Closs, and Katz on chlorophyll *a*,[153] some interesting and important results are emerging from the study of highly ^{15}N-enriched porphyrins and their metalloderivatives. The free bases derive from the porphine nucleus and commonly have substituents (shown as tails) on the eight β carbons of the pyrrole rings. Octaethylporphyrin (OEP) is a model compound of this type, and *meso*-tetraphenylporphyrin (TPP) a related model compound. Earlier studies have used proton and carbon NMR spectroscopy, but nitrogen is of course nearer the active site of the prosthetic group.



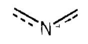
porphine nucleus



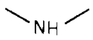
meso-tetraphenylporphyrin (TPP)

Diamagnetic molecules in which porphine nitrogen has been studied now include chlorophyll *a* and its magnesium-free derivative pheophytin *a*;[153] the free bases protoporphyrin IX dimethyl ester and coproporphyrin III tetramethyl ester and their (diprotonated) dications;[154] *meso*-tetraphenylporphyrin (TPP), the dication, and the zinc derivative,[155a] also with various pyridines as axial ligands;[155b] the TPP free base at low temperatures,[156] the cadmium derivative,[157] and iron derivtives;[158] octaethylprophyrin (OEP), the free base, the dication and *N*-methyl compounds, and metalloderivatives (magnesium, iron, cobalt, nickel, zinc, cadmium),[159,161] some with axial ligands;[161] and uroporphyrinogen (uro'gen) in studies of the biosynthesis of porphyrins.[162]

At low temperatures, typically -50 to -80 °C, the free bases show two resonances: a singlet for the "pyridine nitrogen"



and a doublet for the "pyrrole nitrogen"



with a coupling constant ^1J(NH) similar to that in pyrrole itself, -96.5 Hz.[34,163] The "pyridine nitrogen" resonates in the same region as hydrogen-bonded pyridine, about 70 ppm upfield of neat pyridine. The "pyrrole nitrogen" has no n → π^* state (since the nitrogen electron pair which is not involved in σ bonding forms part of the π system) and resonates some 100 ppm upfield of the pyridine nitrogen, 5–20 ppm upfield of neat pyrrole.[152,153,156,159] The dications in CF_3COOH

solution show four pyrrole-type resonances.[154,155a,160]

In the free bases at room temperature there is tautomeric averaging not only of the nitrogen chemical shift but of the NH coupling constant. Under favorable conditions a quintet is observed in proton resonance with ^1J(NH) (ca. 2.4 Hz) one-quarter of the pyrrole value, showing that the dominant exchange process is intramolecular and involves all four nitrogens.[154,156,160] Although exchange broadening can make the nitrogen resonance difficiult to observe,[154] a triplet has been obtained in the ^{15}N resonance at higher temperatures.[160] The free energy of activation is about 50 kJ mol^{-1} at ambient temperatures.[154,156] The NH tautomerism is less symmetrical when the porphine nucleus is less symmetrical, as in pheophytin *a*.[153]

The nitrogen resonances of the metallo derivatives mostly lie between the pyridine or pyrrole-type regions observed for the corresponding free base, as shown in Figure 5. The downfield shift of ca. 60 ppm for pyrrolic nitrogen when pheophytin *a* chelates magnesium to form chlorophyll *a* can be ascribed to anion formation, destabilizing the electron pair previously used to bond hydrogen; similarly, the upfield shift of ca. 40 ppm for the pyridine nitrogen is as expected for stabilization of the "lone pair" electrons by the semipolar bond. The perturbation of the π^* level on complexation seems to be small, since the main red band in the visible spectrum of pheophytin *a*, due to the first $\pi \rightarrow \pi^*$ transition, is blue-shifted by only 5 nm in chlorophyll. ESCA and redox potential measurements are consistent with this picture of charge redistribution on formation of the magnesium chelate, tending to even out the charge density as between the four rings.[153]

In the metalloporphyrins the relaxation of the proton-free ^{15}N may be very slow, making direct observation of the spectrum less useful than the INDOR technique using the methine protons, for which ^3J(NH) $\sim$ 5 Hz.[160,161] A further hazard in the measurement of these compounds is paramagnetic broadening, with the readily oxidizable Fe^{II} species, for example.[158,160]

The chemical shfits measured so far suggest that a very interesting spectrochemical series of the metals will emerge, as more results become available, since metalloporphyrin derivatives are known for almost all metals (other than beryllium and the alkali metals). In OEP complexes the nitrogen shielding decreases in the following sequence (axial ligands, where present, being given in parentheses): $M = Co^{III}(Br^-,py) \gtrsim Ni^{II} \gg Fe^{II}(py_2) > Mg^{II} \sim Zn^{II} > Cd^{II}$, over a range of 190 ppm,[159-161] and in TPP complexes, in the sequence M = Zn > Fe, and Zn > Cd.[155,157,158] Similar nitrogen shifts are observed for the zinc complexes with OEP and with TPP and for the Mg–OEP complex and the nitrogens in chlorophyll *a* (except for the one in the reduced ring IV). In the nickel and cobalt complexes the nitrogen resonance is upfield even of the pyrrole value; cf. the upfield coordination shift of ca. 50 ppm in cobalt(III) amines. The coordination shifts in the OEP complexes have been related to the excitation energies observed in the electronic spectra, and there may be correlations also with M–N bond strengths and stretching frequencies.[160]

In the diamagnetic TPP complexes so far measured the nitrogen shift is not very sensitive to the presence or nature of axial ligands. In Zn–TPP with substituted pyridines as axial ligands the nitrogen line goes downfield with increase in electron donation by the substituent (and increase in stability constant), but the range is only 2.25 ppm.[155b] The range is slightly greater for Fe^{II}–TPP,[158] with cis-inductive effects of axial amine ligands (increased basicity tending to deshield the porphyrin nitrogen). In Fe^{II}–OEP(LL′) the nitrogen shielding decreases in the order L,L′ = py,CO > py,-NCC$_8$H$_{17}$ > py, py, over a range of 40 ppm, indicating π-type ligand bonding.[161]

As the pioneering work on chlorophyll demonstrated,[153] ^{15}N NMR spectroscopy can be a powerful adjunct to the variety of physical methods which aid our understanding of bioinorganic processes such as photosynthesis. One can foresee its extension, as technical problems are overcome, to related metalloporphyrin groups as in the electron-transfer proteins (cytochromes, oxidases, catalases) and oxygen-carrying proteins (hemoglobin, myoglobin) with iron as central metal, to vitamin B$_{12}$ (containing cobalt), and so on. It is equally applicable to the study of nitrogen in axial ligands, which determine the spin state and stereochemistry, notably the coordination number of the metal and its position relative to the porphine plane. ^{15}N shifts in the paramagnetic compounds, also, may be quite sensitive to the various influences on the binding of a ligand, such as cis and trans influences and solvent effects. Work on iron-bound C^{15}N$^-$ in paramagnetic heme derivatives and hemoproteins is described in section IX.

The recent work on the enzymatic conversion of porphobilinogen to uro'gen is no doubt a foretaste of mechanistic studies to come. ^{15}N NMR spectroscopy is being actively applied to amino acids, peptides, and proteins,[6] but such "organic" work has not been covered in this review.

F. Nitrogen–Oxygen Ligands

Earlier ^{14}N studies of nitrosyl, nitro, and nitrato ligands were reviewed in 1973,[3] and ^{15}N measurements are few. For linear nitrosyls, the free ligand is the NO$^+$ ion, which resonates close to NO$_3^-$ and MeNO$_2$.[43,57] Positive and negative coordination shifts of a few tens of ppm have been reported for M–^{14}NO in tetrahedral and octahedral carbonyl and halide complexes of iron, cobalt,[108,123] and ruthenium.[3,123] The range has now been extended downfield with ^{15}N measurements of η^5-cyclopentadienylnitrosyl "piano-stool" complexes of chromium, molybdenum, and tungsten;[164] cf. the low-field resonances of the cyclopentadienyldinitrogen complexes of titanium and zirconium described in section VIII. Whereas nitrosyls of metals to the right of the transition series resonate in the region of NO$^+$, the [(cp)M(CO)$_2$NO] lines are some 50 ppm downfield, between those of NO$^+$ and NOF, and the dinitrosyl [(cp)M(NO)$_2$Cl] lines 150 ppm further downfield,[164] between those of NOF and NOCl. As noted above for protonation shifts, the spread of chemical shifts for a particular group seems to increase the more deshielded the nitrogen.

