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^{15}N NMR AND PHOTOELECTRON SPECTROSCOPIC STUDIES OF SMALL HETEROCYCLES

by

KENNETH CRIMALDI

A dissertation submitted tc the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

1981

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CHAPTER I

INTRODUCTION

^{15}N NMR Spectroscopy

Historical Background

Determination of nitrogen nuclear magnetic resonance (nmr) properties is now recognized to be of great value to chemists. The first example of structure determination using nitrogen chemical shifts (1) appeared in 1957, early in the development of nmr techniques. In that work, as in all of the earlier nitrogen nmr work, the more abundant ^{14}N nucleus was observed. Enrichment with ^{15}N made possible the first detection of ^{15}N resonances in 1964 (2). The beginning of ^{15}N nmr as a practical technique came in 1971-1972 with the observation of ^{15}N resonances at the natural-abundance level. Groups headed by J. D. Roberts, using time-averaging frequency-sweep techniques (3), and E. W. Randall, using the pulsed Fourier-transform method (4), reported the first systematic studies of compounds with the same functional group. In the period following, interest in ^{13}C nmr led to rapid advances in spectrometer technology. Together with insight into the effects of exchange processes, relaxation rates, and the nuclear Overhauser

effect, these advances have made practical (although not trivial) the observation of ^{15}N resonances at the natural-abundance level (5).

NMR Properties of the Nitrogen Nuclei

The nmr properties of ^{14}N and ^{15}N nuclei are collected in Table I. Each nucleus has characteristics which lead to increased experimental difficulties relative to those encountered in observation of ^{1}H or ^{13}C.

Nitrogen-14, although more abundant, has far lower sensitivity than an equal number of protons. Sensitivity, S, is a function of the total number of nuclei N, magnetic field strength B_o, temperature T and magnetogyric ratio γ.

$$S \quad \alpha \quad \frac{N \, B_o^{\,2} \, \gamma^{\,3}}{T}$$

The smaller magnetogyric ratios of both nitrogen nuclei compared to ^{1}H result in their lower sensitivities.

In addition, the ^{14}N nucleus has a spin quantum number I=1. Any nucleus with I>1/2 has a quadrupole moment, which provides the dominant relaxation mechanism. With the exception of compounds where the local electric field gradients are spherically symmetrical, such as ammonium ions and isonitriles, ^{14}N relaxation times are very short and

Table I Comparison of ^{14}N and ^{15}N Nuclear Properties

	^{14}N	^{15}N
Natural abundance	99.64%	0.365%
Spin quantum number	1	1/2
NMR frequency at 2.35 Tesla[a]	7.23 MHz	10.09 MHz
Sensitivity relative to proton for equal number of nuclei	0.00101	0.00104
Sensitivity relative to carbon-13 at natural isotopic abundance	17.22	0.0214
Magnetogyric ratio[b]	1.934×10^3	-2.71×10^3
Electrical quadrupole moment	1.54×10^{-2}	0

a. Magnetic field for proton resonance at 100 MHz.

b. In rad/gauss.

lead to substantial line broadening. This may be alleviated somewhat by decreasing motional correlation times, which increases relaxation times and narrows the resonances. Conditions which favor this process are dilution, decreased viscosity, and higher temperature. The broad peaks usually observed in ^{14}N nmr spectra result in significant uncertanties in chemical shift determination. While functional classes may be distinguished, small variations within a particular class often may not be. Hence, ^{14}N nmr is limited in its applicability compared to nmr studies of nuclei with I=1/2, such as ^{1}H, ^{13}C and ^{15}N. Lacking a quadrupole moment, the latter nuclei give rise to sharp resonances, ideal for high resolution work. The delay in the explcitation of ^{15}N nmr resulted from the low inherent sensitivity and low abundance of the ^{15}N nucleus. These factors combine to give ^{15}N a much lower sensitivity relative to ^{13}C at natural abundance (Table I).

The problems encountered in observing resonances in ^{15}N nmr are cffset by several advantages. The very large (>900 ppm) chemical shift range of ^{15}N coupled with its sensitivity to small structural changes gives this technique great value in structure determination. Even in molecules with several nitrogens, ^{15}N spectra will be less complex than ^{13}C spectra, yet may yield as much or more information about molecular configuration or conformation. Thus, ^{15}N nmr is cften the technique of choice in studies of large

organic molecules.

Nitrogen Chemical Shifts

There is a great deal of similarity in the chemical shift behavior of nitrogen and carbon. Both nuclei have a much larger chemical shift range than hydrogen. Within a class of compounds, additive substituent parameters that predict shifts reasonably well and are of similar magnitude may be derived for both carbon and nitrogen. However, a complicating feature of nitrogen shifts is the possibility of interactions between σ and π orbitals and the lone pair of electrons on nitrogen. Often, conformational changes or protonation perturbs nitrogen resonance positions much more than those of carbons in the same molecule. The magnitude and direction of these changes may be used in structural analysis. Nitrogen chemical shifts are also more sensitive to solvent effects than analogous carbons, giving solvent studies greater usefulness in ^{15}N nmr.

In contrast to many proton chemical shifts, nitrogen chemical shifts in general do not exhibit a dependence on electron density (6). Qualitative correlations can exist over a large (>50 ppm) chemical shift range with electron densities calculated by semiempirical methods.

Although ab initio methods employing extended basis sets

have been impractical for organic molecules (7), semiempirical methods have provided a useful means for rationalizing chemical shifts and, in particular, lone pair influences. The Karplus-Pople relationship (6b) expresses the total nuclear screening constant, σ_{tot} as

$$\sigma_{tot} = \sigma_{dia}^{loc} + \sigma_{para}^{loc} + \sigma_{other}$$

The first term, σ_{dia}^{loc} is the local diamagnetic screening of the nucleus resulting from circulation of electrons in an applied magnetic field. This term is related to electron density and is usually of importance only for proton chemical shifts. While σ_{dia}^{loc} and σ_{para}^{loc} may be comparable in magnitude, σ_{dia}^{loc} is fairly constant (8), and does not affect the total screening significantly. The term σ_{other} includes contributions to the screening not centered at the nucleus, such as anisotropy, field effects, and solvent effects, and is small. Changes in the total screening are dominated by changes in σ_{para}^{loc}. This term is a measure of the deviation of the electron cloud from spherical symmetry and requires electrons with nonzero angular momentum. As a negative term, it causes a decrease in screening, or a deshielding when its absolute value increases.

In the Karplus-Pople formulation, σ_{para}^{loc} is proportional

to three contributing contributing factors :

$$\sigma_{para}^{loc} \quad \alpha \quad \frac{1}{\Delta E} \cdot \left\langle \frac{1}{r^3} \right\rangle \cdot \Sigma Q$$

where ΔE is the average excitation energy, a measure of the accessibility of low-lying excited states; r is the average radius of the (non-s) orbitals influencing the shift; and Q is related to bond order, a measure of multiple bonding to nitrogen.

These factors will lead to deshielding of nitrogen when there is a nearby π-system (or σ^* orbital) that lowers the excited state energies, when there is an orbital on nitrogen with high s-character, or when the nitrogen is multiply bonded. Compounds in Table II display these effects. Aniline is deshielded with respect to ammonia by virtue of lower-energy $n-\pi^*$ transitions involving the adjacent π-system (ΔE) and increased multiple bonding resulting from delocalization (ΣQ). Pyridine has a multiply bonded nitrogen, a π-system (hence a low energy $n-\pi^*$ transition), and a smaller orbital radius; it is even further downfield. Comparison of aniline, pyridine, and azobenzene with their protonated forms shows that increased deshielding from σ_{para}^{loc} is accompanied by a greater shielding on removal of the lone pair by protonation. An exception to the dominance of the σ_{para}^{loc} term is seen in the case of ammonium chloride, which is shifted downfield from ammonia due to a decreased σ_{dia}^{loc}

Table II Illustrative Nitrogen Chemical Shifts[a]

Compound	δ_N, ppm[b]
Ammonia	0.0
Methylamine	2.0
Ammonium Chloride	25.0
Methylamine Hydrochloride	28.0
Anilinium Chloride	48.0
Aniline	52.0
Pyridinium Ion	215.0
Pyridine	317.0
Protonated trans-Azobenzene	358.0
trans-Azobenzene	508.0

a. Taken from Reference 5.

b. Downfield from anhydrous liquid ammonia.

(9).

^{15}N resonances of particular classes of organic compounds fall in characteristic regions, although there is much overlap (10). These are presented in Figure 1. Since there is no discernible isotope effect, ^{14}N and ^{15}N chemical shifts may be compared directly (11).

For aliphatic amines, a system of additive substituent parameters may be derived. Thus, alkyl substitution in the α position often causes deshielding comparable to that observed in ^{13}C shifts of alkanes. Beta substitution usually deshields nitrogen by nearly twice the amount observed for an analogous carbon. Gamma substitution causes a small shielding. These effects are well documented for many amines (12), and depend markedly on geometry.

