Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy. Natural-Abundance Nitrogen-15 Chemical Shifts of Aziridines and Azetidines

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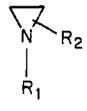
^{15}N chemical shifts of 15 alkylaziridines, eight phenylaziridines, and six *N*-alkylazetidines have been measured at the natural-abundance level. The change in chemical shift with ring size up to seven atoms parallels ^{13}C values of the corresponding carbocycles. The effect of N-methylation on the resonance positions decreases with ring size. *N*-Alkylaziridines display β and γ effects analogous to acyclic amines; the β effect decreases with branching at the α-carbon. Ring alkyl groups also induce typical β and γ shifts, and the effect of γ substitution depends on the degree of β-carbon branching. The influence of ring methyl groups on aziridine shifts is additive except for *cis*-2,3- and -1,2-dimethylaziridine in which steric interactions and distortions of molecular geometry probably play a role. ^{15}N shifts of 2-phenylaziridines appear to display the influence of conjugation between the two rings. The deshielding associated with that interaction is attenuated when the molecular geometry is distorted from the preferred bisected conformation. *N*-Alkylazetidines display normal substituent effects except for *N*-*tert*-butylazetidine, which exhibits a *shielding* β effect. This is associated with steric interactions between the *tert*-butyl methyls and the ring hydrogens.

The usefulness, as well as some of the limitations, of ^{15}N chemical shift measurements for the study of molecular geometry has been amply illustrated.[1-3] With a few scattered exceptions (see below), structural and geometrical effects have been derived from acyclic compounds or from relatively unstrained alicyclics. Indeed, chemical shift data for three- and four-membered nitrogen heterocycles (aziridines and azetidines) are sparse. Aziridine (1) itself

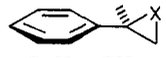


1, $R_1 = R_2 = H$
2, $R_1 = PO(OMe)_2$, $R_2 = CH_3$

is unusually shielded compared with piperidine[4] and in this respect resembles the ^{13}C behavior of cyclopropane compared with cyclohexane.[5] The nitrogen of several ring-methylated aziridine phosphoramidates like **2** is also highly shielded, and the chemical shifts vary slightly with the geometry of methyl substitution.[6] Only one value for an azetidine, that for the phosphoramidate,[6] is known.

Here we present ^{15}N chemical shifts for 15 alkylaziridines, eight phenylaziridines, and six alkylazetidines. We undertook this study in order to further characterize the ^{15}N chemical shift behavior of these strained systems and to determine how the response of the nitrogens to substituents compared with that of unstrained systems. Especially in the aziridines, substituent geometries at the ring are well-defined, so that analysis of geometrical contributions to substituent effects was expected to be reasonably straightforward. Our observations facilitate use of nitrogen chemical shifts for structure analysis in more complex systems which contain aziridine and azetidine rings.

The 2-phenylaziridines are of interest also in connection with the question of conjugation between the phenyl group and three-membered rings. The sterically less favored bisected conformation **3**, in which the Walsh cyclopropane



3, X = CH_2
4, X = NH

orbitals[7] can interact with the benzene π system, has been well established for phenylcyclopropane itself.[8-10] Calculations[9] suggest that a similar conformation is preferred for 2-phenylaziridine, **4**, with conjugative electron donation from the aziridine into the phenyl ring.[10] Faraday-effect measurements indicate extensive conjugation between the rings that is attenuated by geminal- or cis-alkyl substitution.[11] ^{13}C chemical shifts of phenylaziridines[12] have also been interpreted in terms of electron transfer from the aziridine to the phenyl ring. It was our intent to determine if the ^{15}N shifts as well might serve as a probe for this effect.