The N-bonded nitro ligand (in M–NO$_2$) is expected to resonate at medium field in the region of MeNO$_2$ and NO$_3^-$ rather than at low field with nitrite ion in which nitrogen carries a lone pair. Such medium-field resonances were reported[123] for square-planar [M(NO$_2$)$_4$]$^{2-}$ (M = Pd, Pt) and octahedral [Co(NO$_2$)$_6$]$^{3-}$; but this report is corrected, at least for the cobalt complex, by recent ^{14}N work[165] which demonstrates that the reported resonance is due to nitrate formed by the oxidation of dissociated nitrite ion by Co^{III} in the aqueous solution. Broad resonances were observed for the free nitrite, showing exchange averaging and paramagnetic shifts due to interaction with the Co^{II} species. This apparently catalyzes exchange with the Co^{III} complex, with electron transfer.[165]

^{14}N NMR may be useful for the study of nitrates since they give sharp lines, although these are somewhat broadened on covalent bonding to form $XONO_2$. Nitrato complexes of various metals (Al, Ga, Ce, Th, U, Ti, V, Cr, Ru, Co, Au, Zn, Cd, Hg, and Sn) were found[166] to span a range of 25 ppm upfield of nitrate ion. Because the linkage is through oxygen, the shifts are relatively small. The distinction between mono- and bidentate linkage was not possible in ^{14}N resonance[166] but should be possible in ^{15}N resonance, as for covalent carbonates studied by ^{13}C NMR spectroscopy.

Slightly upfield of the range observed for the metallic nitrates is the range for covalent nitrates of nonmetals, the nitrogen shielding tending to increase with increase in electronegativity of the substituent X, as $X = \text{alkyl} < Cl < O_2N < CH_3CO$.[166,109] This may be contrasted with the order observed for covalent nitryl compounds XNO_2, in which there are also conjugative effects of the X substituent, so that the nitrogen shielding increases as $X = ON < O^-$ (i.e., NO_3^-) $< \text{alkyl} < O_2N < H_2N < Ph < Cl < Me_2N < CF_3 < F$.[109] NO_2^+, which is linear, resonates some 125 ppm upfield of NO_3^-,[57,109] and the fast exchange of these two species produces an averaged signal to 100% HNO_3. This is a useful solvent for the nitrato complexes, the ^{14}N study showing nitrate exchange to be absent or very slow.[166]

G. Interstitial Nitrogen

An interesting recent development in coordination chemistry in which NMR spectroscopy can play a key role is the characterization of "interstitial" atoms inside a metal cage in a cluster complex.[167] These structures are studied by X-ray crystallography and vibrational spectroscopy, but the NMR method, in responding only to a given nucleus, is needed for problems such as locating protons, or distinguishing interstitial carbon or nitrogen in a molecule with carbonyl and perhaps nitrosyl ligands and also for studying dynamic processes and solute structures.

So far ^{1}H, ^{13}C, ^{103}Rh, and now ^{31}P, ^{14}N, and ^{15}N NMR spectroscopy have been used to characterize these species when encapsulated. ^{103}Rh within a rhodium cage is strongly deshielded, as in some Rh^{III} species, whereas the cage atoms have upfield resonances more characteristic of Rh^{I}, some even with higher field resonances resembling that of the metal itself.[168,169] Interstitial ^{31}P in rhodium clusters produces the farthest downfield resonances yet observed for this element,[170] but interstitial protons have been observed with high[168] or low[171] shielding.

The carbides so far measured resonate in the low-field region characteristic of carbonium ions R_3C^+ and rhodium carbene complexes: in $[M_6(CO)_{15}C]^{2-}$ anions, which have trigonal-prismatic cages of cobalt or rhodium, the carbide shifts are δ 330 and 265 ppm, respectively.[172] Low-field resonances were therefore expected for the isostructural nitride complexes $[M_6(CO)_{15}N]^-$, but in the event these were found at relatively high field, with $\delta(NH_4^+)$ 176 and 87 ppm, respectively, for the cobalt and rhodium cages.[173] Thus the familiar upfield shift down the group of the transition metal is observed for the carbide and for the nitride resonances. The covalent radius of nitrogen within the cobalt cage, as determined by X-ray crystallography, shows the expected decrease with respect to the radius of interstitial carbide in the isostructural Rh_6C anion.[173]

In the Rh_6 anion the ^{15}N signal showed coupling to six rhodiums, with $^{1}J(Rh^{15}N) = 6.1$ Hz, the reduced coupling constant agreeing with that obtained for the isoelectronic carbide.[172] This coupling constant is rather small, e.g., in comparison with $^{1}J(Rh^{15}N) \simeq 30$ Hz for rhodium dinitrogen complexes, and this may indicate a low s character of the nitrogen bonds, which might be expected.

No structure due to spin–spin coupling was resolved in the ^{14}N or ^{15}N resonances of the cobalt cluster complexes (^{59}Co being quadrupolar) or in the ^{14}N resonance of the rhodium cluster complex. Interestingly, the line widths with unresolved coupling are rather similar in ^{14}N and ^{15}N resonance. Conceivably, similar relaxation mechanisms might be operative, as the high local symmetry makes quadupolar relaxation less favorable, but as recorded in section IIA, this mechanism is dominant even in NH_4^+ in solution, and ^{103}Rh has a very small magnetogyric ratio, about 3% of that of the proton.

IX. Paramagnetic Systems

Under favorable conditions nitrogen NMR can be usefully applied to the study of structure and dynamics in paramagnetic systems, whether the unpaired electron spin is associated with metallic or nonmetallic centres. The resonances are usually broadened by the rather efficient relaxation, but large shifts may compensate for this. Theoretical interpretation is difficult, and interpretation by chemical intuition has its hazards, but chemists have not been deterred unduly by this. The topic has been reviewed in depth[174-176] and with reference to nitrogen NMR studies.[3,5,174,175] A good deal of work has been concerned with weaker interactions, such as solvation and ion-pairing, and with kinetic studies, e.g., of ligand exchange.

NMR shifts in paramagnetic systems, which may[175] (or may not[174]) be called Knight shifts, or (confusingly) isotropic shifts, are expressed relative to the shift in a comparable diamagnetic species. The paramagnetic shift is usually the algebraic sum of two different contributions, both arising from the interaction of the resonant nucleus with unpaired electron spin. *Contact* shifts arise from the Fermi contact (hyperfine, or scalar) interaction of the nucleus with unpaired spin density in s orbitals centered on it. This spin density is transmitted to the resonant nucleus from the paramagnetic center through σ or π bonds, delocalized systems naturally being the more efficient. *Dipolar* or pseudocontact shifts arise from a through-space interaction with magnetically anisotropic spin density (i.e., in p, d, ... orbitals) and may be estimated by a familiar "neighbor anisotropy" formulation, using the anisotropy of the ESR *g* value. Either contribution, contact or dipolar, may have either sign.

Thus the theoretical basis is quite different from that of chemical shifts in diamagnetic systems, which arise from residual, or second-order, paramagnetism, due to the unquenching of orbital angular momentum in the magnetic field. This has a small direct temperature dependence (and is present in paramagnetic molecules also). Paramagnetic (Knight) shifts have a stronger and inverse temperature dependence.

