Nitrogen-15 Magnetic Resonance Spectroscopy. XIV. Natural-Abundance Nitrogen-15 Chemical Shifts of Amines[1]

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Abstract: It has been found possible to measure the shifts of a variety of amines to an accuracy of 0.2 ppm with the isotope at its natural-abundance level. Successful observation of these resonances with our existing equipment is dependent on a favorable nuclear Overhauser effect arising from irradiation of the protons. Chemical exchange of protons directly bound to the amine nitrogen can reduce the signal intensity sufficiently to make detection of the ^{15}N resonance difficult or impossible. The ^{15}N shifts generally correlate linearly with the ^{13}C shifts of alkanes derived by replacing the amine nitrogen with an appropriately substituted carbon. Detailed examination leads to deshielding α and β substituent shift parameters, a shielding γ effect, and possible deshielding associated with hydrogen bonding. Effects of constraints in geometrically rigid systems as well as incorporation of the nitrogen into six-, five-, and three-membered rings are discussed and compared with corresponding ^{13}C shifts. Parallel trends were found for all cases. Natural-abundance ^{15}N spectroscopy is thus a practicable, if far from routine, means of structural analysis.

Recent developments in nmr instrumentation have greatly facilitated the application of ^{13}C spectroscopy to problems in organic chemistry.[2] Characteristic functional group chemical shifts, well-defined substituent and geometrical parameters, the virtual absence of ^{13}C–^{13}C spin–spin coupling in natural abundance, and the favorable Overhauser effect and spectral simplicity associated with proton noise-decoupling to eliminate ^{13}C–^{1}H spin–spin interactions have all contributed to the success which ^{13}C nmr spectroscopy now enjoys. Fourier-transform spectroscopy can be expected to further expand areas of cmr investigations, especially in the biochemical realm. The relatively small use of nitrogen nmr spectroscopy stands in sharp contrast. Even though involved in one of the first applications of nmr to structure elucidation,[3] the spectroscopy of ^{14}N and ^{15}N has nevertheless been relatively little exploited. The reasons for this are straightforward: nitrogen-14, while the dominant isotope (natural abundance = 99.64%), has a large nuclear quadrupole moment associated with its spin quantum number ($I = 1$) which may provide an efficient relaxation mechanism and, when operative, usually results in both large line widths and substantial errors in chemical-shift measurements. Line widths of over 1000 Hz and uncertainties of up to 60 ppm have been reported for ^{14}N resonances.[4,5] As a result, subtle differences in chemical shifts of structurally related compounds are generally undetectable, and only gross correlations between structure and chemical shift have been possible.[4–12] As a further consequence of quadrupole-induced relaxation, nuclear spin–spin coupling is frequently eliminated. A valuable source of structural information is thus lost, except in special cases where the electrical field around the nitrogen is effectively symmetrical, as in some ammonium ions and isocyanides.[13] The presence of residual spin–spin coupling to ^{14}N in the proton spectra of certain compounds, however, has allowed measurement of some ^{14}N chemical shifts by double-resonance methods, but with relatively low accuracy.[14]

The ^{15}N nucleus with spin of $^1/_2$ does not suffer these drawbacks and, in principle, sharp lines are possible, but the low natural abundance (0.36%) and small magnetic moment of this isotope have prevented its use for routine spectra. Nmr studies of both chemical shifts[15,16] and coupling constants[1a,17–24] have employed

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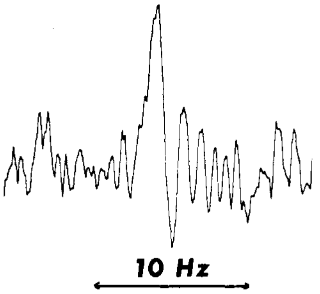

Figure 1. Natural-abundance ^{15}N resonance of cyclobutylamine, obtained after 180 25-sec scans at a sweep rate of 4 Hz/sec.

enriched materials with consequent synthetic and economic limitations.

Application of the techniques which have aided development of ^{13}C spectroscopy (use of an ultrastable digital-sweep spectrometer,[25] and time-averaging of spectra and proton noise decoupling[26] in particular), coupled with knowledge of some of the factors affecting nuclear Overhauser enhancements of ^{15}N resonances,[27] has now enabled us to detect ^{15}N resonances in natural abundance in a relatively routine way and to correlate chemical shifts and structure for several series of related compounds. In this paper we will discuss the techniques and results for aliphatic amines. Subsequent papers will deal with hydrazines and with aromatic amines.