Experimental Section

Materials. Pyrrolidine, *N*-methylpyrrolidine, piperidine, *N*-methylpiperidine, and perhydroazepine (azacycloheptane, **6**) were purchased from Aldrich Chemical Co. 2-Methylaziridine (**1h**) was purchased from Interchemical Co. *N*-Methylazetidine (**5b**) was obtained from Professor A. T. Bottini. *N*-Methylperhydroazepine was obtained by methylation of **6** with formaldehyde and formic acid. All other compounds were prepared according to literature procedures.[13-18] Structures were confirmed by

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(2) Duthaler, R. O.; Roberts, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3889–95.
(3) Fanso-Free, S. N. Y.; Furst, G. T.; Srinivasan, P. R.; Lichter, R. L.; Nelson, R.; Panetta, J.; Gribble, G. W. *J. Am. Chem. Soc.* **1979**, *101*, 1549–53.
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(7) Bernett, W. A. *J. Chem. Educ.* **1967**, *44*, 17–24.
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(11) Martino, R.; Lopez, A.; Castan, P. *Tetrahedron Lett.* **1977**, 3255–8.
(12) Mison, P.; Chaabouni, R.; Diab, Y.; Martino, R.; Lopez, A.; Lattes, A.; Wehrli, F. W.; Wirthlin, T. *Org. Magn. Reson.* **1976**, *8*, 79–89.
(13) (a) Leighton, P. A.; Perkins, W. A.; Renquist, M. L. *J. Am. Chem. Soc.* **1947**, *69*, 1540. (b) Reeves, W. A.; Drake, G. L.; Hoffpauir, C. L. *Ibid.* **1951**, *73*, 3522. (c) Bottini, A. T.; Roberts J. D. *Ibid.* **1958**, *80*, 5203–8.
(14) (a) Fowler, F. W.; Hassner, A.; Levy, L. A. *J. Am. Chem. Soc.* **1967**, *89*, 2077–82. (b) Hassner, A.; Matthews, G. J.; Fowler, F. W. *Ibid.* **1969**, *91*, 5046–54.

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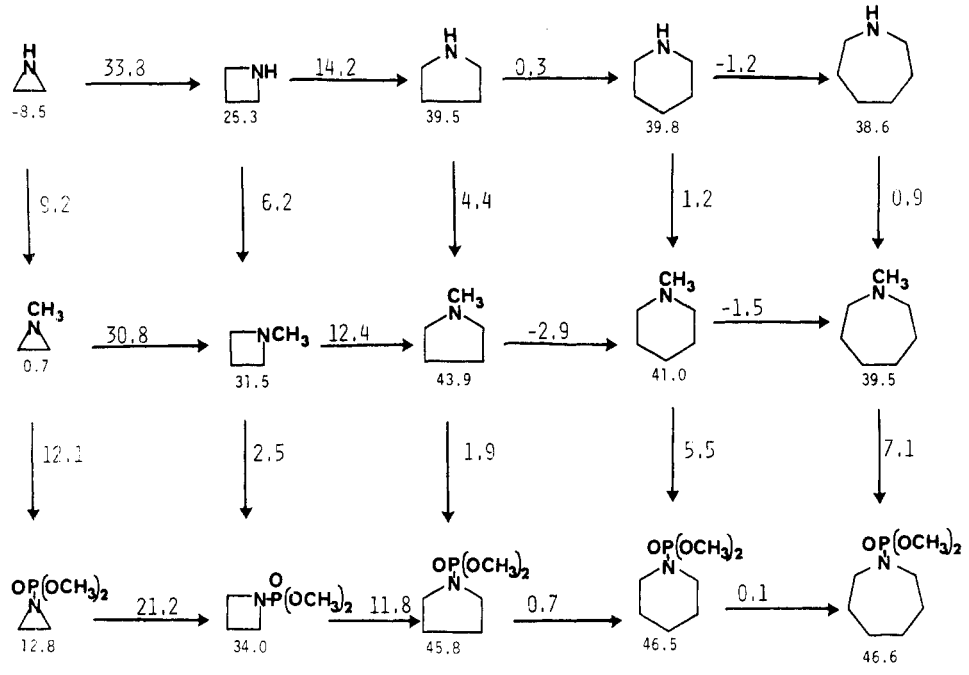
Scheme I



boiling-point comparisons and by determination of ^1H and ^{13}C NMR spectra.