Experimental Considerations

Continuous Wave and Indirect Techniques

In the continuous wave (CW) technique, the frequency (or field) is swept through the region of absorption until nuclei are brought into resonance. For ^{13}C and ^{15}N spectra, either summation of many repeated scans or enrichment in these nuclei is required in order to obtain spectra. Enrichment is expensive and laborious, precluding its use

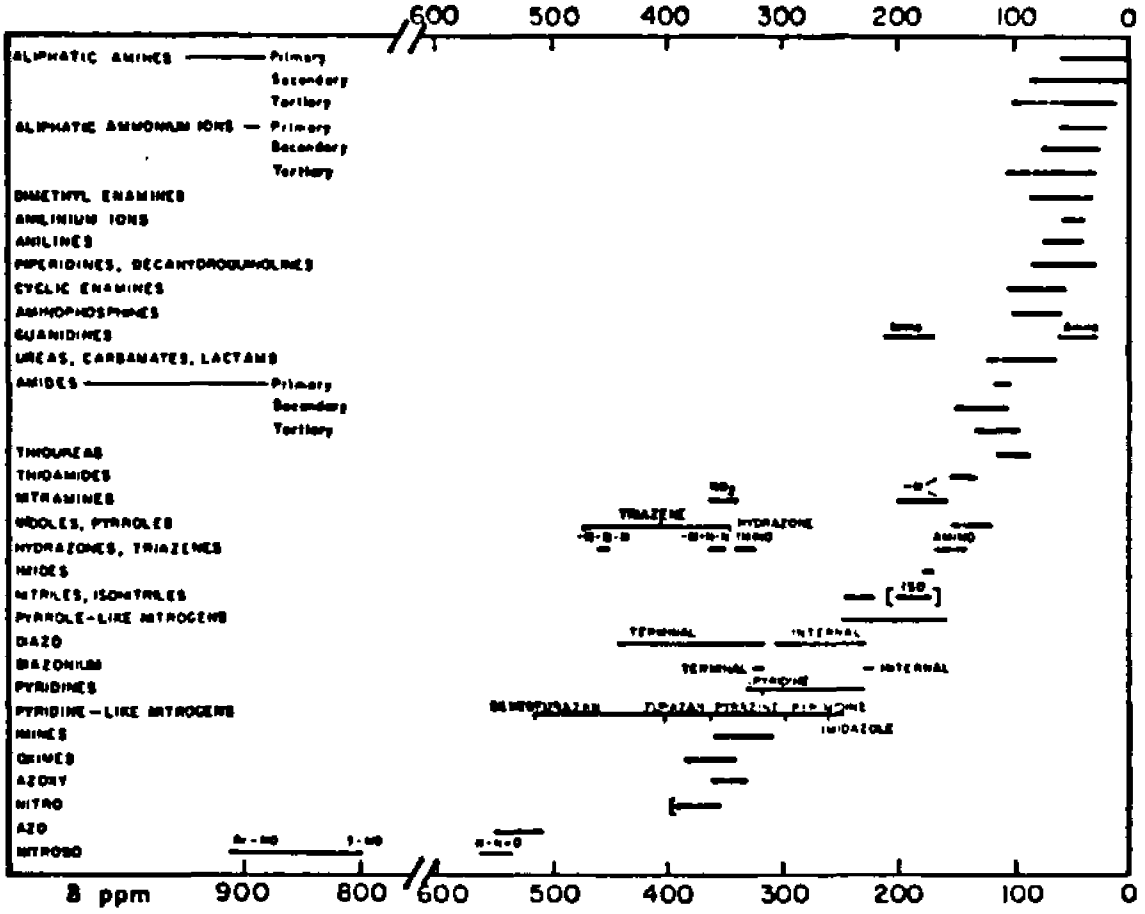


Figure 1. Nitrogen chemical shifts in organic compounds (from Reference 5).

for routine analysis or extensive structural studies. Frequency (or field) sweep methods are time consuming because most of the sweep time is not spent adding to the desired signals.

For enriched compounds in which a proton is coupled to the ^{15}N, the resonance may be detected indirectly. The proton signal is observed while the nitrogen frequency is varied until the proton resonance is decoupled. Indirect measurement of ^{14}N and ^{15}N shifts may also be effected by the INDOR (internuclear double resonance) technique (13).

Fourier Transform nmr Techniques

In FT nmr, the nuclear spins are excited by a short pulse of high power (effectively wideband) radiation in the appropriate frequency range. The resultant magnetization is monitored, and its free induction decay (FID) signal is subjected to Fourier transformation to yield the usual frequency spectrum. This method provides a considerable advantage in sensitivity over CW techniques in that the entire frequency range is monitored simultaneously by FT nmr rather than sequentially. The excitation and FID collection period commonly require about 1 second. Usually, many FIDs are summed in the computer before the Fourier transformation is performed.

In the application of time-averaging methods, signal strength is simply proportional to the number of scans, N, while noise is partially averaged out. Since noise accumulates with $\sqrt{N}$, the signal-to-noise ratio (S:N) increases as a function of $\sqrt{N}$. Typical experiments require 10^3-10^4 scans; a practical upper limit is 10^5-10^6 scans. Thus, improvements in S:N of 50 to several hundred may be attained.

^{15}N Spin Relaxation

Nuclear spin relaxation characteristics play a part in determining experimental conditions for FT nmr. The importance of understanding them increases in ^{13}C nmr as compared with ^{1}H nmr and becomes critical for successful observation of ^{15}N resonances. The reasons for this are discussed in the following two sections.

Spin-Lattice Relaxation

Establishment of, or changes in, the population difference between the two ^{15}N nuclear spin energy levels require transfer of energy between individual spins and the "lattice" or sample heat sink. The spin-lattice relaxation (T_1) process governs the return to the equilibrium energy level population following the rf pulse. It may have contributions from four mechanisms: 1 dipole-dipole

interactions with neighboring magnetic nuclei or unpaired electrons, 2 spin-rotation interactions, 3 chemical shift anisotropy, and 4 scalar interactions.

In many organic molecules, dipole-dipole interactions with nearby protons account for all significant ^{13}C spin-lattice relaxation (14); this is not always true for ^{15}N nuclei. In addition, ^{15}N T_1s vary greatly, commonly being longer than 10 seconds, sometimes longer than 100 seconds. Long T_1s necessitate long waiting times between pulses to allow reequilibration of spin populations. The combination of low abundance, low sensitivity, and long T_1s makes some ^{15}N resonances exceedingly difficult to observe. The use of paramagnetic relaxation reagents (15) to shorten T_1s can alleviate this problem.

The Nuclear Overhauser Effect

Irradiation of protons coupled to nitrogen collapses the nitrogen multiplet, increasing signal intensity. Often, there is an enhancement of this increase resulting from a reorganization of spin level populations. This enhancement, which is only observed if the ^{15}N nucleus under observation relaxes via dipole-dipole interactions with the irradiated protons, is called the nuclear Overhauser effect (NOE) (16). The maximum possible effect is given by :

$$I/I_o = 1 + 0.5 (\gamma_H / \gamma_X)$$

The magnetogyric ratios of the proton and the nucleus under observation are represented by γ_H and γ_X, respectively.

The negative magnetogyric ratio for ^{15}N results in an enhancement, I/I_o of -3.93. If this maximum enhancement is realized, a negative signal is produced. However, contributions from relaxation mechanisms other than the dipolar may decrease I/I_o to near 0, resulting in a nulled signal. Gated decoupling (12) may be applied to overcome this problem.

Photoelectron Spectroscopy

Photoelectron spectroscopy (PES) has considerable potential as a probe of molecular energy levels. Energies of π-type orbitals may be correlated with spectroscopic data, chemical reactivities, and MO calculations. In addition, PES yields information about otherwise relatively inaccessible σ levels. Several reviews (17) discuss the theory and chemical applications of PES. A brief discussion of the basic principles follows.

A photoelectron spectrometer has two basic components : an excitation source and an electron energy analyzer. The most common source of ionizing radiation is the 21.22 eV resonance line of helium. The analyzer, which sorts electrons according to their energies, may be of the electrostatic or magnetic deflection type. The excitation energy produced by the source is sufficient to remove electrons from all valence orbitals of the vaporized sample. The ionization of an electron from a neutral molecule, M, produces a radical cation :

$$M + h\nu \longrightarrow M^{+\cdot} + e^-$$

Kinetic energies of the electrons ejected from orbital n are given by :

$$E_n(e^-) = h\nu - IP_n(M)$$

$IP_n(M)$ is the ionization potential of the n^{th} molecular orbital and $h\nu$ is the energy of the ionizing radiation. Thus, by counting the electrons of a given kinetic energy, a plot of IP vs. electron counts/sec., the photoelectron spectrum, can be obtained. The IP is the energy difference between the radical cation and the ground state. According to the Franck-Condon principle, the excited state vibrational level most similar geometrically to the ground state will be populated most heavily. Since bonding orbitals have larger equilibrium internuclear distances in the excited state, a radical cation in a higher vibrational state is likely to be produced (Figure 2). Ionization to other states produces a broad band whose highest point, corresponding to the most probable ionization process, is known as the vertical ionization potential, IP_n.

IP_n can be correlated with the calculated SCF orbital energies, ϵ_n, by Koopmans' theorem (18) :

$$IP_n = -\epsilon_n$$

It has been pointed out (19) that this theorem is often a bad assumption because it does not account for reorganization of electrons in the radical cation. This process becomes important for orbitals which are highly localized in the ground state. For delocalized orbitals, Koopmans' theorem remains a good approximation.