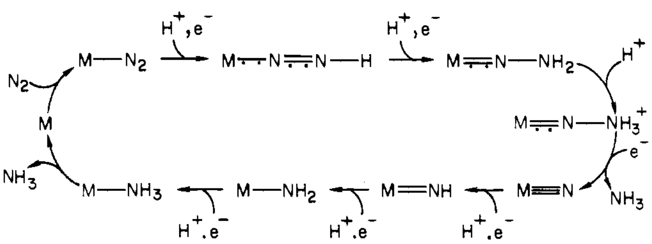
The separation of contact and dipolar contributions to paramagnetic shifts is often difficult, but if it is possible, the contact shift can give interesting information on spin transfer from the paramagnetic center via π and/or σ bonds. Such analyses of spin distribution have been reviewed for η^5-cyclopentadienyl, η^6-arene, and other organometallic compounds[174] and similarly for porphyrins.[177] Several nitrogen donor ligands attached to paramagnetic metal ions have been studied in ^{14}N resonance. For pyridine, shifts of +15.4 ppt (i.e., parts per thousand) were observed on coordination to (octahedral) nickel-d^8 (cf. 12–13 ppt for en ligand); the ^1H, ^{13}C, and ^{14}N contact shifts were used to map the sign density distribution.[178]

Shifts of up to 1 ppt have been observed for ^{14}N in the cyano ligand in Cr, Mn, Fe, Co, and Ni complexes, with concomitant shifts of −2.6 to −8.3 ppt in carbon resonance. The differences in sign and magnitude of the paramagnetic shifts demonstrate the differences in contact interaction, with negative spin density on carbon, the ligating atom, and positive spin density on nitrogen.[12,174]

^{14}N NMR spectroscopy has been used as evidence[135b] in the disputed question of the inner- or outer-sphere character of thiocyanate N-bonded to trivalent lanthanide ions in aqueous solution (as used in group separations of lanthanides and actinides). Shifts of up to −8000 ppm or so were recorded, and across the lanthanide series were found to be maximal at Gd (f^7), changing sign for Pr and Nd (Ce and Lu were not included). The carbon shifts follow the nitrogen shifts, but are an order of magnitude smaller. The nitrogen shifts, and to a lesser extent the carbon shifts, appear to be dominated by the contact interaction. (Gd^{3+} can form magnetically isotropic complexes in which the paramagnetic shifts are wholly due to the contact interaction.) Thus there are negative spin densities in the nitrogen and carbon 2s orbitals (in contrast to the cyano ligand), the carbon value being 10% of the nitrogen value. The nitrogen spin densities are smaller by an order of magnitude than those reported for thiocyanate N-bonded to Co^{II},[179] but comparable to those observed (in ^{17}O studies) for H_2O coordinated to the same lanthanides.

A recent study[180] which demonstrates the potentiality of the method has used ^{15}N-labeled cyanide as a probe to study the effects of ligands bound axially to Fe^{III} in paramagnetic porphyrin derivatives and hemoproteins such as myoglobins and cytochrome *c*. ^{15}N paramagnetic shifts of 500 to 1200 ppm were observed (relative to free cyanide ion, or to diamagnetic $[Fe(CN)_6]^{4-}$), comparable to that of the paramagnetic $[Fe(CN)_6]^{3-}$. These shifts are very sensitive to solvent, but not to substitutions of the porphyrin peripheral groups, which are cis effects. Rather similar shifts, of about 850 ppm, were observed for various hemins with two axial cyano ligands in solution in Me_2SO, but the addition of protic solvents such as methanol shifts the nitrogen line upfield by 200 ppm. Shifts of this magnitude, which contrast with much smaller solvent shifts of the peripheral groups, imply a significant reduction in the *g* value anisotropy plus a decrease in spin transfer from iron to nitrogen, due to the weakening of the axial ligand field and reduction in σ basicity of the ligand consequent on hydrogen bonding from the solvent to the coordinated cyano nitrogen.[180]

Scheme I



Sizeable trans effects were observed, a large downfield shift of cyano nitrogen resulting from the replacement of the other cyano ligand by pyridine. The nitrogen line goes downfield markedly with increasing basicity of the trans ligand, in contrast to the very small cis effect shown by the corresponding monocyanopyridine complexes. It follows that the downfield nitrogen shift from cytochrome *c* to myoglobin cyanides may result from the change in the effective strength of proximal histidine binding to the heme iron rather than from the cis effects of structural changes in the heme peripheral groups. The change in ^{15}N shift with variation in pH of cyanomyoglobin may indicate hydrogen bonding between distal histidine and heme-bound cyanide; and so on. Thus heme ligand–apoprotein interactions, also, may be studied in this way.[180]

X. Nitrogen Fixation

The chemistry of nitrogen fixation[181] is complicated and slow to yield to chemical investigation, but it is likely that nitrogen NMR spectroscopy will play a significant part. On present thinking, molecular nitrogen may be bound in the nitrogenase enzyme at a molybdenum center, perhaps with sulfur coligators, and reduced in an anhydrous pocket, the necessary redox processes being mediated by ferredoxins. Related to the problem of nitrogen fixation in nature is the industrial one, to develop catalytic processes that are economic in energy.

A mechanism for the reduction of ligating dinitrogen to ammonia has been proposed[142,181] on the basis of the isolation of stable complexes (Scheme I). ^{15}N NMR spectroscopy can be used to investigate the nitrogenase action at the molecular level by means of such models if the NMR parameters of likely intermediates are known. So far these have been reported for dinitrogen complexes[140–142] made from molecular $^{15}N_2$, which can be reduced to hydrazine or ammonia, and also for the reduced ligands, diazenido (bent and linear),[149] hydrazido(2−),[139] nitrido, and imido or nitrene,[142] as described in sections VIIIC and VIIID.

XI. Dynamic Processes

Studies of dynamic solution systems in nitrogen resonance are increasing slowly. The fluxional changes in binuclear ($C_5Me_5^-$) dinitrogen complexes of titanium (described in section VIIIC) were elucidated by ^1H and ^{15}N variable-temperature work.[140] Double inversion at two nitrogen centers in bicyclic hydrazines, studied in ^{15}N resonance, gave $\Delta G^\ddagger$ values of 13–15 kcal mol^{-1}, in good agreement with ^1H and ^{13}C NMR results.[182] Proton-transfer reactions have been studied in ^{15}N resonance, e.g., in hydrazines and amides,[183] and in porphyrins (cf. section VIIIE).[154,155a,156,159,160,183] An intermolecular mechanism was established for the tautomeric process in diphenyltriazene at low temperatures from the nitrogen shifts and NH coupling constants. This may involve a hydrogen-bonded dimer in the form of an 8-membered ring.[121c]

Several ligand-exchange studies have used nitrogen resonance. In the Co^{II}–H_2O–NCS^- system, for example, ^{14}N and ^{17}O paramagnetic shifts and line widths were used to assign coordination numbers, determine equilibrium constants, and verify that the ligand shifts are essentially constant for a given nucleus and symmetry of the complex (tetrahedral or octahedral), at constant temperature.[179]

XII. Nitrogen Shielding Tensors

Although qualitative interpretations of chemical shifts have their uses, a fuller understanding of the shielding in anisotropic groups requires knowledge of the shielding tensor[184] which is rotationally averaged in the fluid phase. Experimental values of shielding tensor elements (σ_{xx}, σ_{yy}, σ_{zz}) and anisotropies ($\Delta\sigma$) are given in Table III in order of decreasing isotropic (averaged) shielding σ_{av}, equal to $^1/_3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$. The shielding anisotropy $\Delta\sigma$ may be defined as the largest (absolute) value that can be obtained by subtracting the arithmetic mean of two components from the third. In symmetric-top molecules the nonaxial components ($\sigma_\perp$) are equal and $\Delta\sigma$ is usually defined as ($\sigma_\parallel - \sigma_\perp$), but the practice varies.

For small gaseous molecules the tensor elements may be obtained from the spin-rotation interaction by molecular beam magnetic or electric resonance, or by microwave spectroscopy.[61,184] The spin–rotation constants give experimental values of the components of the paramagnetic (σ_p) shielding tensor which are then combined with theoretical values for the diamagnetic (σ_d) components to give the absolute shielding σ, equal to ($\sigma_d + \sigma_p$). These are the molecular shielding terms of the Ramsey theory.[1] The diamagnetic terms are ground-state functions and are reliably calculated by ab initio or by semiempirical methods[185] so that the limiting error is normally that of the spin–rotation constants. The shielding of the isolated NH_3 molecule thus obtained[50b] forms the basis of an absolute scale for nitrogen shifts,[50a] as mentioned in section IVC. The values of σ given in Table III were obtained from the chemical shift referred to this absolute scale. Differences between σ and σ_{av} may be due to medium effects and (or) to underestimation of errors in the absolute measurements. Even so, some of the discrepancies are surprising.