Spectra. With the exception of **4f**, which was 1.8 M, natural-abundance ^{13}C and ^{15}N spectra of 4–8 M solutions of all the distilled compounds in $CDCl_3$ were determined at 25.03 and 10.09 MHz, respectively, by the pulsed Fourier transform method using a JEOL PS/PFT-100 spectrometer equipped with the JEOL EC-100 data system. For ^{13}C spectra, a spectral width of 5 kHz over 4K or 8K data points was used, with pulse angles of ~20° and a repetition rate of 1–2 s. Chemical shifts were measured with respect to internal $(CH_3)_4Si$. ^{15}N spectra were obtained with a 5-kHz spectral width, 4K or 8K data points, and ~20° pulse angles. For secondary amines a repetition rate of 1–3 s was used. Tertiary amines were run with 10–20 mg of chromium tris(acetylacetonate), $Cr(acac)_3$, to shorten anticipated longer T_1 values. This allowed a repetition rate of 3–5 s to be used. The effect of this amount of $Cr(acac)_3$ is expected to be <0.5 ppm.[19a] Indeed, the combined effects of solvent, relaxation reagent, and bulk susceptibility are expected to introduce an uncertainty of <1 ppm.[19b,c] Chemical shifts were measured with respect to partially enriched $CH_3{}^{15}NO_2$ in a concentric capillary and are reported on the anhydrous ammonia scale.[19d]

Results

^{15}N chemical shifts of *N*-alkylaziridines **1a–g** and ring-methylated aziridines **1h–o** are given in Table I. Similar data for phenylaziridines **4a–h** are presented in Table II. The tables also include for comparison the ^{13}C chemical shifts of carbons in the same compounds occupying corresponding positions. For example, the ^{15}N resonance position in **1l** is compared with the ^{13}C shift of C-3. ^{15}N data for **1d,f,m–o** and **4c–d,f–h** do not lend themselves to these comparisons because the corresponding aziridines listed in the last two columns of Tables I and II were not available (**1d,f**) or were substituted differently at the nitrogens and carbons under comparison.

The value of δ_N for **1a** differs by a few parts per million from the earlier reported value (−11.1 ppm).[4,20] Some of

Table I. ^{15}N Chemical Shifts of Alkylaziridines[a]

no.	R	δ_N	$\Delta\delta_N$[b]	δ_C[c]	$\Delta\delta_C$[b]
1a	H	−8.5	0.0	18.2	0.0
1b	CH_3	0.7	9.2	25.1	6.9
1c	CH_3CH_2	16.4	24.9	31.7	13.5
1d	$CH_3CH_2CH_2$	13.6	22.1		
1e	$(CH_3)_2CH$	30.2	38.7	37.2	19.0
1f	$CH_3(CH_2)_3$	13.6	22.1		
1g	$(CH_3)_3C$	33.5	42.0	39.7	21.5

no.	R	δ_N	$\Delta\delta_N$[b]	δ_C[c]	$\Delta\delta_C$[b]
1h	CH_3	10.5	19.0	25.8	7.6
1i	CH_3CH_2	7.9	16.4	24.7	6.5
1j	$(CH_3)_2CH$	7.3	15.8	24.0	5.8
1k	$(CH_3)_3C$	3.4	11.9	21.4	3.2

no.	R_1	R_2	R_3	R_4	δ_N	$\Delta\delta_N$[b]	δ_C[c]	$\Delta\delta_C$[b]
1l	CH_3	CH_3	H	H	28.6	37.1	32.5	14.3
1m	CH_3	H	H	CH_3	15.9	24.4		
1n	H	CH_3	CH_3	H	30.7	39.2		
1o	CH_3	H	CH_3	H	25.0	33.5		

[a] In parts per million from $NH_3(l)$; see Experimental Section. Positive values denote deshielded nucleus relative to reference. Uncertainty ±0.1 ppm. [b] $\Delta\delta_i = \delta_i - \delta_{1a}$. [c] Reference 12, chemical shifts in parts per million from $(CH_3)_4Si$.

(20) The value for **1a** in ref 4 was converted to the ammonia scale by subtraction of the reported shift from 375.8 ppm. See ref 1, pp 28–33, for a discussion of these conversion constants.