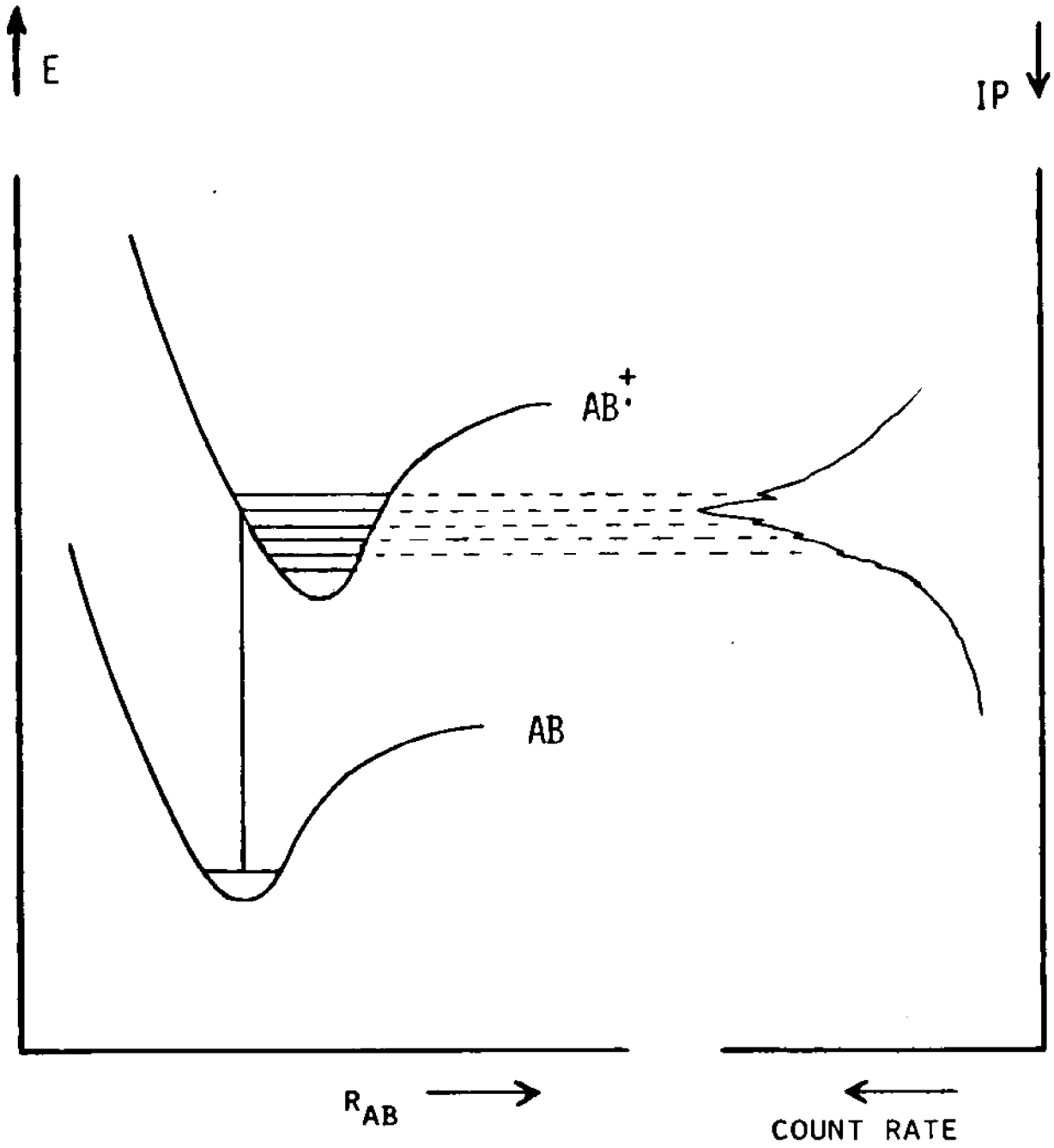


Figure 2. Production of ions in excited vibrational levels causing broadening of PE spectral bands.

Objectives of This Investigation

There were two major motivations for this work. The first was to fill the large gap existing in the ^{15}N chemical shift literature for small-ring compounds. The second was to investigate the utility of ^{15}N nmr as a probe of the unusual geometric and electronic properties of small rings. In the last two series (see below), PES was also used to investigate electronic properties.

The types of compounds under consideration here are as follows :

1. N-Alkylaziridines
2. C-Alkyl and C-phenylaziridines
3. N-Alkylazetidines
4. N-Arylaziridines
5. Alkyl- and arylazirines

CHAPTER II

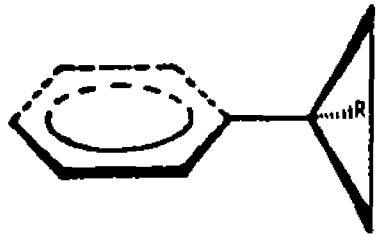
^{15}N CHEMICAL SHIFTS OF AZIRIDINES AND AZETIDINES

Introduction

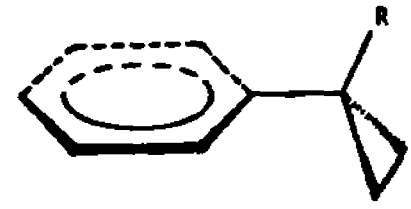
Many of the peculiar physical and chemical properties of three-membered rings resemble those of alkenes (20) more than those of larger rings or acyclic counterparts. Theoretical descriptions of their bonding properties were proposed by Walsh (21) and Coulson (22), and shown to be equivalent (23). In both pictures, orbitals with high p-character are involved in the endocyclic bonding. The highest occupied Walsh-type orbitals are shown below :

An interesting aspect of this bonding is the overlap of the ring orbitals with adjacent π - systems. In the case of phenylcyclopropane, ^{19}F nmr (24), ^{13}C nmr (25), and PES (26) studies have shown the extent of conjugation between cyclopropyl and phenyl rings to be intermediate between vinyl-phenyl and alkyl-phenyl interactions. In order to attain maximum interaction with the Walsh orbitals, which lie in the plane of the small ring, the two rings must be

perpendicular, as in the bisected conformation I.



I



II

Gas-phase electron diffraction (27) has shown that conformation I is present for phenylcyclopropane (R=H). Observation of ^1H chemical shifts for the ortho hydrogens (28) led to the conclusion that conformation I is also preferred in solution and that geminal methyl substitution ($R=CH_3$) rotates the conformation towards II (29). Measurements of dipole moment and the Kerr effect confirmed that I is favored (30a) and that ortho, geminal, or vicinal substitution causes rotation toward the non-bisected form, II (30b). However, a PES study (31) of phenylcyclopropanes with varying geminal- and para-substitution failed to detect any change in conjugation.

Preference of the bisected conformation I is also supported by CNDO/2 (32) and INDO (33) calculations, which indicate that electron density is shifted from the small-ring bonds to the aryl group. The same behavior is predicted to occur to a slightly smaller extent in 2-phenylaziridine. Measurement of ^{13}C chemical shifts of 4-substituted cyclopropylbenzenes (25) confirms these

predictions. The substituent chemical shifts (SCS) are larger for the β carbons than for the α carbon and are larger for substituents which are conjugatively electron-withdrawing than for electron-donating substituents. These observations indicate that cyclopropane enters into conjugation with the benzene ring as an electron donor. ^{13}C chemical shift studies of N-unsubstituted aziridines (34) indicate that the 2-phenyl substituent has an unusually large deshielding effect on the β carbon of the aziridine ring. This effect is attenuated by cis- and, to a lesser extent, by geminal-alkyl substitution. Magnetic rotary polarization (35) (Faraday effect) studies on 2-arylaziridines have revealed a similar pattern. Conjugation is decreased by cis-, geminal-, or ortho-alkyl substitution and slightly enhanced by trans-alkyl substitution. These results suggest that in 2-phenylaziridines, the aziridine ring bonding electrons are delocalized into the benzene π-system and that this conjugation decreases when alkyl substitution favors the non-bisected conformation.

The nmr chemical shifts of cycloalkanes and some heterocycloalkanes have been investigated as a function of ring size. The ^{13}C (36,37), ^{17}O (38), and ^{15}N (39) shifts behave similarly, oscillating slightly among the larger rings, moving slightly to higher shielding for the four-membered ring and drastically for the small ring. This

behavior has not been explained satisfactorily. The ^{15}N data (39) were obtained from a series of cyclic phosphoramidates in which varying degrees of interaction between the nitrogen lone pair and the $P(O)(OCH_3)_2$ group are likely (40). No complete set of ^{15}N shifts for unsubstituted cyclic amines is available. Aziridine itself was reported to be highly shielded (-11.1 ppm) (41,42), about 51 ppm upfield of piperidine.

Alkyl substituent effects on chemical shifts have been determined mainly in acyclic compounds or unstrained rings. Carbon chemical shifts of ring-substituted aziridines (34) with the exception of 2-phenylaziridines (see above) were found to be consistent with known substituent parameters. The effect of ring-methyl groups on the ^{15}N shifts of cyclic phosphoramidates (39) was found to be almost additive. Azetidines have not been examined systematically by either carbon or nitrogen nmr. Consequently, in order to clarify the ^{15}N chemical shift behavior of small rings, a systematic study of these compounds was undertaken, and the results are described in the remainder of this chapter.

Results

Tables III-V list the ^{15}N chemical shifts of compounds 1-5 (see Charts I-II). The tables also include for comparison the ^{13}C chemical shifts of aziridine ring carbons bearing the same substitution pattern. For example, the ^{15}N shift of 3a is compared with the ^{13}C snift of C-3 in the same compound,

3a

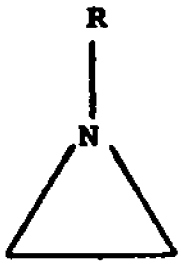
while the ^{15}N shift of 1b is compared to the ^{13}C shift of C-2 in 2a :

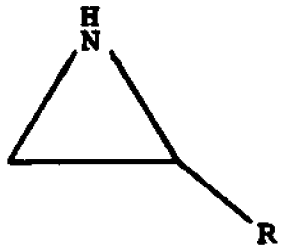
1b 2a

This comparison cannot be made for compounds 1d,f,3b-d and 4 c-d,f-h because the relevant aziridines were not available.

Figure 3 lists ^{15}N shifts and differences in shifts for the series of cyclic amines from 1a through perhydroazepine, their N-rethyl derivatives, and the corresponding phosphoramidates (39).

Chart 1





1 a. R = H

b. R = CH_3

c. R = CH_3CH_2

d. R = $CH_3CH_2CH_2$

e. R = $(CH_3)_2CH$

f. R = $CH_3(CH_2)_3$

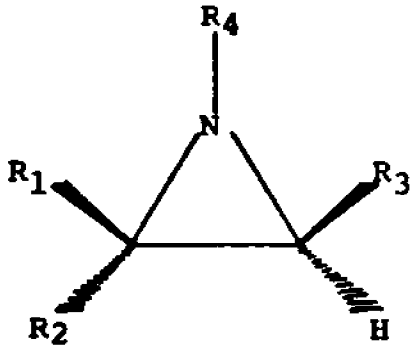
g. R = $(CH_3)_3C$

2 a. R = CH_3

b. R = CH_3CH_2

c. R = $(CH_3)_2CH$

d. R = $(CH_3)_3C$



3 a. R_1, R_2 = CH_3 R_3, R_4 = H

b. R_1, R_4 = CH_3 R_2, R_3 = H

c. R_2, R_3 = CH_3 R_1, R_4 = H

d. R_1, R_3 = CH_3 R_2, R_4 = H

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

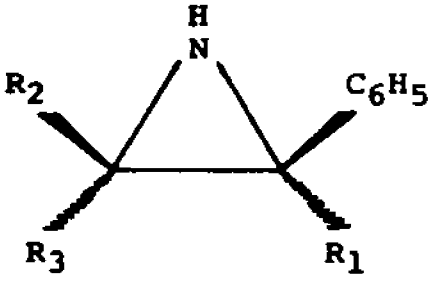
Compound	δ_N	$\Delta\delta_N$[b]	δ_C[c]	$\Delta\delta_C$[b]
1a	-8.5	0.0	18.2	0.0
1b	0.7	9.2	25.1	6.9
1c	16.4	24.9	31.7	13.5
1d	13.6	22.1		
1e	30.2	38.7	37.2	19.0
1f	13.6	22.1		
1g	33.5	42.0	39.7	21.5
2a	10.5	19.0	25.8	7.6
2b	7.9	16.4	24.7	6.5
2c	7.3	15.8	24.0	5.8
2d	3.4	11.9	21.4	3.2
3a	28.6	37.1	32.5	14.3
3b	15.9	24.4		
3c	30.7	39.2		
3d	25.0	33.5		

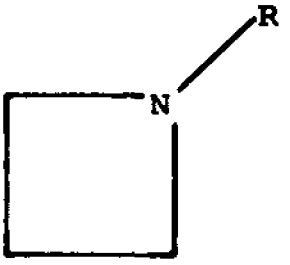
a. In ppm from $NH_3(l)$; see Chapter V.

b. $\Delta\delta_i = \delta_i - \delta_{1a}$

c. Reference 34, in ppm from $(CH_3)_4Si$.