Experimental Section[27a]

The ^{15}N spectra were determined with the Varian DFS-60 spectrometer[25] operating at 6.07 MHz. Samples were run as neat liquids (except for piperazine, which was examined as a saturated solution in dioxane) contained in 10-mm o.d. precision-ground sample tubes at the ambient probe temperature which, with proton decoupling, was 45–55°. Chemical shifts were measured with respect to *ca.* 10 *M* enriched nitric acid contained in a 5-mm o.d. nmr tube centered in the larger tube by means of concentric supporting rings. The choice of this reference was motivated by utilitarian consideration rather than by any desire to establish a new scale for nitrogen chemical-shift measurements.[28] In addition to the availability and ease of handling, the sharp nitrate resonance could be used to monitor the field homogeneity. Signals were generally recorded over sweep widths of 250 or 100 Hz at rates of 10 or 4 Hz/sec, although a few involved either 500- or 50-Hz widths. Line widths were thus dependent on sweep rate, but at the slowest feasible sweep rates (2 Hz/sec) line widths of 1 Hz were obtained, while at a 20-Hz/sec rate line widths were *ca.* 5 Hz. Because of the difficulty in determining optimum rf power levels for each sample, the power was generally set to a level a few decibels below that which could cause saturation of the proton-decoupled ^{15}N resonance of enriched aqueous ammonium chloride. The instrument stability was checked by measuring the position of the nitric acid reference signal before and after recording that of the sample; changes in resonance position were rarely more than 1 Hz (0.16 ppm), and frequently were less. Consequently, the chemical shifts are considered accurate to ±0.2 ppm. The times required to obtain good signal-to-noise ratios varied with the sample and instrument stability, but under optimum conditions, satisfactorily intense signals were obtained in 1–2 hr (Figure 1).

Natural-abundance ^{13}C spectra were determined on neat liquids containing about 10% dioxane as internal reference; the chemical shifts were converted to the CS$_2$ scale by means of the relationship $\delta_{\mathrm{CS_2}} = \delta_{\mathrm{dioxane}} + 125.5$.

Except for (cyclopropylmethyl)amine, which was obtained by lithium aluminum hydride reduction of cyanocyclopropane, all compounds were either commercial products or were available from previous work in these laboratories. Each substance was dried by distillation from sodium or potassium hydroxide pellets (lithium aluminum hydride has been found by Dr. John P. Warren to be useful for the same purpose) immediately before use, but none was degassed.

Results

The nuclear Overhauser effect (NOE) resulting from proton decoupling is extremely important in both ^{15}N and ^{13}C spectroscopy. With the usually encountered mechanism of nuclear relaxation—dipole–dipole interactions between ^{15}N (or ^{13}C) and directly bonded protons—irradiation at the proton frequency causes inversion of ^{15}N resonance signals, because $\gamma_{^{15}\mathrm{N}}$ is negative. For pure dipolar relaxation, a maximum NOE of -3.93 is expected.[27] Protons directly bonded to amine nitrogens can exchange, however, and the ensuing modulation of the spin–spin coupling may provide an additional relaxation pathway. In the case where this mechanism dominates, a noninverted signal is expected.[27] With intermediate rates of exchange, proton irradiation could lead to disappearance of the signal because of the opposing effects produced by the two relaxation mechanisms, and this expectation is, in fact, realized for ammonium ion.[27] We have found for compounds with hydrogens bonded directly to nitrogen that in the absence of proton irradiation no useful natural-abundance ^{15}N signals could be observed with our present spectrometer, while with proton irradiation an inverted ^{15}N signal could be relatively easily detected, provided that the pmr signal of the directly bonded protons was reasonably sharp (half-width ≤ 10 Hz). Clearly, in these circumstances, the exchange rates of the directly bonded protons were sufficiently fast to eliminate spin–spin coupling and

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(27a) NOTE ADDED IN PROOF: Detection of ^{15}N resonances at the natural-abundance level has been reported with the aid of pulse techniques by J. M. Briggs, L. F. Farnell, and E. W. Randall, *J. Chem. Soc. D*, 681 (1971), and P. S. Pregosin, E. W. Randall, and A. I. White, *ibid.*, 1602 (1971). In general, the results agree with these reported here.

(28) Witanowski[6c] has proposed nitromethane as a primary internal reference, while Andersson, *et al.*,[11b] have used saturated aqueous nitrite ion, and Chuck, *et al.*,[22d] report their shifts with respect to external aqueous ammonium ion. The confusion surrounding references for nitrogen chemical shifts has been reviewed by E. D. Becker, *J. Magn. Resonance*, 4, 142 (1971), who proposes the use of tetramethylammonium ion as a primary standard, although this material has a number of drawbacks of its own.