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Table II. ^{15}N Chemical Shifts in 2-Phenylaziridines[a]

no.	R_1	R_2	R_3	δ_N	$\Delta\delta_N$[b,d]	δ_C[c]	$\Delta\delta_C$[b,d]
4a	H	H	H	18.2	26.7	29.2	11.0
4b	CH_3	H	H	33.1	41.6 (45.7)	35.0	16.8 (18.6)
4c	H	CH_3	H	21.5	30.0 (45.7)		
4d	H	H	CH_3	39.3	47.8 (45.7)		
4e	C_6H_5	H	H	36.1	44.6 (53.4)	35.3	17.1 (22.0)
4f	H	C_6H_5	H	22.3	30.8 (53.4)		
4g	H	H	C_6H_5	43.4	51.9 (53.4)		
4h	CH_3	CH_3	H	41.5	50.0 (64.7)		

[a-c] See footnotes to Table I. [d] Parenthesized values are those predicted on the basis of additivity of substituent effects from Table I and from 4a.

Table III. ^{15}N Chemical Shifts of *N*-Alkylazetidines[a]

no.	R	δ_N	no.	R	δ_N
5a	H	25.3	5d	$CH_3CH_2CH_2$	42.4
5b	CH_3	31.5	5e	$(CH_3)_2CH$	56.3
5c	CH_3CH_2	45.0	5f	$(CH_3)_3C$	52.0

[a] See footnote to Table I.

this difference may be attributable to the difference in referencing, but the bulk of it undoubtedly arises from the difference in measurement conditions: the earlier value was for the pure liquid, while the present values are for solutions. Nonetheless, the aziridine nitrogen clearly remains unusually shielded by ~47 ppm compared with that of piperidine (39.8 ppm) measured under the same conditions. Similar behavior is displayed by the aziridine phosphoramidates,[6] which are shielded by ~35 ppm relative to larger rings.

Table III gives the first ^{15}N chemical shifts for *N*-alkylazetidines **5a–f**. Chemical shifts of **6** and its *N*-methyl derivative, of pyrrolidine and of piperidine are reported in Scheme I.

Discussion

Determination of the aziridine and azetidine chemical shifts allows for the first time a comparison of the effect of ring size on nitrogen shifts (Scheme I). Qualitatively, the effect parallels that displayed by cycloalkane ^{13}C shifts: a large shielding difference between the three- and four-membered rings and a much smaller difference from four to five and more ring atoms. Quantitatively, the shifts do not correlate very well with the ^{13}C shifts of the corresponding hydrocarbons. Undoubtedly, the nitrogen lone pair influences the screening in a manner not appropriate for the hydrocarbons. A good correlation would be expected to exist with the corresponding protonated cyclic amines, analogous to what has been demonstrated for acyclic amines.[2]

Scheme I also summarizes the effect of N-methylation as a function of ring size. The magnitude of the deshielding α effect is seen to decrease with an increase in ring size. This behavior is unlike the corresponding ^{13}C behavior. However, the α effect in aliphatic amines is known not to be consistently deshielding.[2,21] Indeed, conversion of primary or secondary amines which are branched at the α-carbon to the corresponding tertiary amines can result in a *shielding* of ~25 ppm. A striking

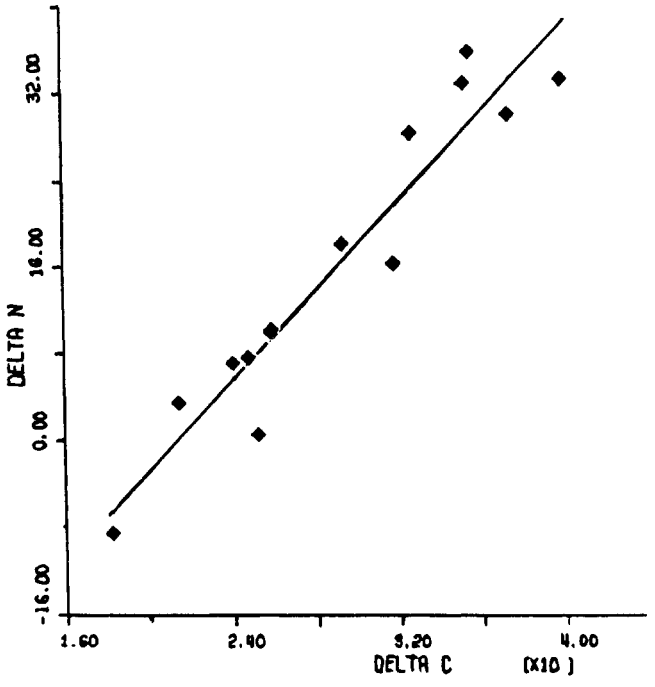
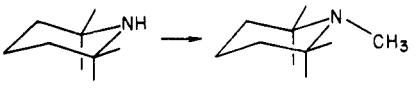