Less accurate values of the shielding tensor elements have been obtained for the heavier molecules N_2,[186] HCN,[187] PN,[188] N_2O,[189,190] and ClCN[191] from the spin–rotation interaction in the isolated molecule.

Shielding anisotropies $\Delta\sigma$ can sometimes be measured for simple molecules dissolved in liquid crystals which align with a magnetic or electric field. The solute molecules becomes partially oriented, the one-dimensional motion causing intermolecular dipolar interactions to average to zero. The method is not without its hazards, but has yielded anisotropy values for CH_3CN,[192] CH_3NC,[193] and N_2O, for which the tensor elements were estimated from the measured anisotropy, the calculated diamagnetic shielding terms, and the chemical shifts.[106]

The NMR spectra of powdered solids show the tensor elements separately, or superposed if the lines overlap, but there is a major problem of line broadening by the direct (dipolar) coupling that is averaged to zero by molecular motion in the fluid phase. Waugh and coworkers[53a,194] have used double-resonance techniques to study isotopically or chemically dilute nuclei through their spin–spin coupling to an abundant nucleus, usually protons or fluorine. ^{15}N in natural abundance is a suitable candidate, and was studied in CH_3CN[53a] and NH_4NO_3. Three shielding tensor elements were observed for the nitrate ion in NH_4NO_3 in which one N–O bond is 0.02 Å shorter than the other two, as shown by X-ray crystallography.[194]

The shielding tensors for two aromatic molecules in the solid (frozen) state, pyridine[195] and nitrobenzene,[196] have been measured by Schweitzer and Spiess, who found that the shielding anisotropy is much greater than the dipolar line broadening at high magnetic field, 7.5 T. The method does not give the assignment of the individual elements to the molecular axes, but this has now been done for nitrobenzene from relaxation measurements which give the rotational diffusion tensor in solution.[197] For solid $^{15}N_2$ at 4.2 K, the shielding anisotropy could be measured from the variation in the dipolar coupling with increasing field.[198]

The uses of experimental values of the shielding tensor elements and anisotropies are various. We observed the relevance to magnetic relaxation in section IIIA. Since the rate of relaxation by the shielding anisotropy mechanism is given (for linear molecules) by

$$1/T_{1sa} = {}^2/_{15}\gamma^2 B_0^2 (\Delta\sigma)^2\tau \qquad (5)$$

this mechanism becomes more important for the more anisotropic groups and at higher fields B_0. Measures of $\Delta\sigma$ may be obtained from studies at different field strengths if the relevant correlation times τ are known. The connection with studies of molecular tumbling and diffusion in fluids is exemplified by the work on nitrobenzene referred to above.[197]

For quantum mechanical studies of nuclear magnetic shielding, comparison of the calculated values for the tensor elements or anisotropies with experimental values[184] affords a more stringent test of the theory than comparisons of the averaged (isotropic) shieldings, in which important information has been lost.

Knowledge of the tensor components is of particular interest to the physical picture of nuclear magnetic shielding since this is a geometrical phenomenon. In linear groups, as in the molecules N_2O, ClCN, CH_3CN, HCN, N_2, CH_3NC, and PN in Table III, the values of the parallel shielding component $\sigma_\parallel$ are all positive and similar in magnitude, lying within the range 335–370 ppm. The reason for this near-constancy is that the magnetically induced electron circulation about the axis of a linear molecule resembles that in the free atom, being unimpeded by the presence of other nuclei. The paramagnetic component $\sigma_{\parallel}{}^{p}$ is therefore zero, so that $\sigma_{\parallel}$ is equal to the diamagnetic component $\sigma_{\parallel}{}^{d}$. This term is not very sensitive to changes along the axis and is, of course, positive.

The perpendicular shielding component $\sigma_{\perp}$ is negative for the end nitrogen since rotation about a perpendicular axis mixes the n(σ) and π^* orbitals. $\sigma_{\perp}$ is negative, or small and positive, for middle nitrogen, as in NNO or CH_3NC, because of the relatively small σ–π HOMO–LUMO separations. Table III shows that the linear groups may have high shielding anisotropies, but the high electronic symmetry for the axial direction makes the overall electronic symmetry fairly high.

In planar groups, as in nitrate ion or benzene, the highest shielding is perpendicular to the plane. This is because the electronic circulations about this axis that reinforce the applied field use σ(HOMO) and σ^*-(LUMO) orbitals for which the splitting ΔE is relatively large. The circulations about the in-plane axes, however, result from the mixing of σ and π orbitals ($\pi \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$) for which ΔE is smaller, corresponding to stronger deshielding. The ring current in benzene makes a small diamagnetic contribution which is significant only in proton shielding. For pyridine, similarly, the most shielded direction is likely to be the one perpendicular to the plane, corresponding to in-plane $\sigma \rightarrow \sigma^*$ circulations, with relatively high ΔE and shielding. The strongest deshielding is likely to be associated with the in-plane axis which is perpendicular to the molecular (C_{2v}) axis, since rotation about this (in-plane) perpendicular axis mixes the lone pair (n_N) and π^* orbitals with low ΔE. Thus $\sigma_{\parallel}$, associated with the C_{2v} axis direction, is expected to be the intermediate tensor element.

From the pyridine analogy, the most shielded direction in nitrobenzene was expected to be the one perpendicular to the molecular plane, but experimental evidence suggests that it is parallel to the C_{2v} molecular axis.[197] The shielding difference may be relatively small.

Spiess[199] has tabulated some ratios of experimental shielding anisotropies for nitrogen and carbon in pairs of isoelectronic compounds; the ratios are 3.7 for pyridine/benzene, 3.5 for nitrobenzene/benzoate, 2.8 for nitrate/carbonate, and 1.6 for N_2/CO. As mentioned in section VD, such ratios may be compared with the ratio of the radial factors, $\langle r^{-3}\rangle_{N2p}/\langle r^{-3}\rangle_{C2p}$, which has a value of about 2 for the free atoms. The radial factor is expected to be relatively small for nitrogen in pyridine compared with carbon in benzene, because of the partial negative charge on nitrogen (increasing r_{2p} and decreasing $\langle r^{-3}\rangle_{N2p}$). Since the $\Delta\sigma$ ratio is large for pyridine/benzene, the dominant factor must be the inverse ΔE term, which is relatively small for pyridine because the nitrogen carries a lone pair of electrons. As to the N_2/CO pair, the CO polarity is very small (and not of the sign predicted by electonegativity arguments), but the electronegative partner would be expected to bring down the carbon LUMO relative to the HOMO, consistent with the relatively large shielding anisotropy for carbon in CO compared with that for nitrogen in N_2. In this way shielding anisotropies can provide a useful test of predictions based on a physical model of nuclear magnetic shielding.