Chart 2





4 **a**. R_1, R_2, R_3 = H

b. R_1 = CH_3 R_2, R_3 = H

c. R_2 = CH_3 R_1, R_3 = H

d. R_3 = CH_3 R_1, R_2 = H

e. R_1 = C_6H_5 R_2, R_3 = H

f. R_2 = C_6H_5 R_1, R_3 = H

g. R_3 = C_6H_5 R_1, R_2 = H

h. R_1, R_2 = CH_3 R_3 = H

5 **a**. R = H

b. R = CH_3

c. R = CH_3CH_2

d. R = $CH_3CH_2CH_2$

e. R = $(CH_3)_2CH$

f. R = $(CH_3)_3C$

Table IV ^{15}N Chemical Shifts of 2-Phenylaziridines[a]

Compound	δ_N	$\Delta\delta_N$[b,d]	δ_C[c]	$\Delta\delta_C$[b,d]
4a	18.2	26.7	29.2	11.0
4b	33.1	41.6 (45.7)	35.0	16.8 (18.6)
4c	21.5	30.0 (45.7)		
4d	39.3	47.8 (45.7)		
4e	36.1	44.6 (53.4)	35.3	17.1 (22.0)
4f	22.3	30.8 (53.4)		
4g	43.4	51.9 (53.4)		
4h	41.5	50.0 (64.7)		

a-c. As in Table III.

d. Parenthesized values are those predicted on the basis of additivity of substituent effects from Table III and from 4a.

Table V ^{15}N Chemical Shifts of N-Alkylazetidines[a]

Compound	δ_N
5a	25.3
5b	31.5
5c	45.0
5d	42.4
5e	56.3
5f	52.0

a. As in Table III.

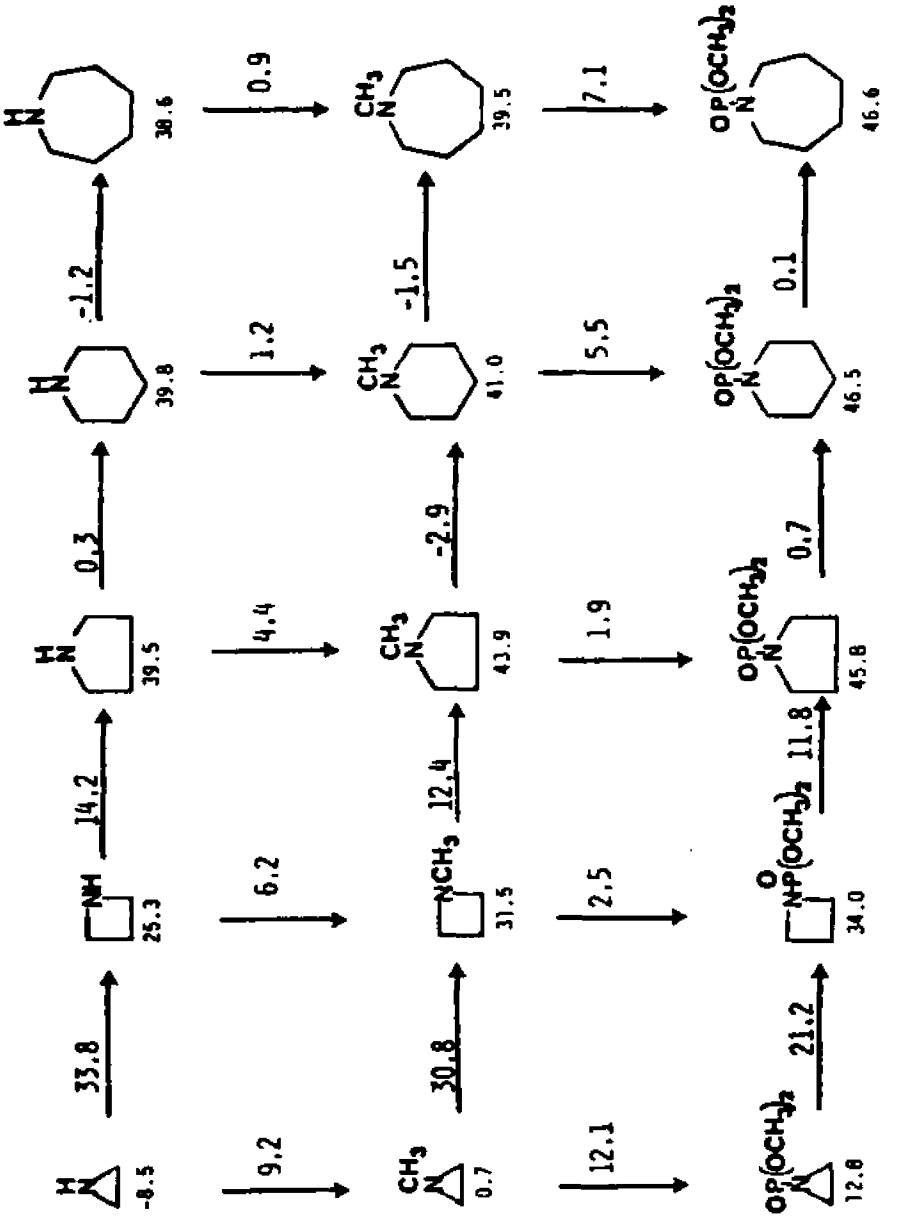


Figure 3. Scheme of ring-size and N-substituent effects on ^{15}N chemical shifts.

The value of δ_N for the parent 1a given in Table III differs slightly from the earlier reported value (-11.1 ppm) (41). The difference may be attributed to the difference in referencing and solvent : the earlier value was obtained from the neat liquid, while the present one was determined from a solution of aziridine in chloroform. It is well known (5) that ^{15}N resonance positions can vary with solvent.

Discussion

Effect of Ring Size on ^{15}N Chemical Shifts

Qualitatively, the ^{15}N shifts of the cyclic amines shown in Figure 3 parallel the ^{13}C shifts of cycloalkanes : a large difference between three- and four-membered rings, a smaller one between four- and five-membered rings, and nonsystematic small variations subsequently. Quantitatively, the shifts do not correlate very well with ^{13}C or ^{17}O shifts cited above. Possibly, this stems from n-σ^* interactions between the nitrogen lone pair and C-C bonds that is not present for the other nuclei.

The effect of N-methylation as a function of ring size is also displayed in Figure 3. The magnitude of the deshielding α effect decreases with increasing ring size, in contrast to the ^{13}C chemical shift behavior of cycloalkanes. However, α substitution on amines does not always lead to deshielding (43,44). Methylation of primary or secondary amines branched at the α-carbon can result in a shielding of up to 25-30 ppm. The same behavior is exhibited by the phosphoramidates (Figure 3) : the deshielding compared with the unsubstituted cyclic amines also decreases with ring size. Since any delocalization of the lone pair into the P-O bond will be greater in the larger rings (40), it would seem that the parallel results

in the two series are the result of a common change in the σ skeleton on N-substitution.

Aziridines

In general, ^{15}N shifts of aziridines parallel the ^{13}C shifts of identically substituted aziridine carbons. Figure 4 shows a plot of the 13 compounds where this comparison can be made; the correlation coefficient is 0.953 and the slope is 2.1 ppm N/ppm C. This value, reflecting the greater sensitivity of the nitrogen nucleus to structural changes, is typical of ^{15}N-^{13}C correlations (41,43). The ^{15}N shifts of 1a, 2a, 3a,c,d correlate with the ^{13}C shifts of the corresponding cyclopropanes (45) with a correlation coefficient of 0.997 and a slope of 2.16 ppm N/ppm C (Figure 5). If 4a and 4e are included (46) in this comparison, the correlation coefficient drops to 0.979 and the slope increases to 2.34 ppm N/ppm C (Figure 6). These results indicate that nitrogen and carbon in three-membered rings are affected similarly by substituents.