Figure 1. Plot of ^{15}N chemical shifts of ring-substituted aziridines vs. ^{13}C chemical shifts of the corresponding carbons (see text).

example exists in 2,2,6,6-tetramethylpiperidine, N-methylation of which shields the nitrogen by −31 ppm.[22]



$\Delta\delta$ = −31 ppm

These results have been discussed in terms of possible changes in lone-pair σ-bond interactions and putative steric interactions between the *N*-methyl and axial 2-methyl groups. The situation is clearly highly complex. Hybridization–and hence electronic description around the nitrogen–changes as a function of ring size, as do the lone-pair orientation and the degree of flattening of nitrogen, so no obvious single explanation emerges. It is interesting that the same trend exists for the phosphoramidates[6] (Scheme I): the deshielding compared with the parent amines also decreases with ring size. Here, the nitrogen lone pairs in the five- and six-membered rings are expected to interact more strongly with the $P(O)(OCH_3)_2$ group and thus be less easily characterized according to spatial orientation.[23] The parallel results in the two series

(21) Reference 1, p 41.

(22) Duthaler, R. O.; Williamson, K. L.; Giannini, D. D.; Bearden, W. H.; Roberts, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 8406–12.

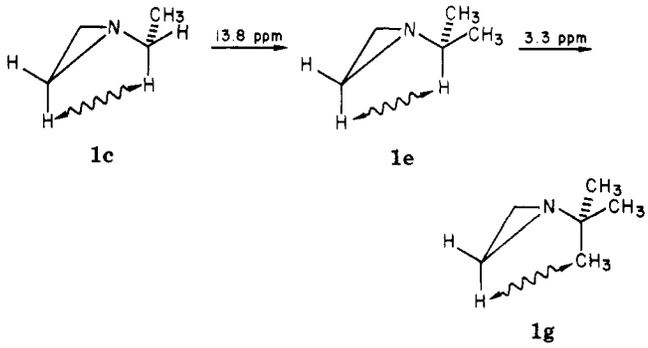
suggest that the difference in the α effects is related more to changes relating to the σ skeleton than to any lone-pair interactions.

Aziridines. In general, aziridine ^{15}N shifts parallel the ^{13}C shifts of corresponding carbons in the same compounds. Figure 1 shows a plot of the 13 compounds where these structural conditions are met; the correlation coefficient is 0.953, and the slope is 2.1 ppm N/ppm C. This value is characteristic of that observed for many ^{15}N–^{13}C correlations.[2-4] The ^{15}N shifts of **1a,h,l,n,o** also correlate (r = 0.997, slope = 2.16 ppm N/ppm C) with the ^{13}C shifts of the corresponding cyclopropanes.[24,25]

It is also interesting to note that there is a relationship between the ^{15}N shifts of **1a,h,l, 5a**, and pyrrolidine and the corresponding reported photoelectron (PE) ionization potentials of the lone-pair electrons.[26a] The direction of the trend is such that lone-pair electrons are removed more easily from the less highly shielded nitrogen. We have shown previously that PE ionization potentials and ^{15}N chemical shifts can correlate in cases where lone-pair delocalization is important.[26b] An explanation for the aziridines and azetidines is less straightforward. The change in the ionization potential with ring size is consistent with increased p character in the lone-pair orbital. That, however, is expected to increase the average orbital radius and hence shield the nitrogen,[1] contrary to observation. A simple diamagnetic effect, associated with decreased electron density because of the change in lone-pair character, cannot be excluded. However, this seems unlikely because that effect is justifiably believed not to be large enough to account for the experimental observations.