XIII. References

(1) J. Mason, *Adv. Inorg. Chem. Radiochem.*, **22**, 199 (1979), and references therein.
(2) E. W. Randall and D. G. Gillies, *Prog. NMR Spectrosc.*, **6**, 119 (1970).
(3) N. Logan, "^{14}N NMR Data in the Study of Inorganic Molecules", Chapter 6 in ref 4.
(4) M. Witanowski and G. A. Webb, Eds., "Nitrogen NMR", Plenum Press, London, 1973.
(5) M. Witanowski, L. Stefaniak and G. A. Webb, *Annu. Rep. NMR Spectrosc.*, **7**, 117 (1977).
(6) G. C. Levy and R. L. Lichter, "^{15}N NMR Spectroscopy", Wiley-Interscience, New York, 1979.
(7) (a) F. Bloch, *Pure Appl. Chem.*, **32**, 1 (1972); (b) W. G. Proctor and F. C. Yu, *Phys. Rev.*, [2] **77**, 717 (1950).
(8) D. Herbison-Evans and R. E. Richards, *Mol. Phys.*, **8**, 19 (1964) (^{14}N).
(9) R. K. Harris and B. E. Mann, Eds., "NMR and the Periodic Table", Academic Press, 1978.
(10) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance", McGraw-Hill, New York, 1959.
(11) D. Gust, R. B. Moon, and J. D. Roberts, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 4696 (1975) (^{15}N).
(12) M. Shporer, G. Ron, A. Loewenstein, and G. Navon, *Inorg. Chem.*, **4**, 358 (1965) (^{14}N).
(13) J. P. Kintzinger and J. M. Lehn, *Helv. Chim. Acta*, **58**, 905 (1975) (^{14}N); C. Deverell, *Prog. NMR Spectrosc.*, **4**, 235 (1969).
(14) Y. Yamamoto and J. Uzawa, *Chem. Lett.*, 1213 (1978) (^{14}N).
(15) J. Browning, P. L. Goggin, and R. J. Goodfellow, *J. Chem. Res., Miniprint*, 4201 (1978) (^{14}N).
(16) O. R. Chambers, M. E. Harman, D. S. Rycroft, D. W. A. Sharp, and G. M. Winfield, *J. Chem. Res., Miniprint*, 1849 (1977) (^{14}N).
(17) W. Becker, W. Beck, and R. Rieck, *Z. Naturforsch. B*, **25B**, 1332 (1970) (^{14}N).
(18) M. L. Buess and G. L. Petersen, *Rev. Sci. Instrum.*, **49**, 1151 (1978).
(19) W. McFarlane and C. J. Turner, *Bull. Soc. Chim. belg.*, **87**, 271 (1978) (^{14}N).
(20) W. C. Bailey and H. S. Story, *J. Chem. Phys.*, **60**, 1952 (1974) (^{14}N).
(21) W. B. Moniz and H. S. Gutowsky, *J. Chem. Phys.*, **38**, 1155 (1963) (^{14}N).
(22) D. Herbison-Evans and R. E. Richards, *Mol. Phys.*, **7**, 515 (1964) (^{14}N).
(23) J. P. Kintzinger and J. M. Lehn, Chapter 3 in ref 4 (^{14}N).
(24) A. Abragam, "The Principles of Nuclear Magnetism", Clarendon Press, Oxford, 1961.
(25) A. Loewenstein and M. Brenman, *J. Magn. Reson.*, **34**, 193 (1979) (^{14}N).
(26) J. M. Anderson, J. D. Baldeschwieler, D. C. Dittmer, and W. D. Phillips, *J. Chem. Phys.*, **38**, 1260 (1963) (^{14}N).
(27) J. B. Lambert and D. A. Netzel, *J. Magn. Reson.*, **25**, 531 (1977) (^{15}N).
(28) E. Lippmaa, T. Saluvere, and S. Laisaar, *Chem. Phys. Lett.*, **11**, 120 (1971) (^{15}N).
(29) L. M. Ishol, T. A. Scott, and M. Goldblatt, *J. Magn. Reson.*, **23**, 313 (1976) (^{14}N and ^{15}N).
(30) T. Saluvere and E. Lippmaa, *Chem. Phys. Lett.*, **7**, 545 (1970) (^{15}N).
(31) G. C. Levy, J. J. Dechter, and J. Kowalewski, *J. Am. Chem. Soc.*, **100**, 2308 (1978) (^{15}N).
(32) G. E. Hawkes, E. W. Randall, and W. E. Hull, *J. Chem. Soc., Perkin Trans. 2*, 1268 (1977) (^{15}N).
(33) G. A. Morris and R. Freeman, *J. Am. Chem. Soc.*, **101**, 760 (1979) (^{15}N).
(34) H. J. Jakobsen and W. S. Brey, *J. Am. Chem. Soc.*, **101**, 774 (1979) (^{15}N).
(35) R. D. Bertrand, W. B. Moniz, A. N. Garroway, and G. C. Chingas, *J. Am. Chem. Soc.*, **100**, 5227 (1978), and references therein (^{13}C).
(36) J. P. Marchal and D. Canet, *J. Magn. Reson.*, **31**, 23 (1978) (^{15}N).
(37) E. D. Becker, R. B. Bradley, and T. Axenrod, *J. Magn. Reson.*, **4**, 136 (1971); R. Price, Ph.D. Thesis, Queen Mary College, London, 1969 (^{14}N, ^{15}N).
(38) C. J. Jameson, *J. Chem. Phys.*, **66**, 4983 (1977); *Bull. Magn. Reson.*, **2**, 0000, (1980).
(39) H. Batiz-Hernandez and R. A. Bernheim, *Prog. Nucl. Magn. Reson. Spectrosc.*, **3**, 63 (1967).
(40) C. J. Jameson, A. K. Jameson, H. Parker, S. M. Cohen, and C. L. Lee, *J. Chem. Phys.*, **68**, 2861 (1978).
(41) H. Schultheiss and E. Fluck, *Z. Naturforsch. B*, **32B**, 257 (1977) (^{15}N).
(42) L.-O. Andersson and J. Mason, *J. Chem. Soc., Chem. Commun.*, 99 (1968) (^{14}N).

(43) L.-O. Andersson, J. Mason, and W. van Bronswijk, *J. Chem. Soc. A*, 296 (1970) (^{14}N).

(44) I. A. Stenhouse, personal communication.

(45) W. M. Litchman, A. Alei, and A. E. Florin, *J. Chem. Phys.*, **50**, 1897 (1969) (^{15}N).

(46) R. O. Duthaler and J. D. Roberts, *J. Magn. Reson.*, **34**, 129 (1979) (^{15}N).

(47) J. Kroner, W. Schneid, N. Wiberg, B. Wrackmeyer, and G. Ziegleder, *J. Chem. Soc., Faraday Trans. 2*, **74**, 1909 (1978) (^{14}N).

(48) J. M. Briggs and E. W. Randall, *Mol. Phys.*, **26**, 699 (1973) (^{15}N).

(49) E. D. Becker, *J. Magn. Reson.*, **4**, 142 (1971) (^{14}N).

(50) (a) C. J. Jameson, A. K. Jameson, D. Oppusunggu, S. Wille, P. M. Burrell, and J. Mason, *J. Chem. Phys.*, **74**, 81 (1981); (b) S. G. Kukolich, *J. Am. Chem. Soc.*, **97**, 5704 (1975); (c) J. Mason, *J. Chem. Soc., Faraday Trans. 2*, **73**, 1464 (1977); (d) *ibid.*, **75**, 607 (1979); (e) D. M. Kanjia, J. Mason, I. A. Stenhouse, R. E. Banks, and N. D. Venayak, *J. Chem. Soc., Perkin Trans.*, in press (^{15}N).

(51) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963); J. A. Pople, *Mol. Phys.*, **7**, 301 (1963-4); *Discuss. Faraday Soc.*, **34**, 7 (1962).

(52) R. G. Barnes and W. V. Smith, *Phys. Rev.*, **93**, 95 (1954).

(53) (a) S. Kaplan, A. Pines, R. G. Griffin, and J. S. Waugh, *Chem. Phys. Lett.*, **25**, 78 (1974); (b) L. M. Ishol and T. A. Scott, *J. Magn. Reson.*, **27**, 23 (1977) (^{15}N).

(54) M. B. Robin, "Higher Excited States of Polyatomic Molecules", Academic Press, New York, 1974.

(55) J. Mason and W. van Bronswijk, *J. Chem. Soc. A*, 791 (1971); J. Mason and J. G. Vinter, *J. Chem. Soc., Dalton Trans.*, 2522 (1975) (^{14}N).

(56) J. Mason, W. van Broswijk, and J. G. Vinter, *J. Chem. Soc., Perkin Trans. 2*, 469 (1977) (^{14}N).

(57) G. A. Olah, B. G. Balaram Gupta, and S. C. Narang, *J. Am. Chem. Soc.*, **101**, 5317 (1979) (^{15}N).

(58) J. D. Baldeschwieler and E. W. Randall, *Proc. Chem. Soc.*, 303 (1961) (^{14}N).

(59) B. Wrackmeyer, *J. Magn. Reson.*, **27**, 345 (1977) (^{14}N).

(60) G. A. Olah and T. E. Kiovsky, *J. Am. Chem. Soc.*, **90**, 4666 (1968) (^{15}N).