For small groups of compounds such as 1a, 2a, 3a, and 1a, 5a, pyrrolidine, a relationship exists between the ^{15}N shifts and the photoelectron ionization potentials for the lone-pair electrons (47). It has been shown that ionization potentials and ^{15}N chemical shifts can correlate in cases where lone-pair delocalization is important (48). In this

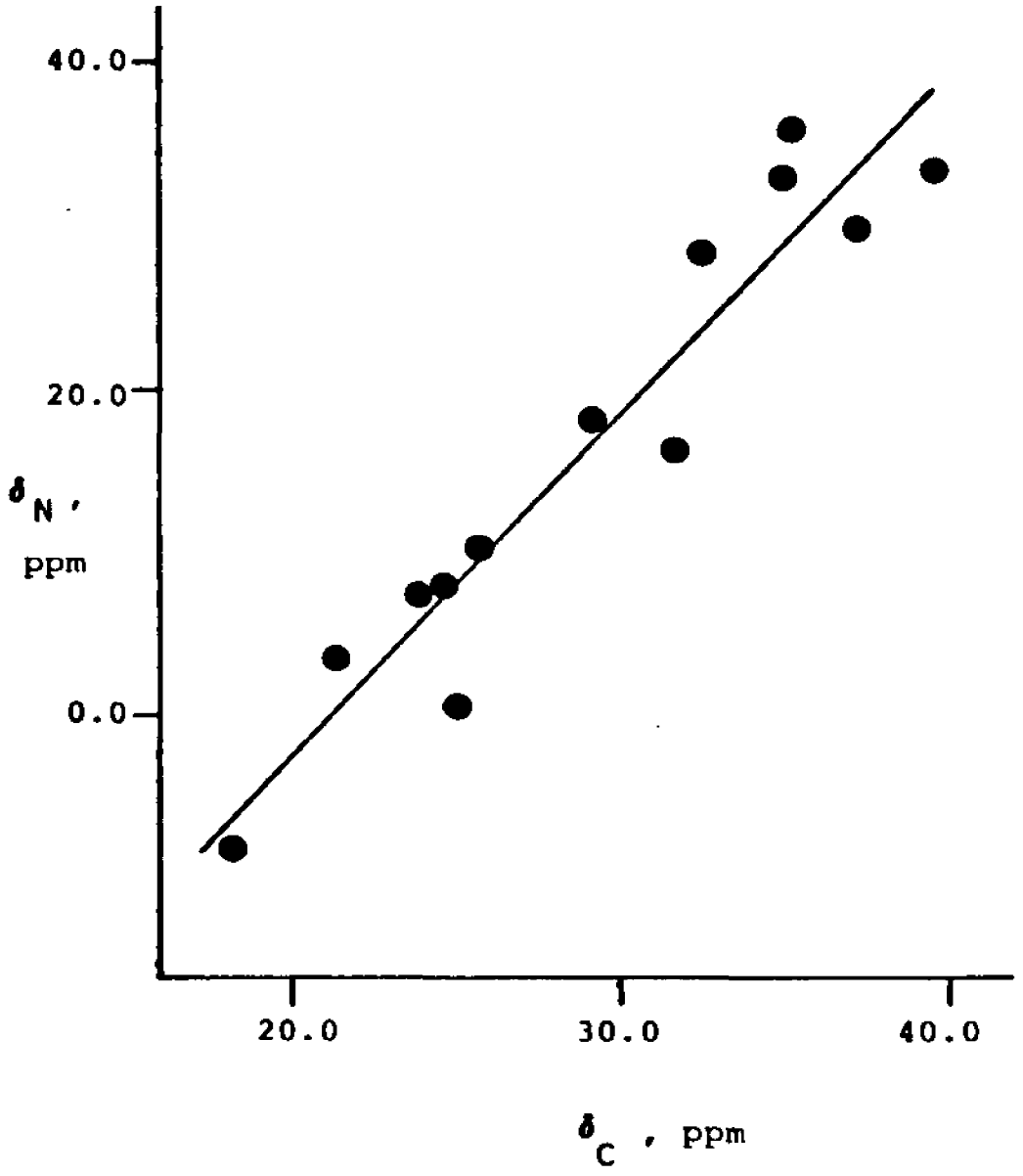


Figure 4. ^{15}N Chemical shifts of ring-substituted aziridines vs. ^{13}C shifts of corresponding carbons (see text).

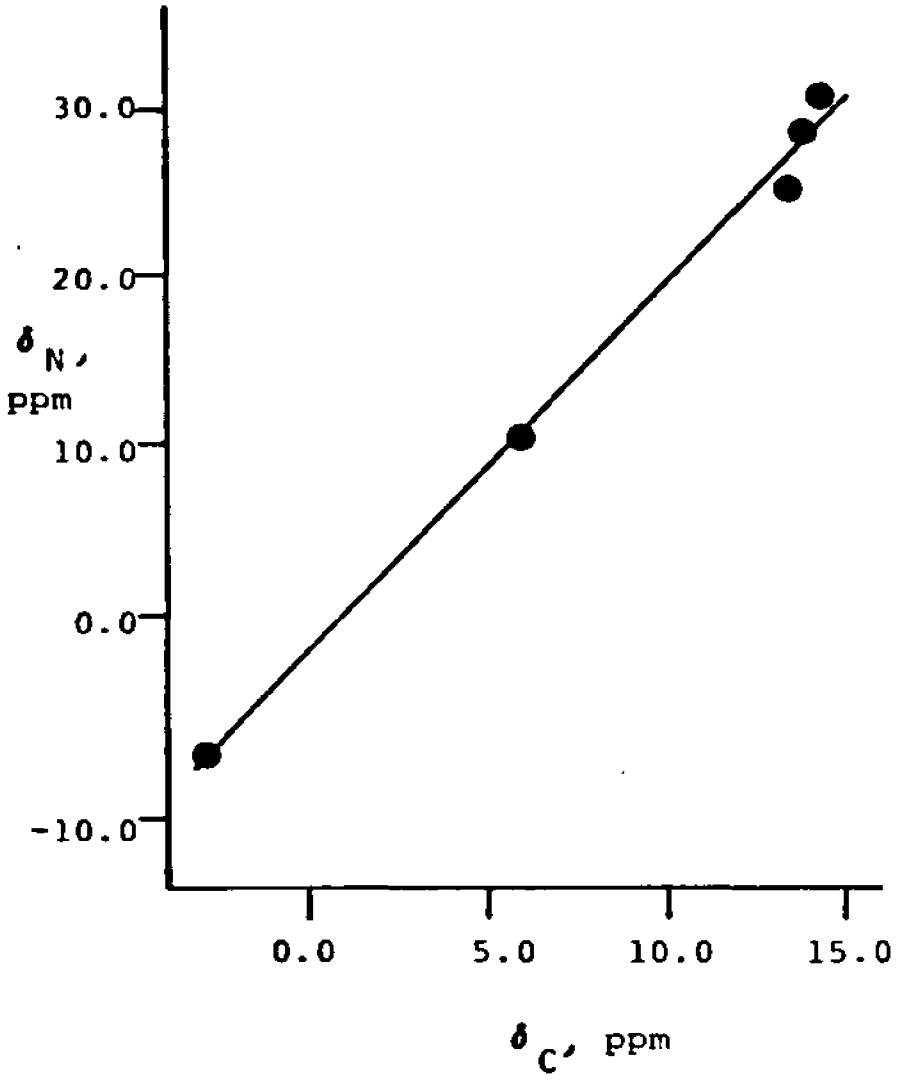


Figure 5. ^{15}N Chemical shifts of aziridines vs. ^{13}C chemical shifts of the corresponding cyclopropanes.

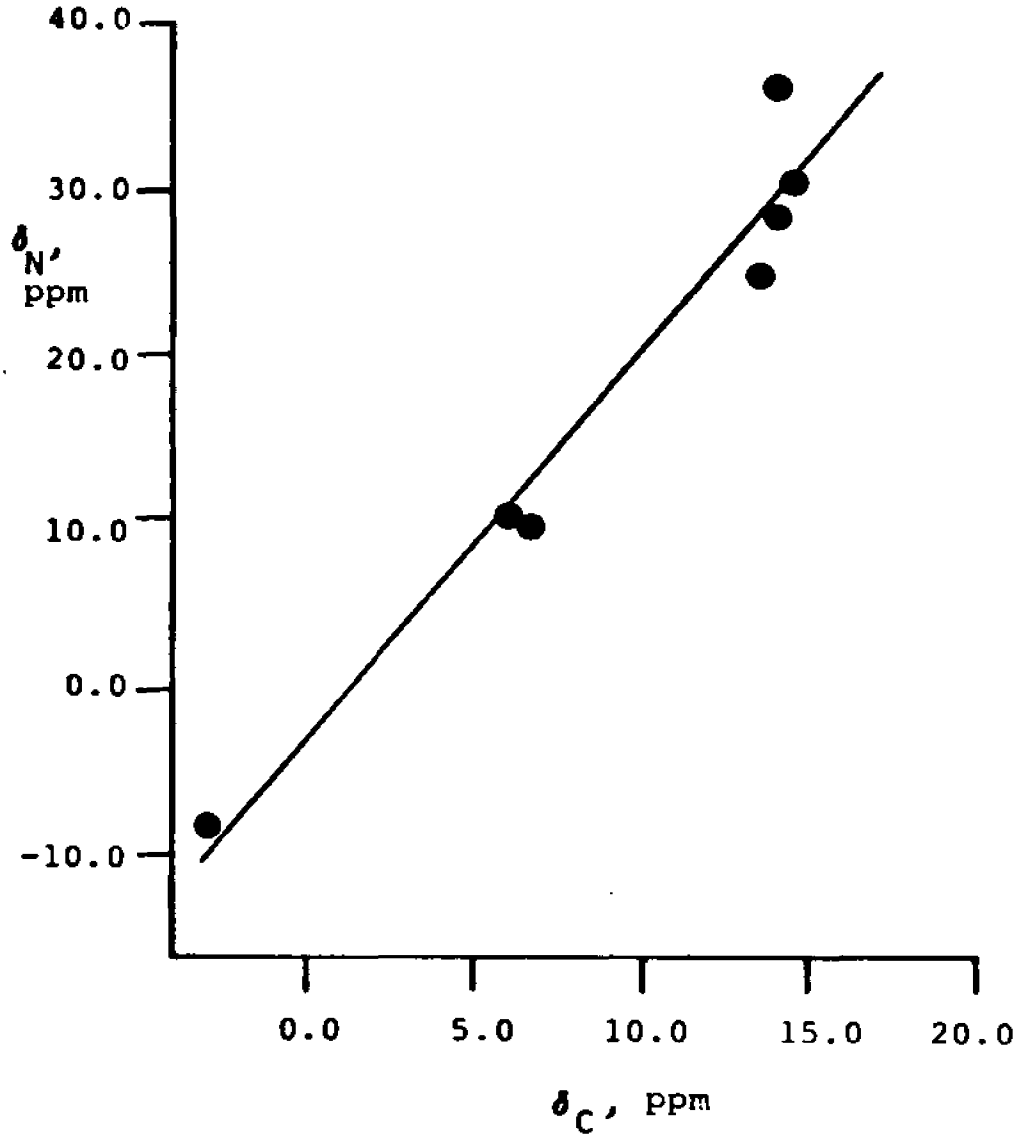


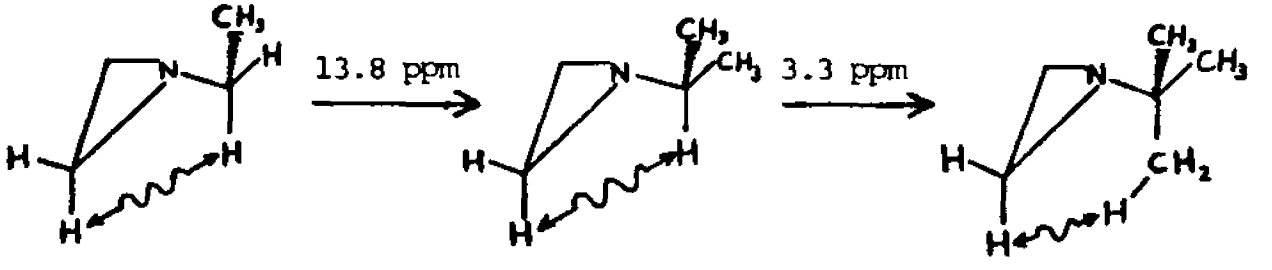
Figure 6. ^{15}N Chemical shifts of aziridines vs. ^{13}C chemical shifts of the corresponding cyclopropanes.

case, however it is difficult to explain why lower ionization potential corresponds to deshielded ^{15}N nuclei. The decrease in ionization potential in each of the two groups is consistent with increased p-character in the lone-pair orbital. This would be expected to decrease the $\langle r^3 \rangle^{-1}$ term in the chemical shift expression (see Chapter 1) and shield the nitrogen, which is contrary to observation. A diamagnetic effect, associated with changes in electron density is possible, but usually unlikely for nitrogen shifts.