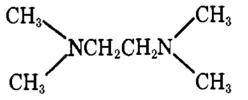
Table I. Natural-Abundance ^{15}N Chemical Shifts[a]

Compound	$\delta_{^{15}N}$, ppm	$\delta_{^{14}N}$, ppm[b]	$\delta_{^{13}C}$, ppm[c]
$(CH_3CH_2)_2NH$	327.9	332	158.72[d]
$CH_3(CH_2)_2NH_2$	356.0	359	180.03[d]
$CH_3(CH_2)_3NH_2$	352.3	359	179.52[e]
$CH_3(CH_2)_4NH_2$	353.6		179.37[e]
$(CH_3)_2CHNH_2$	332.2	334	168.90[d]
$[(CH_3)_2CH]_2NH$	298.3[f]		144.05[d]
$(CH_3)_3CNH_2$	317.4	319	161.78[d]
$CH_3CH_2CH(CH_3)NH_2$	335.4		171.22[d]
$CH_3CH(CH_3)CH_2NH_2$	357.4		181.73[d]
$CH_3CH_2CH_2CH(CH_3)NH_2$	333.1		170.72[d]
$H_2N(CH_2)_2NH_2$	358.7	363	182.41[e]
$H_2N(CH_2)_3NH_2$	354.2		179.75[e]
$H_2N(CH_2)_4NH_2$	353.9	360	
$H_2N(CH_2)_5NH_2$	353.9		
$H_2N(CH_2)_6NH_2$	353.6		
$(CH_3)_2NCH_2CH_2N(CH_3)_2$	353.5		
$HOCH_2CH_2NH_2$	359.6	364	183.36[e]
$CH_3OCH_2CH_2NH_2$	361.7		
$NCCH_2CH_2NH_2$	355.6		180.54[e]
$C_6H_5CH_2CH_2NH_2$	354.5		179.66[e]
$HOCH_2CH(CH_3)NH_2$	339.9[f]		173.6[d]
$HOCH_2CH(CH_2CH_3)NH_2$	344.9		177.24[d,e]
$HOCH_2C(CH_3)_2NH_2$	326.8		166.94[d,e]
$C_6H_5(CH_2)_3NH_2$	352.8		179.53[e]
$C_6H_5CH_2NH_2$	352.4	356	177.82[e]
$C_6H_5CH(CH_3)NH_2$	332.0		168.91[e]
$C_6H_5NH_2$	319.3	319	171.74[e]
$CH_2{=}CHCH_2NH_2$	355.5	360	
Cyclopropylamine	346.5		
(Cyclopropylmethyl)amine	352.8		180.21
Cyclobutylamine	331.6		
trans-1,2-Diaminocyclobutane	335.9		
cis-1,2-Diaminocyclobutane	349.4		
Cyclopentylamine	336.9		173.04[c]
Cyclohexylamine	333.3	337	169.8[d]
Ethylenimine	387.2		196.3[d]
Pyrrolidine	337.3	340[g]	166.99[e]
Piperidine	336.5		165.78[e]
Morpholine	343.7		168.96[e]
Piperazine	340.3[h]		167.21[e]
Nicotine (**2**)	55.8 (N_1) 321.8 ($N_{1'}$)		
Pyridine	56.8[i]		64.55

[a] Upfield from external $H^{15}NO_3$, ±0.2 ppm. [b] Reference 5. [c] See text. [d] Reference 30, and converted from benzene to CS_2 reference by relationship $\delta_{CS_2} = \delta_{C_6H_6} + 64.55$. [e] This work. [f] Kindly determined by Dr. John P. Warren. [g] Reference 4, in ether. [h] Saturated solution in dioxane. [i] Signal was not inverted.

broaden the nitrogen lines, but not fast enough to afford an important relaxation mechanism. A dramatic example of this effect is provided by 1,4-butanediamine:[27] when the substance was examined without purification, no ^{15}N signal could be observed even after many hours of spectral accumulation, while a strong signal was easily detected in less than an hour after the material had been carefully distilled. More strikingly, the pmr spectrum of *tert*-butylamine displayed a weak broad signal for the N–H proton even after purification, and attainment of a ^{15}N resonance was possible only after over 1000 scans. It was primarily for this reason that every substance was distilled just prior to use, and it was deemed expedient to determine the pmr spectrum of each substance to confirm the sharpness of the N–H resonance.

The importance of NOE is illustrated by comparison of the spectra obtained with *N,N,N′,N′*-tetramethylethylenediamine (**1**) and nicotine (**2**), for neither of which is relaxation possible through ^{15}N to H dipole–dipole interactions with directly bound protons. With **1**, only a weak, noninverted signal was obtained after about 1200 scans, while stronger inverted signals were obtained for each of the nitrogens of **2** after a comparable number of scans. It is conceivable that the nitrogen nuclei of **2** are able to relax *via* an intermolecular dipole–dipole mechanism,[27] while those of the diamine are not. Interestingly, no ^{15}N signal was detectable from *N*-methylpyrrolidine.