***N*-Alkylaziridines.** Comparison of compounds **1b,c,d,f** shows that β and γ substitution deshield and shield the nitrogen by 15.7 and −2.8 ppm, respectively, while substitution δ to the nitrogen has no influence. These effects are comparable to those observed for *unbranched* acyclic aliphatic amines.[2] The chemical shifts of these compounds may be compared profitably with the corresponding *N,N*-dimethylalkylamines, i.e., the compounds derived by formal opening of the aziridine ring. The shifts of aziridines **1b,c,f** differ by a relatively constant amount, −8.2 to −8.6 ppm, from those of the comparison compounds so derived.[2,27] Thus, while the chemical shift region of the aziridine nitrogen is characteristic of the three-membered ring, the response of the nitrogen to alkyl substituents is normal. This is also the case for ring-methyl aziridines (see below).

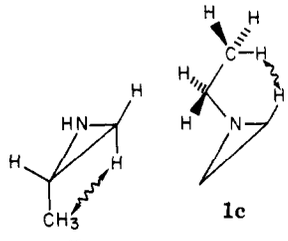
The β effect on the chemical shifts deserves somewhat closer scrutiny. In the series **1b → 1c → 1e → 1g**, the additional deshielding diminishes progressively; the smallest effect, 3.3 ppm, exists for **1g** compared with **1e**. This decrease in the β effect with increased branching at the α-carbon has been noted in both ^{13}C[28] and ^{15}N[2] shifts and, of most relevance to the discussion here, in the ^{13}C shifts of secondary aziridines.[12] It has been associated with an increase in the likelihood of steric interactions between



1c **1e** **1g**

the β methyl carbons and ring hydrogens. Staggered conformations which minimize these interactions are possible in **1c** and **1e** but are less likely in **1g**. A very similar argument was presented to rationalize analogous trends in a series of *N*-alkylacetamides.[29]

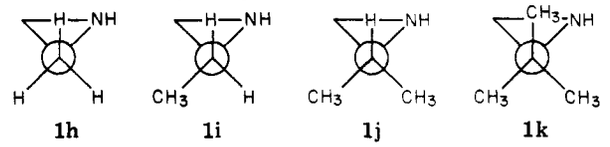
2-Alkylaziridines. Effects of monoalkyl substitution on the ring may be compared with those of *N*-alkyl substitution. The methyl group in 2-methylaziridine (**1h**) is a β substituent, whose 19.0-ppm deshielding of the nitrogen is larger than the 15.7 ppm arising in going from **1b** to **1c**. Qualitatively, a similar but smaller effect is seen in the corresponding ^{13}C shifts (**1b → 1c** = 6.6 ppm, **1a → 1h** = 7.6 ppm). Examination of models shows that the rigid ring of **1h** holds the C-2 methyl further from the hydrogen at C-3 compared with distances which are accessible in the torsionally more flexible **1c**. To the extent that these



1h **1c**

interactions lead to shielding of the nitrogen, the influence would be larger in **1c** than in **1h**; hence the β effect in **1h** is more deshielding. Support for this picture is seen in the ^{13}C shift of C-2 in *N*-methylaziridine (**1b**) (27.9 ppm) compared with that in aziridine (**1a**) (18.2 ppm). Here, the 9.7-ppm β effect on C-2 in **1b** is larger than that on C-3 in 2-methylaziridine (**1h**), 7.6 ppm. Because of the ability of the nitrogen geometry to distort, the *N*-methyl group is expected to be held further away from the C(2)–H bond and hence to induce a smaller opposing shielding interaction.