N-Alkylaziridines

Examination of the chemical shift differences among compounds 1b, 1c, 1d, and 1f reveals β, γ, and δ substitution effects of 15.7 ppm, -2.8 ppm and 0.0 ppm, respectively. The latter two values are comparable to those observed for acyclic amines (42,43). In fact, the chemical shifts for 1c, 1d, and 1f differ from those of the corresponding tertiary acyclic amines ($R\text{-}N(CH_3)_2$) by a relatively constant amount, -8.2 to -8.6 ppm, which demonstrates the similarity between γ and δ effects in the two series. The β effect requires more careful examination. In the series 1b $\longrightarrow$ 1c $\longrightarrow$ 1e $\longrightarrow$ 1g, the successive deshielding diminishes progressively, the smallest effect existing for conversion of 1e to 1g. The diminution of β deshielding with increased branching at the

α carbon has been observed in both ^{13}C (49) and ^{15}N (43) chemical shift behavior, and, most appropriately, in the ^{13}C shifts of secondary aziridines (34). This effect has been associated with the geometric proximity of the hydrogens on the β methyl carbons to those on the α ring carbons. Similar interactions in the trans-decahydroquinolines have been accounted for in a regression analysis by a term $\alpha_e\beta_e$ = -5.3 ppm (43b). Staggered conformations which minimize these interactions are more likely in 1c and 1e than in 1g. A similar argument was presented to rationalize analogous



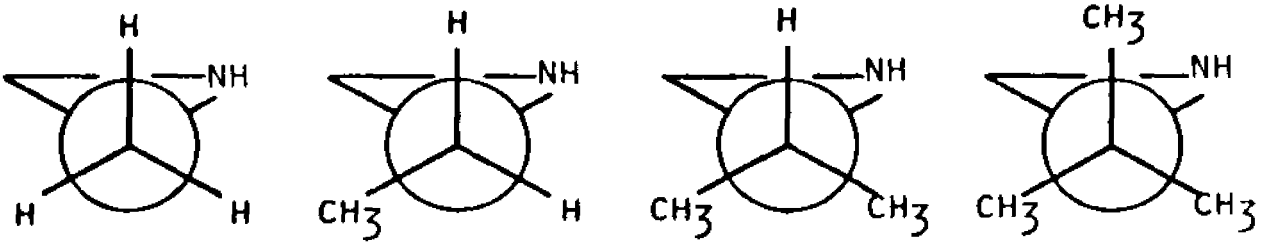
1c 1e 1g

trends in a series of N-alkylacetamides (50). In both acetamides and aziridines, the smallest change in the deshielding β effect occurs with the third methyl group. For tertiary acyclic amines, the deshielding β effects of both the first and second β methyl groups are smaller than those observed in the acetamides or aziridines. Possibly, the greater potential for steric crowding in the acyclics, compared to amides or aziridines, leads to a reduction in the β effect.

2-Alkylaziridines

Examination of shift data for 2-alkyl substituted aziridines allows comparison with substituent effects observed for N-alkyl substitution. The methyl group of 2-methylaziridine (2a), a β substituent, deshields the nitrogen by 19.0 ppm. This is identical to the value obtained on β-methyl substitution of acetamide (50), but larger than the 15.7 ppm deshielding of 1c relative to 1b. The carbon shifts of the aziridines with corresponding substitution (Table III) parallel the ^{15}N shifts, although the values are smaller. This is consistent with the smaller β effect on ^{13}C shifts : 1b ⟶ 1c = 6.6 ppm, 1a ⟶ 2a = 7.6 ppm. Models show that the rigid structure of 2a holds the methyl substituent further from the C-3 hydrogen than does the torsionally more flexible 1c. These 1,3 H-H interactions appear to shield nitrogen, either by steric perturbation of electron distribution or by conformation-induced changes in orbital interactions involving nitrogen. Thus, the observed β effect is diminished more in 1c than in the more rigid 2a or N-ethylacetamide. Further support for this interpretation is found by comparing the β effects on ^{13}C shifts induced by N-methyl (9.7 ppm) and 2-methyl (7.6 ppm) substitution. Because of the conformational mobility of nitrogen substituents, the N-methyl group may be held further from the ring hydrogens than the 2-methyl group, and hence induce a smaller shielding interaction.

Replacement of methyl with ethyl at C-2 (2a → 2b) results in a shielding γ effect of -2.6 ppm that is comparable to the value in acyclic amines. Additional shielding induced by successive γ methyl groups reaches a minimum of -0.6 ppm at two γ substituents and increases to -3.9 ppm with the third methyl group. The same trend is seen for the ^{13}C shift behavior of C-3 in the same compounds. As shown in the depictions of the conformations expected to be most stable,



2a 2b 2c 2d

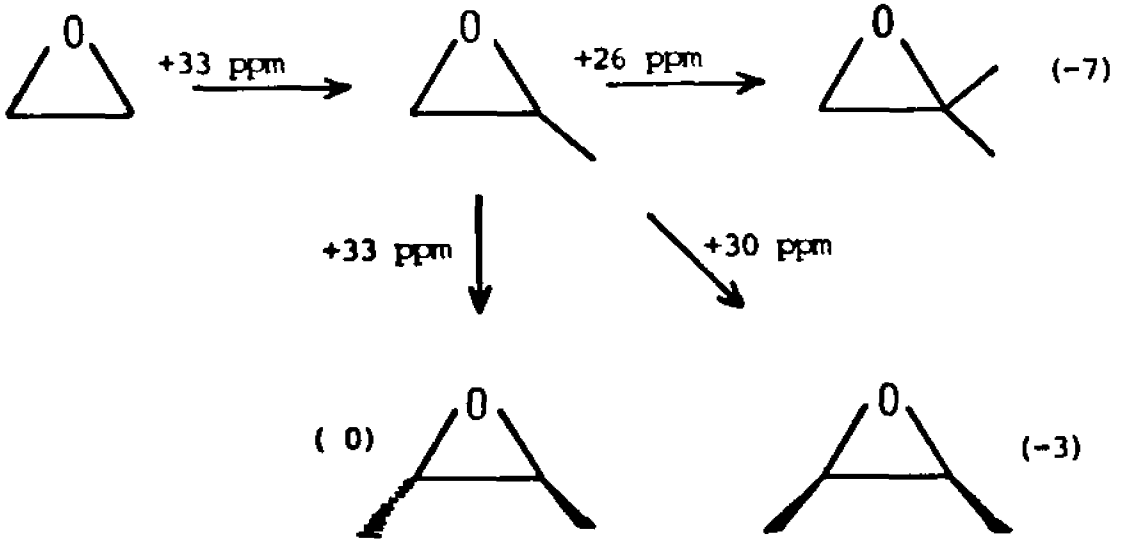
the ethyl and isopropyl groups in 2b and 2c may adopt conformations in which the γ-methyl groups are oriented away from the aziridine ring atoms. This is not possible for the tert-butyl group of 2d, which always has a methyl group quasisynclinal to the ring; hence the shielding is largest in this case.

If substituent effects were precisely additive, $\Delta\delta_N$ values for ring-dimethylaziridines should be twice that of 2a. Geminal and trans vicinal dimethyl substitution induce effects which are nearly additive. The deviation from additivity for 3a is -0.9 ppm, identical to the deviation

displayed by the corresponding aziridine ^{13}C shift. Trans-disubstituted 3c displays a small positive deviation of 1.2 ppm. Only cis-disubstituted 3d displays a substantial deviation of -4.5 ppm. This additional shielding is comparable to that observed in piperidines (43c) and decahydroquinolines (43b) in which there are gauche CH_3-CH_3 interactions.

The deviation (-3.8 ppm) of $^{\Delta}\delta_N$ for N,2-dimethyl-aziridine (3b) from the value (28.2) expected on the basis of the shifts of 1b and 2a is comparable to that for 3d. The fact that it is 0.7 ppm less for 3b may be significant since 3b is not restricted to a cis conformation.

The data for ring-methylated aziridines contrast with recently published ^{17}O shifts of methyloxiranes (51), which display the pattern of shift deviations outlined below :



As in the aziridines, the effects of trans-dimethyl

substituents are nearly additive. In the oxiranes, however, geminal dimethyl substitution induces a larger upfield deviation from additivity than cis-dimethyl substitution. Since deviations of the ^{13}C shift of C-3 in 1,1- and 1,2-dimethylcyclopropanes (45) resemble more closely those of the aziridine nitrogen shifts and the geometries of cyclopropane, aziridine, and oxirane are very similar, this is puzzling.