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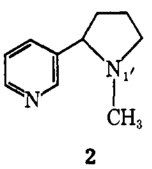

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The chemical shifts obtained for the amines studied in this investigation are given in Table I together with corresponding values of ^{14}N chemical shift, where known. No isotope effect is expected,[29] and the differences are expected to arise from differences in reference used and in the measurement conditions. In addition to the nitrogen shifts, Table I lists ^{13}C chemical shifts of those carbons in alkanes derived from the corresponding amines by replacing the amine function with an appropriate carbon unit. Thus, for a given amine, $R{-}NH_2$, the ^{13}C shift listed is that of the methyl resonance of $R{-}CH_3$. These values will be used later in the discussion and have been obtained from the literature[30] or were measured in this laboratory.

Discussion

Prior considerations of nitrogen chemical shifts[4–12] have focussed on the relative importances of the various terms in the Ramsey equation, where, as is general for second-row elements, the paramagnetic term dominates.[31] In an LCAO–MO treatment,[32] this term is approximated by eq 1, where ΔE is an "average"

$$\sigma_p^{AA} = -\frac{e^2\hbar^2}{2m^2c^2}\frac{1}{\Delta E}\left\langle\frac{1}{r^3}\right\rangle\sum_{B} Q_{AB} \qquad (1)$$

excitation energy, $\langle 1/r^3\rangle$ is the average value of the non-s-orbital radius, and the Q_{AB}'s are the elements of the "charge-density bond order" matrix of the LCAO molecular orbitals. While this approach may be useful from a theoretical point of view and for explaining large differences in chemical shifts, we feel an empirical discussion is potentially more useful for structure–chemical shift correlations and predictions. A treatment of this type is facilitated if a correlation between ^{15}N shifts and the ^{13}C shifts of the alkanes derived as discussed above can be demonstrated, because the factors affecting ^{13}C shifts have been extensively investigated and

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(31) (a) N. F. Ramsey, *Phys. Rev.*, *78*, 699 (1950). (b) Recently it has been shown that diamagnetic terms can account for some of the anomalies in ^{13}C structure–shift correlations. Similar considerations are expected to be important for ^{15}N. See R. Gunter and J. Mason, *J. Chem. Soc. A*, 2196 (1971), and J. Mason, *ibid.*, 1038 (1971).

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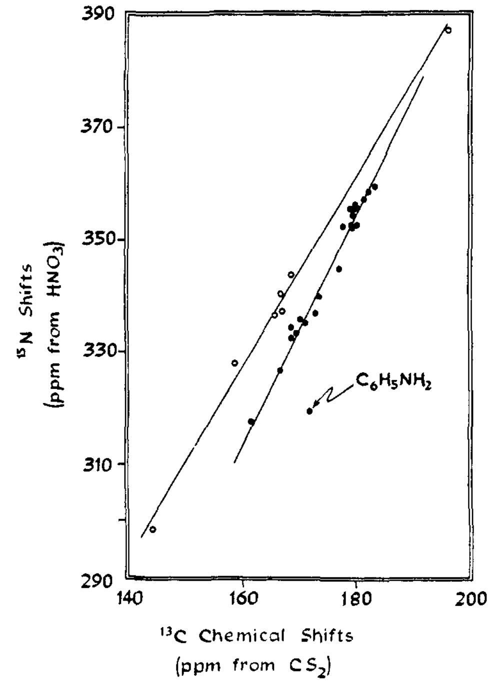


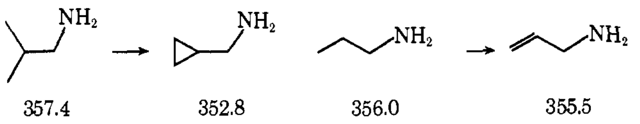
Figure 2. Correlation between ^{13}C and ^{15}N chemical shifts in structurally similar compounds. The open circles represent secondary amines, while the solid circles correspond to primary amines.