(61) J. Mason, *Adv. Inorg. Chem. Radiochem.*, **18**, 197 (1976).

(62) W. Beck, W. Becker, H. Nöth, and B. Wrackmeyer, *Chem. Ber.*, **105**, 2883 (1972).

(63) H. Nöth and B. Wrackmeyer, *Chem. Ber.*, **107**, 3070 (1974) (^{14}N).

(64) H. Nöth and B. Wrackmeyer, *Chem. Ber.*, **107**, 3089 (1974) (^{14}N).

(65) H. Nöth and B. Wrackmeyer, *Chem. Ber.*, **106**, 1145 (1973) (^{14}N).

(66) K. Barlos and H. Nöth, *Z. Naturforsch. B*, **35B**, 125 (1980) (^{14}N).

(67) H. Nöth and B. Wrackmeyer, *Chem. Ber.*, **110**, 1086 (1977) (^{14}N).

(68) H. Nöth and B. Wrackmeyer, *Chem. Ber.*, **109**, 3480 (1976) (^{14}N).

(69) H. Nöth and W. Storch, *Chem. Ber.*, **110**, 1636 (1977); **109**, 884 (1976) (^{14}N).

(70) E. F. Mooney and M. A. Qaseem, *J. Inorg. Nucl. Chem.*, **30**, 1439 (1968) (^{14}N).

(71) M. R. Collier, M. F. Lappert, J. Mason, and W. van Bronswijk, unpublished work (^{14}N).

(72) K. Hensen and K. P. Messer, *Theor. Chim. Acta*, **9**, 17 (1967) (^{14}N).

(73) R. Prinz and H. Werner, *Angew. Chem., Int. Ed. Engl.*, **6**, 91 (1967) (^{14}N).

(74) H. Nöth, W. Tinhof, and B. Wrackmeyer, *Chem. Ber.*, **107**, 518 (1974) (^{14}N).

(75) H. Nöth, W. Tinhof, and T. Taeger, *Chem. Ber.*, **107**, 3113 (1974) (^{14}N).

(76) K. Barlos, G. Hübler, H. Nöth, P. Wanninger, N. Wiberg, and B. Wrackmeyer, *J. Magn. Reson.*, **31**, 363 (1978) (^{14}N).

(77) D. W. W. Anderson, J. E. Bentham, and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1215 (1973) (^{15}N).

(78) M. L. Filleux-Blanchard and Nguyen Dinh An, *Org. Magn. Reson.*, **12**, 12 (1979) (^{15}N).

(79) M. Witanowski, L. Stefaniak, H. Januszewski, M. G. Voronkov, and S. N. Tandura, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **24**, 281 (1976) (^{14}N).

(80) (a) V. A. Pestunovich, S. N. Tandura, B. Z. Shterenberg, V. P. Baryshok, and M. G. Voronkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2159 (1979); (b) E. E. Liepin'sh, I. S. Birgele, G. I. Zelchan, and E. Lukevits, *Zh. Obshch. Khim.*, **49**, 1537 (1979) (^{15}N).

(81) K. Jurkschat, C. Mugge, A. Tzschach, A. Zschunke, G. Engelhardt, E. Lippmaa, M. Magi, M. F. Larin, V. A. Pestunovich, and M. G. Voronkov, *J. Organomet. Chem.*, **171**, 301 (1979) (^{15}N).

(82) K. Barlos, H. Nöth, and B. Wrackmeyer, *Z. Naturforsch. B*, **33B**, 515 (1978) (^{14}N).

(83) D. E. Arnold and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 889 (1975) (^{15}N).

(84) J. Mason, W. van Bronswijk, and J. G. Vinter, *J. Chem. Soc., Dalton Trans.*, 2337 (1977) (^{14}N).

(85) B. Thomas, G. Seifert, G. Grossmann, and D. Scheller, *Z. Phys. Chem. (Leipzig)*, **260**, 225 (1979); B. Thomas and G. Grossmann, *Z. Anorg. Allg. Chem.*, **448**, 107 (1979) (^{15}N).

(86) G. A. Gray, G. W. Buchanan, and F. G. Morin, *J. Org. Chem.*, **44**, 1768 (1979) (^{15}N).

(87) H. Saito, Y. Tanaka, and S. Nagata, *J. Am. Chem. Soc.*, **95**, 324 (1973) (^{14}N).

(88) A. J. Banister, *Nature (London) Phys. Sci.*, **237**, 92 (1972).

(89) D. A. Armitage, J. Mason, J. G. Vinter, *Inorg. Chem.*, **17**, 776 (1978) (^{14}N).

(90) I. Yavari, J. S. Staral, and J. D. Roberts, *Org. Magn. Reson.*, **12**, 340 (1979) (^{15}N).

(91) J. Mason, W. van Bronswijk, and O. Glemser, *J. Phys. Chem.*, **82**, 463 (1978) (^{14}N).

(92) J. Nelson and H. G. Heal, *J. Chem. Soc. A*, 136 (1971) (^{14}N).

(93) I. Yavari, R. E. Botto, and J. D. Roberts, *J. Org. Chem.*, **43**, 2542 (1978) (^{15}N).

(94) N. Logan and W. L. Jolly, *Inorg. Chem.*, **4**, 1508 (1965) (^{15}N).

(95) J. Mason, *J. Chem. Soc. A*, 1567 (1969) (^{14}N).

(96) O. J. Scherer and G. Wolmershäuser, *Angew. Chem., Int. Ed. Engl.*, **14**, 485 (1975) (^{14}N).

(97) T. Chivers, R. T. Oakley, O. J. Scherer, and G. Wolmershäuser, *Inorg. Chem.*, in press (^{15}N).

(98) A. J. Banister and J. Mason, unpublished work (^{15}N).

(99) R. L. Lichter and J. D. Roberts, *J. Am. Chem. Soc.*, **94**, 4904 (1972) (^{15}N).

(100) I. Yavari and J. D. Roberts, *J. Am. Chem. Soc.*, **100**, 4662 (1978) (^{15}N).

(101) J. Mason and W. van Bronswijk, *J. Chem. Soc., Chem. Commun.*, 357 (1969) (^{14}N).

(102) J. H. Noggle, J. D. Baldeschwieler, and C. B. Colburn, *J. Chem. Phys.*, **37**, 182 (1962) (^{14}N).

(103) A. M. Qureshi, J. A. Ripmeester, and F. Aubke, *Can. J. Chem.*, **47**, 4247 (1969) (^{14}N).

(104) F. Aubke, F. G. Herring, and A. M. Qureshi, *Can. J. Chem.*, **48**, 3504 (1970) (^{14}N).

(105) J. E. Kent and E. L. Wagner, *J. Chem. Phys.*, **44**, 3530 (1966) (^{14}N).

(106) P. K. Bhattacharyya and B. P. Dailey, *J. Chem. Phys.*, **59**, 5820 (1973) (^{15}N).

(107) M. Christl, J. P. Warren, B. L. Hawkins, and J. D. Roberts, *J. Am. Chem. Soc.*, **95**, 4392 (1973) (^{15}N).

(108) W. Becker and W. Beck, *Z. Naturforsch. B*, **25B**, 101 (1970) (^{14}N).

(109) J. Mason and W. van Bronswijk, *J. Chem. Soc. A*, 1763 (1970) (^{14}N).

(110) E. Tannenbaum, E. M. Coffin, and A. J. Harrison, *J. Chem. Phys.*, **21**, 311 (1953).

(111) I. Yavari and J. D. Roberts, *J. Org. Chem.*, **43**, 4689 (1978) (^{15}N).

(112) K. F. Chew, W. Derbyshire, N. Logan, A. H. Norbury, and A. I. P. Sinha, *J. Chem. Soc., Chem. Commun.*, 1708 (1970) (^{14}N).

(113) O. W. Howarth, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.*, 3335 (1964) (^{14}N).

(114) H. Böhland and E. Mühle, *Z. Anorg. Allg. Chem.*, **379**, 273 (1970) (^{14}N).

(115) J. Müller, *Z. Naturforsch. B*, **34B**, 437 (1979) (^{15}N).

(116) J. Müller and H. F. Schröder, *Z. Anorg. Allg. Chem.*, **450**, 149 (1979) (^{15}N).