Replacement of methyl with ethyl at C-2 (**1h → 1i**) induces a shielding γ effect of −2.6 ppm, a value comparable to that in acyclic amines. A branching effect exists with further γ substitution, in which a minimum in the extent of shielding is observed with two γ substituents. The largest effect arises with three such substituents. The same trend is seen in the corresponding ^{13}C shifts. As shown in the depictions of the staggered conformations expected to be most stable, the ethyl and isopropyl groups in **1i** and **1j** may adopt conformations in which the γ-



1h **1i** **1j** **1k**

methyl groups are oriented away from the ring nitrogen

(23) Buchanan, G. W.; Morin, R. G. *Can. J. Chem.* **1979**, *57*, 21–6.
(24) Monti, J. P.; Faure, R.; Vincent, E. J. *Org. Magn. Reson.* **1975**, *7*, 637–8.
(25) Inclusion of **4a** and **4e** in the comparison (Subbotin, O. A.; Kozmin, A. S.; Grishin, Y. K.; Sergeyev, N. M.; Bolesov, I. G. *Org. Magn. Reson.* **1972**, *4*, 53–62) lowers the correlation coefficient to 0.979 and increases the slope to 2.34 ppm N/ppm C.
(26) (a) Yoshikawa, K; Hashimoto, M.; Morishima, I. *J. Am. Chem. Soc.* **1974**, *96*, 288–9. (b) Sibi, M. P.; Lichter, R. L. *J. Org. Chem.* **1977**, *42*, 2999–3004; **1979**, *44*, 3017–22.
(27) The chemical shifts reported in ref 2 were converted to the ammonia scale by subtraction from 374.0 ppm.
(28) Grutzner, J. B.; Jautelat, M.; Dence, J. B.; Smith, R. A.; Roberts, J. D. *J. Am. Chem. Soc.* **1970**, *92*, 7107–20.
(29) Westerman, P. W.; Roberts, J. D. *J. Org.* Chem. **1978**, *43*, 1177–9.

and carbon atoms. The *tert*-butyl group of **1k**, however, always has a methyl group which is quasi-synclinal to the ring atoms; hence the shielding is expected to be largest in this compound.

Geminal and trans vicinal dimethyl substitution induce effects which are nearly additive. For **1l**, the difference between the observed chemical shift and that calculated from **1h** is −0.9 ppm, which is fortuitously identical with the corresponding deviation between the observed and calculated ^{13}C chemical shifts. Similarly, the corresponding deviation between calculated and observed ^{15}N shifts for trans-disubstituted **1n** is also small. Only in the cis-disubstituted **1o** does a substantial deviation, −4.5 ppm, arise. This additional shielding undoubtedly reflects sterically induced changes in both the bond angles and the dihedral angles of the methyl groups with respect to the ring, compared with the monomethyl compound.

The deviation (−3.8 ppm) of *N*,2-dimethylaziridine (**1m**) from the value anticipated by comparison of **1b** and **1h** is comparable to that for **1o**. Aziridine **1m** would not be expected to be constrained in a cis arrangement. These results reaffirm the sensitivity of nitrogen chemical shifts to changes in geometry.

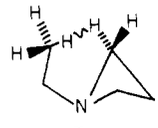
2-Phenylaziridines. One object of this study was to determine whether ^{15}N resonance positions of 2-phenylaziridines reflect conjugation between the phenyl group and the π-type orbitals of the three-membered ring. A possible indication of this may be seen by comparing the shift difference between phenylaziridine (**4a**) and aziridine (**1a**), 26.7 ppm, with that between 1-phenylethylamine and ethylamine, 18.7 ppm.[1,4] It is tempting to attribute the additional 8-ppm deshielding to this type of conjugative interaction which, from Faraday-effect studies,[11] has been suggested to be intermediate between styrene and allylbenzene.

These influences require the bisected conformation **4** and hence should be attenuated by steric interactions with appropriately placed ring methyl groups. As noted above, effects of ring-methyl substitution on the nitrogen shifts are additive, except for cis vicinal methyl groups, where a deviation from additivity of −4.5 ppm arises. On the basis of additivity, the chemical shifts of the methylphenylaziridines **4b–d** are expected to be 45.7 ppm. The trans vicinally substituted **4d** displays a positive deviation of +2.1 ppm, which is in the same direction as the +1.2-ppm deviation of **1n**. While the deviation for **4d** is very small, it is consistent with increased interaction between the rings inferred from Faraday-effect measurements on *trans*-3-alkyl-2-phenylaziridines.[11] The deviations for the geminal **4b** and cis vicinal **4c** are −4.1 and −15.7 ppm, respectively. It is likely that these larger deviations for the methylphenylaziridines may be ascribed to sterically inhibited conjugation between the two ring systems. This would be expected to be smaller for the geminal **4b** in which the substituents are widely separated.[30] Similarly, severe steric interactions in **4c** would more substantially inhibit delocalization and hence shield the nitrogen. In the trisubstituted **4h**, the measured ^{15}N shift deviates by −14.7 ppm from the predicted value of 64.7 ppm, assuming perfect substituent additivity. When compared with the −15.7-ppm deviation for **4c**, the effect of geminal substitution on the carbon which bears a phenyl group that is already torsionally distorted appears to be essentially negligible. Since the deviation for **4b**, some of which may arise from geometrical distortions of the phenyl group, is itself small, this conclusion is reasonable. Indeed, the effect of an additional trans vicinal methyl group on **4c** (**4c** → **4h**, 20.0 ppm) is identical with that arising without a phenyl group (**1h** → **1n**, 20.2 ppm).