a correlation would imply that the same factors are likely to affect both. To this end, the nitrogen shifts in Table I were plotted against the corresponding carbon shifts, with the result shown in Figure 2. The existence of two correlation lines is clearly evident. One which includes all of the primary amines, except aniline, has a slope of 2.05, intercept of -15.5, and $r = 0.993$. The other, which correlates a smaller number of secondary amines, has a slope of 1.67, intercept of 58.5, and $r = 0.998$. The difference between these plots with primary and secondary amines might be the result of differences in hydrogen bonding or some other factor as yet not understood. In this connection, it seems significant that the ^{15}N shifts of ethylenediamine and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine are nearly equal. However, in any case, these apparently linear ^{15}N–^{13}C shift correlations are consistent with the idea that the substituent-induced chemical-shift changes result from external perturbations which are common to several nuclei.[30d,33,34] It is possible that the substituent effects manifest themselves in the $\langle 1/r^3\rangle$ and ΣQ_{AB} terms in eq 1, rather than in significantly affecting ΔE. The deviation of aniline from the primary amine line can be rationalized in terms of a substantial lowering of ΔE brought about by the interaction of the nitrogen lone pair with the ring,[15a] which is, of course, not possible in the carbon analog (toluene). If this interpretation is correct, it is noteworthy that the interaction is large enough to dominate the nitrogen shift, but has no effect on the one-bond ^{15}N–H coupling constant. The reported value, -78.5 Hz, is consistent with simple hybridization arguments in which the nitrogen is sp^3 hybridized.[35]

Considering only the primary alkylamines, substituent parameters can be derived following the method of Grant and Paul.[30a,36] The relevant compounds and chemical shifts are summarized in Table II, together with the coefficient matrix corresponding to the number of substituents in the α through ϵ positions. Linear regression analysis of the data with a constant term of 379 ppm[37] yields $\alpha = -8.7$ ppm, $\beta = -18.2$ ppm, $\gamma = +2.7$ ppm, $\delta = -3.0$ ppm, and $\epsilon = +1.8$ ppm. The standard deviation from the calculated values was 1.1 ppm and the correlation coefficient was 0.997.[38] Because of the rather small number of experimental chemical-shift values, the actual values of the parameters are likely to be uncertain, but the trends seem significant and serve to emphasize the suggestions derived from the correlation in Figure 2. Nitrogen chemical shifts are seen to be susceptible to the same kinds of electronic and steric influences as ^{13}C shifts: deshielding α and β effects,[30a] as well as a shielding, presumably sterically induced, γ effect[39] can be discerned. In analogy to the ^{13}C results,[30d] the δ-substituent effect appears to be deshielding. Consistent with the presence of a steric γ effect, constraint of the *gem*-methyl group of isobutylamine by conversion to (cyclopropylmethyl)amine results in a downfield shift of 4.6 ppm, presumably because the γ-methyl groups can no longer interact with the nitrogen. Moreover, the near identity of the nitrogen resonance positions in allylamine and *n*-propylamine may be rationalized in a similar manner, if the downfield shift expected on removal of the γ effect in *n*-propylamine is offset by an upfield shift associated with the electronegativity of the vinyl substituent (see below).

Table II. ^{15}N Chemical Shifts of Alkylamines

Compound	δ_N, ppm	Coefficients α	β	γ	δ	ϵ
$CH_3CH_2CH_2NH_2$	356.0	1	1	1	0	0
$CH_3CH_2CH_2CH_2NH_2$	352.3	1	1	1	1	0
$CH_3CH_2CH_2CH_2CH_2NH_2$	353.6	1	1	1	1	1
$(CH_3)_2CHNH_2$	332.2	1	2	0	0	0
$(CH_3)_3CNH_2$	317.4	1	3	0	0	0
$CH_3CH_2CH(CH_3)NH_2$	335.4	1	2	1	0	0
$CH_3CH(CH_3)CH_2NH_2$	357.4	1	1	2	0	0
$CH_3CH_2CH_2CH(CH_3)NH_2$	333.1	1	2	1	1	0



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(33) B. F. Spielvogel and J. M. Purser, *J. Amer. Chem. Soc.*, **89**, 5294 (1967).

(34) J. M. Purser and B. F. Spielvogel, *Chem. Commun.*, 386 (1968); *Inorg. Chem.*, 7, 2156 (1968).

(35) E. W. Randall, J. J. Ellner, and J. J. Zuckerman, *J. Amer. Chem. Soc.*, **88**, 622 (1966). See, however, G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *ibid.*, **92**, 1, 11 (1970), for criticisms of the simple hybridization approach.

(36) For a thorough discussion of substituent parameters in rigid systems, see J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *ibid.*, **92**, 7107 (1970).

(37) The constant term corresponds to the chemical shift of ammonia and was corrected from the reported[5] ^{14}N value (383 ppm) to an approximate ^{15}N value appropriate to the present experimental conditions by substraction of the *ca.* 4-ppm difference between the ^{14}N and ^{15}N chemical shifts given in Table I.