(117) J. Müller, *Z. Naturforsch. B*, **33B**, 993 (1978) (^{15}N).

(118) (a) R. O. Duthaler, H. G. Förster, and J. D. Roberts, *J. Am. Chem. Soc.*, **100**, 4974 (1978); (b) R. L. Lichter, P. R. Srinivasan, A. B. Smith, R. K. Dieter, C. T. Denny, and J. M. Schulman, *J. Chem. Soc., Chem. Commun.*, 366 (1977); (c) D. G. Morris and A. M. Murray, *J. Chem. Soc., Perkin Trans. 2*, 1579 (1976); (d) A. Fadini, E. Glozbach, P. Krommes and J. Lorberth, *J. Organomet. Chem.*, **149**, 297 (1978) (^{15}N)

(119) (a) A. L. Blumenfeld, V. C. Lenenko, B. Lorentz, I. Möbius, M. Wahren, V. B. Shur, and M. E. Vol'pin, *Dokl. Akad. Nauk SSSR*, **251**, 611 (1980); (b) N. N. Bubnov, K. A. Bilevitch, L. A. Poljakova, and O. Yu. Okhlobystin, *J. Chem. Soc., Chem. Commun.*, 1058 (1972) (^{15}N).

(120) C. H. Bradley, G. E. Hawkes, E. W. Randall, and J. D. Roberts, *J. Am. Chem. Soc.*, **97**, 1959 (1975) (^{15}N).

(121) (a) C. Casewit and J. D. Roberts, *J. Am. Chem. Soc.*, **102**, 2364 (1980); (b) T. Axenrod, P. Mangiaracina, and P. S. Pregosin, *Helv. Chim. Acta*, **59**, 1655 (1976); (c) A. N. Nesmeyanov, E. V. Borisov, A. S. Peregudov, D. N. Kravtsov, L. A. Federov, Z. I. Fedin, and S. A. Postovoi, *Dokl. Akad. Nauk SSSR*, **247**, 1154 (1979) (^{15}N).

(122) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 4461 (1955); 3203 (1958).