2-Phenylaziridines

The effect of conjugation between the rings in 2-phenylaziridines may be appreciated by comparing the shift difference between 2-phenylaziridine (4a) and aziridine (1a), 26.7 ppm, with that between 1-phenylethylamine and ethylamine, 18.7 ppm (41,42). The large $\Delta\delta_N$ observed for 2-phenylaziridine is also substantially larger than that for any other 2-alkyl group (Table III). This behavior resembles that of the β carbon chemical shifts in 2-phenylaziridines (34) and cyclopropylbenzenes (25). In all these cases, the additional deshielding of the β ring atoms may be attributed to conjugative delocalization of electrons from the small ring Walsh orbitals to the benzene π orbitals. This would decrease electron density in the π-like Walsh orbitals and deshield the nitrogen.

The bisected conformation I must be attained in order for

delocalization to be effective. If this is prevented by appropriately placed substituents, significant chemical shift changes should occur. As described above, effects of methyl substitution on C-2 and C-3 are additive, except for cis-vicinal methyl groups, where a deviation of -4.5 ppm arises. If additivity were observed for the methylphenylaziridines 4b-d, their $\Delta\delta_N$ values would be that of 2a + 4a, or 45.7 ppm. Substitution of a methyl group trans to phenyl results in a deviation of +2.1 ppm for 4d. While this is rather small, and comparable to the +1.2 ppm deviation of 3c, it is consistent with the slightly increased interaction between the rings inferred from Faraday-effect measurements on trans-3-alkyl-2-phenylaziridines (35). The Faraday-effect data also suggest that methyl substitution geminal or cis to the phenyl group decreases the conjugative interaction to a small, but approximately equal amount in the two cases. The ^{15}N shifts show large, but unequal deviations of -4.1 ppm for geminal 4b and -15.7 ppm for cis 4c. Since geminal substituents in aziridine are expected to be at least 115° apart (52), it seems reasonable that the deviation for geminal substitution might be smaller. In fact, the ^{13}C shifts of aziridine ring carbons (34) display a larger negative deviation from additivity for cis-methyl phenyl substitution than for geminal-methyl phenyl substitution. In the trisubstituted 4h, the ^{15}N shift deviates by -14.7 ppm from the value of 64.7 ppm expected from perfect substituent additivity. Thus

it seems that the combined effect of geminal and cis methyl groups is comparable to that of a cis methyl group alone. Apparently the cis methyl is sufficient to completely prevent the attainment of the bisected conformation required for delocalization. Indeed, the effect of an additional trans methyl group on 4c (4c → 4h, 20.0 ppm) is identical to that arising without a phenyl group (2a → 3c, 20.2 ppm).

The discussion above interprets the negative (shielding) deviations from additivity as arising from steric inhibition of a deshielding conjugative interaction between the rings. It is also possible that a γ effect may be contributing; the ortho phenyl carbons are γ to the nitrogen, and their geometrical disposition may affect the ^{15}N resonance position.

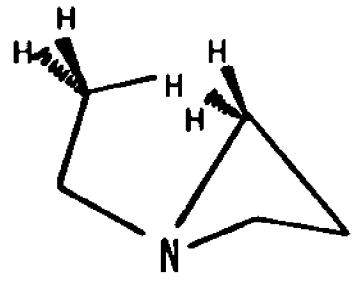
The effect of an additional phenyl substituent on the ^{15}N shift of 2-phenylaziridine parallels the methyl substituent effects. Chemical shifts of 4e-4g correlate remarkably well with those of 4b-4d (r = 1.00, slope = 1.19). Deviations from the additive value of $\Delta\delta_N$ = 53.4, twice that of 4a, are larger fcr 4e (-8.8 ppm) and 4f (-22.6 ppm). The Faraday-effect results for these compounds (35b) show that conjugation in 4e is reduced to the same extent as in 4b and 4c, but that 4f is more strongly conjugated than 4a. The authors suggest that either the phenyl groups can twist slightly, as in cis-stilbene, avoiding steric interactions

while reraining in conjugation to a large degree, or that the conjugation observed is a through-space interaction between the two aromatic rings. Molecular models suggest that the geometry of aziridine and the requirement of a bisected conformation are not compatible with the type of conformation observed in cis-stilbene. Even if this situation existed, it could not explain the enhancement of conjugation beyond that in 4a. Through-space interaction between the phenyl groups is a much more convincing explanation, especially in view of the even greater enhancement observed for cis-2-benzyl-3-phenylaziridine. The increased negative deviations of the ^{15}N shifts for the phenyl contrasted with the methyl substituents clearly reflect the greater steric constraints on the phenyl group. The deviation of 4g from additivity is small (-1.5 ppm) and may be rationalized in terms of competitive cross conjugation of the two rings with the aziridine ring. Such interactions are consistent with slightly decreased interaction inferred from Faraday-effect measurements (35b).

N-Alkylazetidines

The values given in Table V are the first reported for alkylazetidines. The effect of N-methylation was discused above in connection with ring size. Comparison of the shifts of 5b-5d reveals β and γ substituent effects of 13.5 and -2.6 ppm, respectively. The effect of γ

substitution is similar to that in aziridines and acyclic amines, but the β effect is rather small compared to that for N-ethylaziridine, 1b (15.7 ppm). In addition, a second β substituent (5e) deshields the nitrogen by only 11.3 ppm relative to 5c. Replacement of the last β hydrogen with methyl in 5f actually shields the nitrogen by -4.3 ppm relative to 5e. This is the only known example of a shielding β effect on a saturated ^{15}N or ^{13}C atom. To rationalize the low value of the β effect, as well as its rapid decrease with branching at the α carbon, a compensating shielding arising from 1,3 H - H interactions between the β C - H and the C-(2) - H bonds may be visualized. Molecular models indicate that these interactions are at least as likely in puckered azetidines (53a) as in aziridines (see N-alkylaziridines section) :



To the extent that this conformation is attainable, it may lead to shielding of the nitrogen. It is also possible, especially for 5f, that progressive flattening of the azetidine ring may occur, resulting in shielding through changes in bonding and geometry about the nitrogen (53b).

CHAPTER III

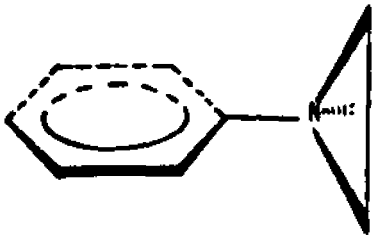
^{15}N CHEMICAL SHIFTS AND IONIZATION POTENTIALS OF N-ARYLAZIRIDINES

Introduction

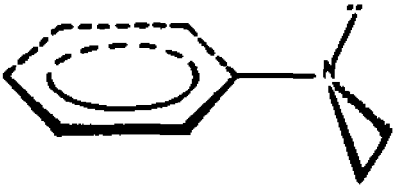
In the previous chapter, substituent effects on the ^{15}N chemical shifts of small rings were examined in terms of the anomalous geometry and conjugative ability of these systems. This chapter will examine the conjugative interaction of the nitrogen lone pair of aziridine with the π orbitals of benzene substituted in the 4 or 2 position. Results from ^{15}N nmr and PES will be used to explore the nature and extent of this interaction.

In the parent molecule, N-phenylaziridine, two minimum-energy conformations are likely : the bisected conformation, in which the axis of the nitrogen lone pair orbital is in the plane of the ring (I), and the perpendicular conformation, in which the lone pair is effectively perpendicular to the benzene plane (II). The bisected conformation, which allows overlap of the small-ring Walsh orbitals with the benzene system, is preferred in phenylcyclopropane and 2-phenylaziridine (see Chapter II). However, in N-phenylaziridine, electron diffraction

studies in the gas phase (54), and dipole moment and Kerr constant measurements in solution (55), all point exclusively to the perpendicular conformation II, which optimizes lone pair delocalization.



I



II

Previous work has shown the extent of this conjugation in N-phenylaziridines appears to be less than that in anilines. Thus, results from ^{19}F chemical shifts (56) and infrared intensities (57) suggest that the 1-aziridinyl group is not as conjugatively electron-donating as either the amino or the dimethylamino group. Other studies, including ^{13}C nmr (58), infrared intensities (57), and uv spectroscopy (59), all show that N-phenylaziridine is the least conjugated of the series of N-phenyl cyclic amines.

Magnitudes of ^{15}N chemical shifts are useful in estimating the degree of n-π interaction, which may be influenced by 4-substituents (60) and by steric hindrance (48) to conjugation in anilines. Shielding of the nitrogen in N,N-dimethylanilines upon 2,6-dimethyl substitution or upon 4-substitution by electron-donating groups is

attributable to decreased electron delocalization. Substituent chemical shifts in 4-substituted anilines and N,N-dimethylanilines have been correlated with σ_I and σ_R^- values in a dual substituent parameter (DSP) analysis (60b, 61).

The DSP equation [1] of Taft (10) was developed because

$$P_i - P_o = \rho_I \sigma_I + \rho_R \sigma_R \qquad [1]$$

of the inability of the single-parameter Hammett equation (62) to correlate physical property measurements in some systems with σ. In equation [1], P_i is a physical property or rate measurement in the presence of substituent i, and P_o is the value when i = H. σ_I and σ_R are measures of the substituent effect transmitted inductively or by resonance, respectively, and ρ_I and ρ_R are the corresponding sensitivities of the measured property.

Hammett's σ constants, derived from ionization constants of substituted benzoic acids, do not fit data from substituted benzenes with very different electron distributions. Taft's equation uses one of four σ_R parameters : σ_R^{BA}, σ_R^+ , σ_R^- , σ_R^o . The first, σ_R^{BA} is used for benzoic acids or other slightly electron-deficient systems. Benzenes which are extremely electron-deficient or electron-rich require the use of σ_R^+ or σ_R^- , respectively. The σ_R^o values are appropriate for relatively unperturbed benzenes.

They have been used extensively for ^{19}F and ^{13}C chemical shifts (61). These σ_R parameters are not to be confused with the plethora of σ constants proposed (64) for use in the single-parameter equation (σ^+, σ^-, σ^*, etc.). Other DSP equations have been proposed (65), all with a single resonance parameter for all molecular systems.