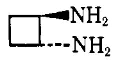
(38) Substituent parameters for ^{13}C shifts have been improved by addition of branching parameters,[30a] and presumably a similar improvement would obtain here. However, the small number of values at hand makes such a treatment of limited utility.

(39) (a) D. M. Grant and B. V. Cheney, *J. Amer. Chem. Soc.*, **89**, 5315 (1967); (b) B. V. Cheney and D. M. Grant, *ibid.*, **89**, 5319 (1967).

While the directions of the alkyl substituent effect parallel those observed in ^{13}C spectroscopy, the magnitudes differ considerably: α_N is somewhat smaller than α_C (-9.1 ppm), while β_N is almost twice as large as β_C (-9.40 ppm).[30a] It has been suggested[36] that both parameters arise in part *via* an inductive mechanism characteristic of the substituent, and in part *via* a substituent-induced distortion of the α–β bond. In the present case, a substituent-induced polarization of the lone-pair electrons could play an additional role.[40] In this connection, it is interesting to note that an even more marked effect is observed in the alkylhydrazines,[41] in which nitrogen is incorporated in one of the α–β bonds: $\alpha_N = -3.2$ ppm, $\beta_N = -24.4$ ppm. Clearly, the magnitude of the effect is atom dependent.

Further examination of the data allows extraction of some other approximate substituent constants for groups other than alkyl. Thus, $\gamma_{NH_2} = 5.2$ ppm, $\gamma_{OR} = 6.1$–9 ppm, $\gamma_{C_6H_5} = 0.8$ ppm, and $\gamma_{CN} = 2.1$ ppm. The influence of the amino and phenyl groups is rapidly attenuated as the number of intervening carbons increases beyond two. Results here and those previously reported[5] for amino alcohols and for phenylethylamine reveal a reasonable degree of additivity of substituent effects.

The γ effects of substituents cited here are all upfield shifts which seem to increase with increasing substituent electronegativity. Similar observations have been made in the ^{13}C spectra of the geometrically rigid norbornyl system and attributed to stereoelectronic perturbations of the ^{13}C shielding.[36] Such perturbations are unlikely to be the sole factor with ^{15}N shifts and, in particular, effects arising from inter- and intramolecular association are probably important, especially in the neat liquids where hydrogen bonding is expected to be extensive. Such interactions are known to influence nitrogen resonance-line positions,[42] generally resulting in downfield shifts. This factor may cause the pronounced chemical-shift difference between *cis*- and *trans*-1,2-diaminocyclobutane. The 13.5-ppm difference is similar in direction, although hardly in magnitude, to the 3.6-ppm difference between the methyl carbon resonances of *cis*- and *trans*-1,2-dimethylcyclopentane.[43] Although the geometry of the cyclobutane ring differs from that of the cyclopentane ring, so that the spatial relationships between the amino groups on the one ring do not quite correspond to those between the methyl groups on the other, hydrogen bonding is possible in the amines, both inter- and, in the cis compound, intramolecular. The difference between the two diamines will reflect a balance of steric, stereoelectronic,[36] and hydrogen-bonding effects, but the simplest interpretation is a dominant steric effect in the cis isomer.

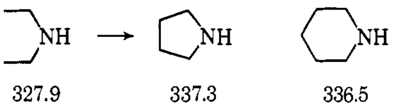


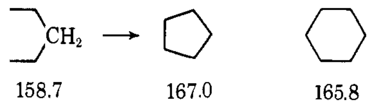
335.9 ppm

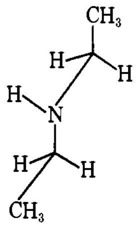
349.4 ppm

There is a marked downfield shift of about 20 ppm of the resonances associated with the conversion $CH_3(CH_2)_{n-1}NH_2 \rightarrow (CH_2)_nCHNH_2$. This is fundamentally a β effect and is rather small for the three-carbon case (-9.5 ppm). The corresponding conversions to the cyclic amines from the corresponding 2-aminoalkanes are γ effects and are accompanied by small ^{15}N chemical-shift changes in the five- and four-carbon cases, but a large upfield shift (14.3 ppm) with cyclopropylamine. The effect of the cyclopropane ring is probably too large to be ascribed to the influence of a diamagnetic ring current.[44] There may also be an inductive effect associated with the cyclopropyl group.

The effect of ring closure in which nitrogen is part of the ring rather than external to it is seen by comparing diethylamine with pyrrolidine and piperidine: the *ca.* 10-ppm upfield shift induced and the closeness of the pyrrolidine and piperidine values parallel the behavior of the ^{13}C shifts in the analogous hydrocarbons and it seems possible that constraint of the otherwise freely rotating alkyl groups into a ring induces some kind of steric shift, or else there is a large upfield shift associated with elimination of extended conformations of the type **3**.