(123) R. Bramley, B. N. Figgis, and R. S. Nyholm, *J. Chem. Soc. A*, 861 (1967) (^{14}N).
(124) J. W. Lehman and B. M. Fung, *Inorg. Chem.*, **11**, 214 (1972) (^{15}N).
(125) Y. Nakashima, M. Muto, I. Takagi, and K. Kawano, *Chem. Lett.*, 1075 (1975) (^{15}N).
(126) M. Alei, P. J. Vergamini, and W. E. Wageman, *J. Am. Chem. Soc.*, **101**, 5415 (1979) (^{15}N).
(127) W. M. Litchman, M. Alei, and A. E. Florin, *J. Am. Chem. Soc.*, **91**, 6574 (1969) (^{15}N).
(128) M. Alei, A. E. Florin, and W. M. Litchman, *J. Am. Chem. Soc.*, **92**, 4828 (1970) (^{15}N).
(129) R. Hagen, J. P. Warren, D. H. Hunter, and J. D. Roberts, *J. Am. Chem. Soc.*, **95**, 5712 (1973) (^{15}N).
(130) E. H. Curzon, J. Herron, and P. Moore, *J. Chem. Soc., Dalton Trans.*, 721 (1980) (^{15}N).
(131) B. M. Fung, S. C. Wei, T. H. Martin, and I.-Y. Wei, *Inorg. Chem.*, **12**, 1203 (1973) (^{15}N).
(132) B. M. Fung and S. C. Wei, *J. Magn. Reson.*, **3**, 1 (1970) (^{14}N).
(133) K. S. Bose and E. H. Abbott, *Inorg. Chem.*, **16**, 3190 (1977) (^{15}N).
(134) H. Motschi, P. S. Pregosin, and L. M. Venanzi, *Helv. Chim. Acta*, **62**, 667 (1979) (^{15}N).
(135) (a) P. S. Pregosin, H. Streit, and L. M. Venanzi, *Inorg. Chim. Acta*, **38**, 237 (1980) (^{15}N); (b) C. Musikas, C. Cuillerdier, and C. Chachaty, *Inorg. Chem.*, **17**, 3610 (1978), and references therein (^{14}N, ^{15}N).
(136) J. Müller, *Z. Naturforsch. B*, **34B**, 531 (1979) (^{15}N).
(137) J. Müller, *Z. Naturforsch. B*, **34B**, 536 (1979) (^{15}N).
(138) Unpublished observations by J. Dilworth, R. L. Richards, and J. Mason (^{15}N).
(139) J. Chatt, M. E. Fakley, R. L. Richards, J. Mason, and I. A. Stenhouse, *J. Chem. Res. Synop.*, 322 (1979), and references therein (^{15}N).
(140) J. M. Manriquez, D. R. McAlister, E. Rosenberg, A. M. Shiller, K. L. Williamson, S. I. Chan, and J. E. Bercaw, *J. Am. Chem. Soc.*, **100**, 3078 (1978), and references therein (^{15}N).
(141) J. Chatt, M. E. Fakley, R. L. Richards, J. Mason, and I. A. Stenhouse, *J. Chem. Res., Synop.*, 44 (1979) (^{15}N).
(142) J. R. Dilworth, S. Donovan-Mtunzi, C.-T. Kan, R. L. Richards, and J. Mason, *Inorg. Chim. Acta*, in press (^{15}N).
(143) L. J. Todd and J. R. Wilkinson, *J. Organomet. Chem.*, **77**, 1 (1974) (^{13}C).
(144) H. Mahnke, R. K. Sheline, and H. W. Spiess, *J. Chem. Phys.*, **61**, 55 (1974) (^{13}C).
(145) D. L. Thorn, T. H. Tulip, and J. A. Ibers, *J. Chem. Soc., Dalton Trans.*, 2022 (1979).
(146) (a) C. Busetto, A. D'Alfonso, F. Maspero, G. Perego, and A. Zazzetta, *J. Chem. Soc., Dalton Trans.*, 1828 (1977); (b) K. Jonas and C. Krüger, *Angew. Chem., Int. Ed. Engl.*, **19**, 520 (1980).
(147) K. R. Laing, S. D. Robinson, and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 2713 (1973).
(148) A. P. Gaughan and J. A. Ibers, *Inorg. Chem.*, **14**, 352 (1975).
(149) J. R. Dilworth, C.-T. Kan, R. L. Richards, J. Mason, and I. A. Stenhouse, *J. Organomet. Chem.*, **20**, C24 (1980) (^{15}N).
(150) R. O. Duthaler and J. D. Roberts, *J. Am. Chem. Soc.*, **100**, 4969 (1978) (^{15}N).
(151) L. H. Staal, D. J. Stufkens, and A. Oskam, *Inorg. Chim. Acta*, **26**, 255 (1978) (^{15}N).
(152) (a) J. A. Happe and M. Morales, *J. Am. Chem. Soc.*, **88**, 2077 (1966) (^{15}N); (b) M. Alei, L. O. Morgan, and W. E. Wageman, *Inorg. Chem.*, **17**, 2288 (1978) (^{15}N); (c) M. Alei, W. E. Wageman, and L. O. Morgan, *Inorg. Chem.*, **17**, 3314 (1978) (^{15}N).
(153) S. G. Boxer, G. L. Closs, and J. J. Katz, *J. Am. Chem. Soc.*, **96**, 7058 (1974) (^{15}N).
(154) C. S. Irving and A. Lapidot, *J. Chem. Soc., Chem. Commun.*, 184 (1977) (^{15}N).
(155) (a) D. Gust, and J. D. Roberts, *J. Am. Chem. Soc.*, **99**, 3637 (1977); (b) D. Gust and D. N. Neal, *J. Chem. Soc., Chem. Commun.*, 681 (1978) (^{15}N).
(156) H. J. C. Yeh, M. Sato, and I. Morishima, *J. Magn. Reson.*, **26**, 365 (1977) (^{15}N).
(157) D. D. Dominguez, M. M. King, and H. J. C. Yeh, *J. Magn. Reson.*, **32**, 161 (1978) (^{15}N).
(158) I. Morishima, T. Inubushi, and M. Sato, *J. Chem. Soc., Chem. Commun.*, 106 (1978) (^{15}N).
(159) K. Kawano, Y. Ozaki, Y. Kyogoku, H. Ogoshi, H. Sugimoto, and Z.-I. Yoshida, *J. Chem. Soc., Chem. Commun.*, 226 (1977) (^{15}N).
(160) K. Kawano, Y. Ozaki, Y. Kyogoku, H. Ogoshi, H. Sugimoto, and Z.-I. Yoshida, *J. Chem. Soc., Chem. Commun.*, 1319 (1978) (^{15}N).
(161) Y. Ozaki, Y. Kyogoku, H. Ogoshi, H. Sugimoto, and Z.-I. Yoshida, *J. Chem. Soc., Chem. Commun.*, 76 (1979) (^{15}N).
(162) G. Burton, H. Nordlov, S. Hosozawa, H. Matsumoto, P. M. Jordan, P. E. Fagerness, L. M. Pryde, and A. I. Scott, *J. Am. Chem. Soc.*, **101**, 3114 (1979); but see A. R. Battersby, R. G. Brereton, C. J. R. Fookes, E. McDonald, and G. W. J. Matcham, *J. Chem. Soc., Chem. Commun.*, 1124 (1980) (^{15}N).
(163) J. M. Briggs, E. Rahkamaa, and E. W. Randall, *J. Magn. Reson.*, **12**, 40 (1973) (^{15}N).
(164) R. E. Botto, B. W. S. Kolthammer, P. Legzdins, and J. D. Roberts, *Inorg. Chem.*, **18**, 2049 (1979) (^{15}N).
(165) K. D. Rose and R. G. Bryant, *Inorg. Chem.*, **18**, 2130 (1979) (^{14}N).
(166) K. F. Chew, M. A. Healy, M. I. Khalil, and N. Logan, *J. Chem. Soc., Dalton Trans.*, 1315 (1975) (^{14}N).
(167) P. Chini, G. Longoni, and V. G. Albano, *Adv. Organomet. Chem.*, **14**, 285 (1976).
(168) S. Martinengo, B. T. Heaton, R. J. Goodfellow, and P. Chini, *J. Chem. Soc., Chem. Commun.*, 39 (1977); B. T. Heaton, C. Brown, D. O. Smith, L. Strona, R. J. Goodfellow, P. Chini, and S. Martinengo, *J. Am. Chem. Soc.*, **102**, 6175 (1980) (^{1}H, ^{13}C, ^{103}Rh).
(169) O. A. Gansow, D. S. Gill, F. J. Bennis, J. R. Hutchison, J. L. Vidal, and R. C. Schoening, *J. Am. Chem. Soc.*, **102**, 2449 (1980) (^{103}Rh).
(170) J. L. Vidal, W. E. Walker, R. L. Pruett, and R. C. Schoening, *Inorg. Chem.*, **18**, 129 (1979); P. Chini, G. Ciani, S. Martinengo, A. Sironi, L. Longhetti, and B. T. Heaton, *J. Chem. Soc., Chem. Commun.*, 188 (1979) (^{31}P, ^{13}C).
(171) D. W. Hart, R. G. Teller, C. Y. Wei, R. Bau, G. Longoni, S. Campanella, P. Chini, and T. F. Koetzle, *Angew. Chem., Int. Ed. Engl.*, **18**, 80 (1979) (^{1}H).
(172) V. G. Albano, P. Chini, S. Martinengo, D. J. A. McCaffrey, D. Strumolo, and B. T. Heaton, *J. Am. Chem. Soc.*, **96**, 8106 (1974); V. G. Albano, P. Chini, G. Ciani, M. Sansoni, D. Strumolo, B. T. Heaton, and S. Martinengo, *J. Am. Chem. Soc.*, **98**, 5027 (1976) (^{13}C).
(173) D. Martinengo, G. Ciani, A. Sironi, B. T. Heaton, and J. Mason, *J. Am. Chem. Soc.*, **10**, 7095 (1979) (^{14}N, ^{15}N, ^{13}C).
(174) G. N. La Mar, W. DeW. Horrocks, and R. H. Holm, Eds., "NMR of Paramagnetic Molecules", Academic Press, 1973; in particular, Chapter 14, Section IIIC (B. R. McGarvey and R. J. Kurland) (^{14}N, etc.).
(175) K. E. Schwarzhans, *Angew. Chem., Int.* Ed. *Engl.*, **9**, 946 (1970) (^{14}N, etc.).
(176) R. S. Drago, J. I. Zink, R. M. Richman, and W. D. Perry, *J. Chem. Educ.*, **51**, 37, 464 (1974).
(177) G. N. La Mar and R. A. Walker (Jensen), in D. Dolphin, Ed., *Porphyrins*, 4, Chapter 2 (1979).
(178) Yu. N. Molin, P. V. Schastnev, and N. D. Chuvylkin, *Zh. Strukt. Khim.*, **12**, 402 (1971), and references therein (^{14}N).
(179) A. H. Zeltmann and L. O. Morgan, *Inorg. Chem.*, **9**, 2522 (1970) (^{14}N, ^{17}O).
(180) I. Morishima and T. Inubushi, *J. Am. Chem. Soc.*, **100**, 3568 (1978), and references therein (^{15}N).
(181) R. N. F. Thorneley, J. Chatt, R. R. Eady, D. J. Lowe, M. J. O'Donnell, J. R. Postgate, R. L. Richards, and B. E. Smith, "Nitrogen Fixation", Vol. 1, W. E. Newton and W. H. Orme-Johnson, Eds., University Park Press, 1980, p 171.
(182) Y. Nomura and Y. Takeuchi, *J. Chem. Soc., Chem. Commun.*, 295 (1979) (^{15}N).
(183) J. D. Roberts, *Pure Appl. Chem.*, **51**, 1037 (1979) (various nuclei).
(184) B. R. Appleman and B. P. Dailey, *Adv. Magn. Reson.*, **7**, 231 (1974).
(185) T. D. Gierke and W. H. Flygare, *J. Am. Chem. Soc.*, **94**, 7277 (1972).
(186) S. I. Chan, M. R. Baker, and N. F. Ramsey, *Phys. Rev. A*, **136**, 1224 (1964); M. R. Baker, C. H. Anderson, and N. F. Ramsey, *ibid.*, **133**, 1533 (1964) (^{15}N).
(187) R. M. Garvey and F. C. De Lucia, *J. Mol. Spectrosc.*, **50**, 38 (1974) (^{14}N).
(188) J. Raymonda and W. Klemperer, *J. Chem. Phys.*, **55**, 232 (1971) (^{14}N).
(189) K. H. Casleton and S. G. Kukolich, *J. Chem. Phys.*, **62**, 2696 (1975) (^{14}N).
(190) J. M. L. J. Reinartz, W. L. Meerts, and A. Dynamus, *Chem. Phys.*, **31**, 19 (1978) (^{14}N).
(191) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy", McGraw-Hill, (1955) (^{14}N).
(192) J. D. Kennedy and W. McFarlane, *Mol. Phys.*, **29**, 593 (1975) (^{15}N).
(193) C. S. Yannoni, *J. Chem. Phys.*, **52**, 2005 (1970) (^{14}N).
(194) M. G. Gibby, R. G. Griffin, A. Pines, and J. S. Waugh, *Chem. Phys. Lett.*, **17**, 80 (1972) (^{15}N).
(195) D. Schweitzer and H. W. Spiess, *J. Magn. Reson.*, **15**, 529 (1974) (^{15}N).
(196) D. Schweitzer and H. W. Spiess, *J. Magn. Reson.*, **16**, 243 (1974) (^{15}N).
(197) R. E. Stark, R. L. Vold, and R. R. Vold, *Chem. Phys.*, **20**, 337 (1977) (^{14}N).
(198) L. M. Ishol and T. A. Scott, *J. Magn. Reson.*, **27**, 23 (1977) (^{15}N).
(199) H. W. Spiess, *Ber. Bunsenges. Phys. Chem.*, **79**, 1009 (1975) (^{15}N).