While the discussion above has focussed on sterically inhibited conjugation as the origin of the extra shielding, it should be recognized that some of the influence may arise from a "γ effect" analogous to that in the aliphatic amines. This is because the ortho carbons of the phenyl group are γ to the aziridine nitrogen, and their influence on the ^{15}N resonance positions will depend very much on their geometrical disposition.

The chemical shifts of diphenylaziridines **4e–g** correlate remarkably well with those of **4b-d** (r = 1.00, slope = 1.19), but the deviations from additivity (based on **4a**) are much larger for **4e** (−8.8 ppm) and **4f** (−22.6 ppm). The deviation from additivity for **4g** is small (−1.5 ppm) and may be rationalized in terms of competitive cross conjugation of the two rings with the aziridine ring.

***N*-Alkylazetidines.** The values given in Table III are the first reported for alkylazetidines. The effect of N-methylation was discussed above in connection with ring size. Single β and γ substituents (**5c** and **5d**) respectively deshield and shield the nitrogen by amounts comparable to those in the aziridines, although the β effect is somewhat smaller for the azetidines (13.5 vs. 15.7 ppm). A second β substituent (**5e**) deshields the nitrogen by an additional but lesser amount (11.3 ppm; cf. **1e**, shift = 13.8 ppm). Surprisingly, the third β substituent in **5f** actually *shields* the nitrogen by −4.3 ppm. To our knowledge, this is the first example of a shielding β effect in ^{15}N or ^{13}C NMR spectroscopy. To rationalize the decreasing β effect with increased α-carbon branching in the aziridines, a compensating shielding arising from 1,3 H···H interactions between the β C–H and the C(2)–H bonds was proposed. Molecular models show that such interactions could be possible also in the puckered azetidines.[31] The proton on C-2 can be held in a more pseudoaxial position, placing it closer to the methyl group in the conformation shown in **5c**. To the extent that this interaction is attainable, it may lead to additional shielding.



5c

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Registry No. **1a**, 14942-88-2; **1b**, 72443-20-0; **1c**, 72443-21-1; **1d**, 72443-22-2; **1e**, 72443-23-3; **1f**, 72443-24-4; **1g**, 72443-25-5; **1h**, 72443-26-6; **1i**, 72443-27-7; **1j**, 72443-28-8; **1k**, 72443-29-9; **1l**, 72443-30-2; **1m**, 72443-31-3; **1n**, 72443-32-4; **1o**, 72443-33-5; **4a**, 72443-34-6; **4b**, 72443-35-7; **4c**, 72443-36-8; **4d**, 72443-37-9; **4e**, 72443-38-0; **4f**, 72443-39-1; **4g**, 72467-42-6; **4h**, 72443-40-4; **5a**, 72443-41-5; **5b**, 72443-42-6; **5c**, 72443-43-7; **5d**, 72443-44-8; **5e**, 72443-45-9; **5f**, 72443-46-0.

(30) The H–C–H bond angle for aziridine itself is reported to be 115°; this would be expected to widen somewhat upon geminal substitution: Bak, B.; Skaarup, S. *J. Mol. Struct.* **1971**, *10*, 385.

(31) Mastryukov, V. S.; Dorofeeva, O. V.; Vilkov, L. V. *J. Mol. Struct.* **1976**, *34*, 99.