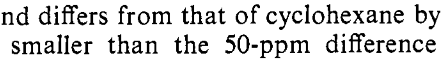






3

In comparison to the 10-ppm shift induced on formation of the five- and six-membered rings from their acyclic precursors, closure of dimethylamine[45] to ethylenimine causes an upfield shift of about 19 ppm, which agrees well with the difference between the carbon shifts of C_2 of propane[30a] and cyclopropane[30c] carbon shifts. The resonance position of the latter compound differs from that of cyclohexane by 30 ppm, a value smaller than the 50-ppm difference between piperidine and ethylenimine. Coming at about 8 ppm higher field than that for ammonia, the imine nitrogen



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(40) (a) In rigid systems, geminal and vicinal ^{15}N–H coupling constants depend on lone-pair "orientation," which may, in fact, reflect a more subtle distortion of the lone-pair orbital;[20,23] (b) see also R. S. Mulliken, *J. Chem. Phys.*, **36**, 3428 (1962).

(41) R. L. Lichter and J. D. Roberts, *J. Amer. Chem. Soc.*, in press.

(42) (a) H. Kamei, *Bull. Chem. Soc. Jap.*, 41, 1030 (1968); (b) W. M. Litchman, M. Alei, Jr., and A. E. Florin, *J. Amer. Chem. Soc.*, **91**, 6574 (1969); (c) M. Alei, Jr., A. E. Florin, and W. M. Litchman, *ibid.*, **92**, 4828 (1970); (d) L. Paolillo and E. D. Becker, *J. Magn. Resonance*, **2**, 168 (1970).

(43) M. Christl, H. J. Reich, and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 3463 (1971).

(44) (a) G. E. Maciel and G. B. Savitsky, *J. Phys. Chem.*, **69**, 3925 (1965); (b) P. H. Weiner and E. R. Malinowski, *ibid.*, 71, 2791 (1967); (c) K. M. Crecely, R. W. Crecely, and J. H. Goldstein, *ibid.*, 74, 2680 (1970).

(45) The shift for dimethylamine from ref 4 was corrected by subtracting 4 ppm to account for the apparent differences in referencing.

shift is the highest so far known for a neutral organic compound. The general correspondence with the cyclopropane carbon shift, which has been interpreted in terms of ring current induced diamagnetic shielding,[30c] suggests a similar explanation for nitrogen resonance as well. Whether this is correct or not, the ^{15}N shifts correspond to the substantial diamagnetic shieldings observed for the ^{13}C resonances of aziridine.

Catalytic Mode, Solvent Isotope Effects, and Transition-State Structure in Hydride Expulsion from Silicon[1,2]

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Richard L. Schowen,*[3] and J. K. Lee

Contribution from the Department of Chemistry, University of Kansas,
Lawrence, Kansas 66044. *Received May 12, 1971*

Abstract: Triphenylsilane, tribenzylsilane, and tributylsilane are methanolyzed to hydrogen and the methoxysilanes in a specific methoxide catalyzed reaction ($\beta > 0.8$ for triphenylsilane, > 0.5 for tribenzylsilane, > 0.7 for tributylsilane in phenol–phenoxide buffers). Deuterated silanes react more slowly by factors of 1.20 ± 0.08, 1.35 ± 0.09, and 1.40 ± 0.10, respectively. The protiated compounds have $\Delta G^*_{298} = 18.17 \pm 0.02, 20.33 \pm 0.02, 21.89 \pm 0.02$ kcal/mol, $\Delta H^* = 9.4 \pm 0.3, 11.4 \pm 0.3, 12.3 \pm 0.5$ kcal/mol, and $\Delta S^* = -29.5 \pm 1.8, -30.0 \pm 1.8, -32.1 \pm 3.2$ gibbs/mol, respectively. For triphenylsilane, the second-order rate constants k_n in mixtures of CH_3OH and CH_3OD (mole fraction n) are given by $k_n = k_0(1 - n + 0.22n)/(1 - n + 0.76n)^3$. The transition state strongly resembles a quinquevalent-silicon compound, the Si–H bond being strong and the H–H bond of the product still weak. The absence of a nonbonded electron pair on the leaving group prevents electrophilic assistance by prior-protonation or solvation-catalysis mechanisms, forcing concerted donation of a solvent proton to the hydride in the course of its departure. Proton transfer to this very basic species is little advanced in the transition state so that the reaction is unselective and general acids do not compete with solvent.

Understanding the catalysis of very unfavorable processes is central to development of a comprehensive theory of catalytic action. The hydride ion, H^-, is a very poor leaving group because it is extremely basic and because, when bonded, it has no lone pair of electrons for attachment of an acid catalyst to aid its departure. Nevertheless, it is displaced by nucleophiles from silicon centers with simultaneous bonding to a solvent proton to form a hydrogen molecule.[4] The nucleophile must bind tightly to the silicon in order to effect this displacement, as shown by the strong acceleration produced by electron withdrawal at silicon (Hammett ρ values of $+2$ to $+5$).[5] Since donation of nucleophile lone-pair electons into silicon d orbitals could give relative negative charge at silicon even if the leaving group bond is broken considerably, the degree to which the Si–H bond has been broken and the H–H bond formed in the transition state is not known. The hydride isotope effects,[6] k_{SiH}/k_{SiD} (*e.g.*, 1.15 for triphenylsilane in wet piperidine at 25°), are small compared to the maximum estimated from complete loss of the isotopic zero-point energy in the reactant stretching mode (k_H/k_D about 4)[7] so that it has been presumed that the transition state is unsymmetrical, *i.e.*, either very reactant-like (strong Si–H, weak H–H) or very product-like (weak Si–H, strong H–H). Kaplan and Wilzbach[6b] suggested that the H–H bond is completely formed on the basis of simple model calculations, but their only "reactant-like" model was hydride-ion-like rather than having a strong Si–H bond. Thornton[8] arrived at the opposite conclusion (strong Si–H bond, weak H–H bond) by estimating the equilibrium isotope effect for complete formation of products as $K_H/K_D = 1.7$. If the isotope effect indeed passes smoothly from 1.00 for an exactly reactant-like transition state through a maximum of about 4 for a "symmetrical" transition state and down to 1.7 for an exactly product-like structure, then the observed isotope effect of 1.15, being less than 1.7, could correspond only to a reactant-like structure. The problem with this conclusion is that the assumption of the smooth rise and fall of the isotope effect about

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(1) Catalysis in Organosilicon Chemistry. III. For part II, see R. L. Schowen and K. S. Latham, *J. Amer. Chem. Soc.*, **89**, 4677 (1967).

(2) This research was supported by the National Science Foundation and the National Aeronautics and Space Agency (University of Kansas Institutional Grant). Data reduction was carried out at the University of Kansas Computation Center. For further details, see K. O'Donnell, Ph.D. Thesis, University of Kansas, 1968, and R. Bacon, M.S. Thesis, University of Kansas, 1970.

(3) Holder of a Research Career Development Award of the National Institute of General Medical Sciences.

(4) (a) R. L. Schowen and R. Bacon, *Tetrahedron Lett.*, 4177 (1970), demonstrated the bonding of solvent proton to expelled hydride to be concerted with Si–H cleavage. The reaction has long been known. Its fundamental aspects were reviewed in (b) C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, Chapter 6.

(5) (a) H. Gilman and G. E. Dunn, *J. Amer. Chem. Soc.*, **73**, 3404 (1951); (b) G. Schott and C. Harzdorf, *Z. Anorg. Allg. Chem.*, **306**, 180 (1960); (c) O. W. Steward and O. R. Pierce, *J. Amer. Chem. Soc.*, **83**, 1916 (1961); (d) G. Schott and D. Gutschick, *Z. Anorg. Allg. Chem.*, **325**, 175 (1963); (e) J. Hetflejs, F. Mares, and V. Chvalovsky, *Collect. Czech. Chem. Commun.*, 30, 1643 (1965); (f) G. Schott, P. Hansen, S. Kuhla, and P. Zwierz, *Z. Anorg. Allg. Chem.*, 351, 37 (1967).

(6) (a) L. Kaplan and K. E. Wilzbach, *J. Amer. Chem. Soc.*, **74**, 6152 (1952); (b) L. Kaplan and K. E. Wilzbach, *ibid.*, **77**, 1297 (1955); (c) C. Brynko, G. E. Dunn, H. Gilman, and G. S. Hammond, *ibid.*, **78**, 4909 (1956); (d) L. H. Sommer, D. R. Weyenberg, and P. G. Campbell, Abstracts of the 135th Meeting of the American Chemical Society, Boston, Mass., 1959, p 23M.

(7) The stretching frequencies are 2120 cm^{-1} ($(C_6H_5)_3SiH$) and 1549 cm^{-1} ($(C_6H_5)_3SiD$), as determined in this work and in agreement with L. Kaplan, *J. Amer. Chem., Soc.*, **76**, 5880 (1954).

(8) E. R. Thornton, *J. Org. Chem.*, **27**, 1943 (1962).