Also of interest in connection with ^{15}N shifts of N-arylaziridines is the fact that, in many instances, ^{15}N chemical shifts correlate with photoelectron spectroscopic ionization potentials. For example, the ^{15}N shifts of methyl-substituted formamides and acetamides correlate separately with the ionization potentials of the nitrogen lone pair (48). However, in ureas (48) an "average ΔIP" for the two lone-pair-like orbitals does not correlate with δ_N; rather, only a general trend is displayed. ^{15}N chemical shifts of 2,6-dialkyl-N,N-dimethylanilines correlate well with the difference in IP between π_2 and π_4, the orbitals arising by interaction between the nitrogen lone pair and the appropriate benzene π orbital (Figure 7). However, only a moderate correlation is exhibited with π_2, the orbital considered to have the greater lone-pair contribution. While δ_N of 4-substituted N,N-dimethylanilines does not correlate with either π_2 or π_4 (60b), the shifts for a series of 4-substituted benzamides (66) display a good correlation with the IP of the nitrogen lone pair.

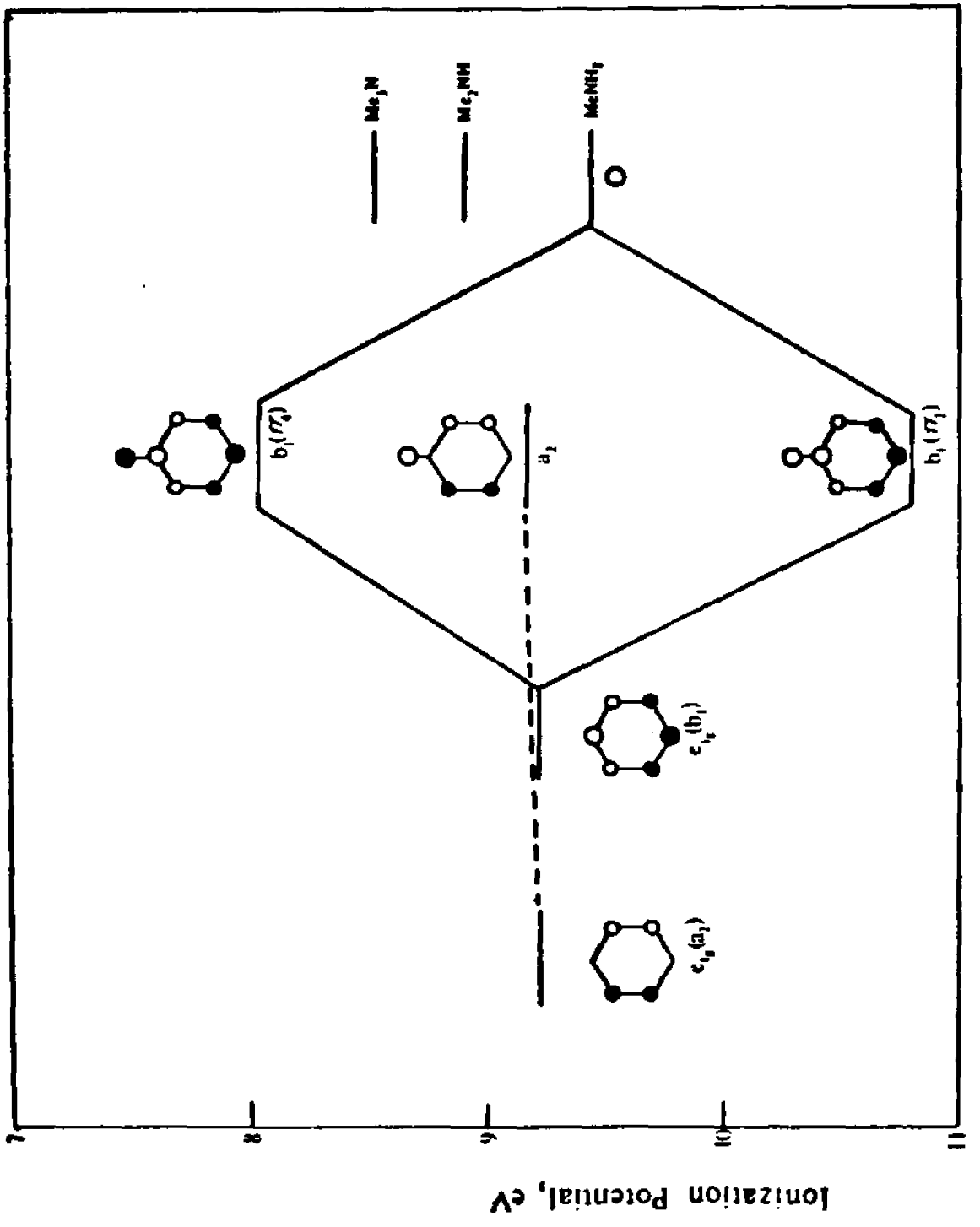


Figure 7. Orbital interactions in anilines.

The goal of this study was to measure the ^{15}N chemical shifts and photoelectron vertical ionization potentials of a series of N-arylaziridines and, by correlating the shifts with DSP parameters and with IPs, to describe the n-π interaction. Unfortunately, the shifts do not correlate well with the IPs. Possible reasons for this are discussed below.

Results

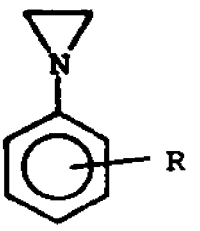
Two new compounds, N-(2,6-dimethylphenyl)aziridine and N-(4-dimethylaminophenyl)aziridine have been synthesized using procedures from the literature (see Experimental Methods). ^{15}N chemical shifts of N-arylaziridines, 6a-6j, along with values for the corresponding N,N-dimethylanilines (from Reference 60b) are listed in Table VI. The vertical ionization potentials of the three highest occupied orbitals are listed in Table VII.

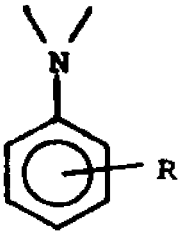
Discussion

^{15}N Chemical Shifts

The range of ^{15}N chemical shifts spanned by aziridines 6a-j (Table VI) is substantially less than the range (51.8 ppm) for the corresponding N,N-dimethylanilines. Exclusion of anilines in which conjugation is known to be sterically hindered, and which correspond to 6i and 6j, still affords a larger chemical shift range (28.1 ppm) than for the aziridines. Thus, consistent with earlier studies, the aziridine nitrogen appears to interact less extensively with the benzene ring than other aniline nitrogens. Nonetheless, the manner in which the phenylaziridine and aniline nitrogen nuclei respond to substituents seems to be parallel. The aziridine values correlate well (r = 0.988, standard

Table VI ^{15}N Chemical Shifts of N-Arylaziridines[a]





	R	δ_N	$\Delta\delta_N$[b]	δ_N[c]	$\Delta\delta_N$[b]
6a	H	39.8	0.0	44.9	0.0
6b	4-$N(CH_3)_2$	35.0[d]	-4.8	42.6	-2.3
6c	4-OCH_3	36.1	-3.7	40.8	-4.1
6d	4-CH_3	38.0	-1.8	42.8	-2.1
6e	4-F	37.4	-2.4	40.5	-4.4
6f	4-Cl	39.6	-0.2	49.1	4.2
6g	4-CN	45.7[e]	5.9	59.6	14.8
6h	4-NO_2	47.3[f]	7.5	68.6	23.7
6i	2-CH_3	37.9	-1.9	33.8[g]	-11.1
6j	2,6-$(CH_3)_2$	37.8	-2.0	16.8[g]	-28.1

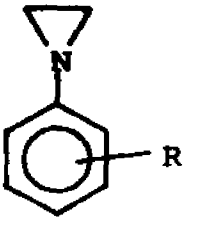
a. As in Table III.

b. $\Delta\delta_{N_R} = \delta_{N_R} - \delta_{N_H}$ c. Reference 60b, DMSO solutions. d. $\delta_{N(CH_3)_2}$ = 41.5 ppm.

e. δ_{CN} = 254.4 ppm. f. δ_{NO_2} = 370.1 ppm.

g. Reference 48a.

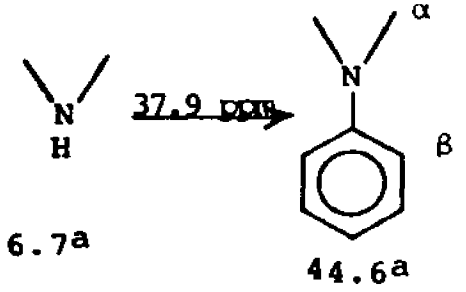
Table VII Vertical Ionization Potentials of N-Arylaziridines (in eV)



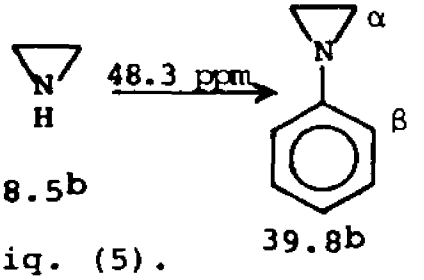
R	π_2	π_3	π_4	$\pi_2 - \pi_4$
H	10.3	9.1	8.1	2.2
4-$N(CH_3)_2$	10.4	9.0	7.1	3.3
4-OCH_3	9.7	9.1	7.6	2.1
4-CH_3	10.1	9.2	8.0	2.1
4-F	10.4	9.5	8.2	2.2
4-Cl	10.3	9.6	8.3	2.0
4-CN	10.5	9.7	8.5	2.0
4-NO_2	11.0	10.0	8.9	2.1
2,6-$(CH_3)_2$	10.1	8.6	7.9	2.2

deviation = 0.69 ppm, Figure 8), and moderately well (r = 0.957, standard deviation = 1.3 ppm, Figure 9) with those for primary and N,N-dimethylanilines, respectively. The slope of the latter correlation line, 0.414 ppm (aziridine)/ppm (aniline), also points to attenuated interaction with the benzene ring; indeed, the behavior more nearly resembles that of 4-substituted N,N-2,6-tetramethylanilines (60b). Interestingly, the aziridine values in Table VI correlate well (r = 0.988, standard deviation = 0.63 ppm, Figure 10) with ^{17}O shifts of corresponding anisoles (67), and yield a slope similar to that of the aniline plot, 0.422 ppm N/ppm O.

The discussion so far supports the idea that N-phenylaziridine nitrogens interact less effectively with a benzene ring than do aniline nitrogens. This inference seems at variance with the following phenyl substituent effects :



6.7[a] 44.6[a]



-8.5[b] 39.8[b]

a. Neat liq. (5).

b. $CDCl_3$ solution, this work.

c. C_6H_{12} solution (5).

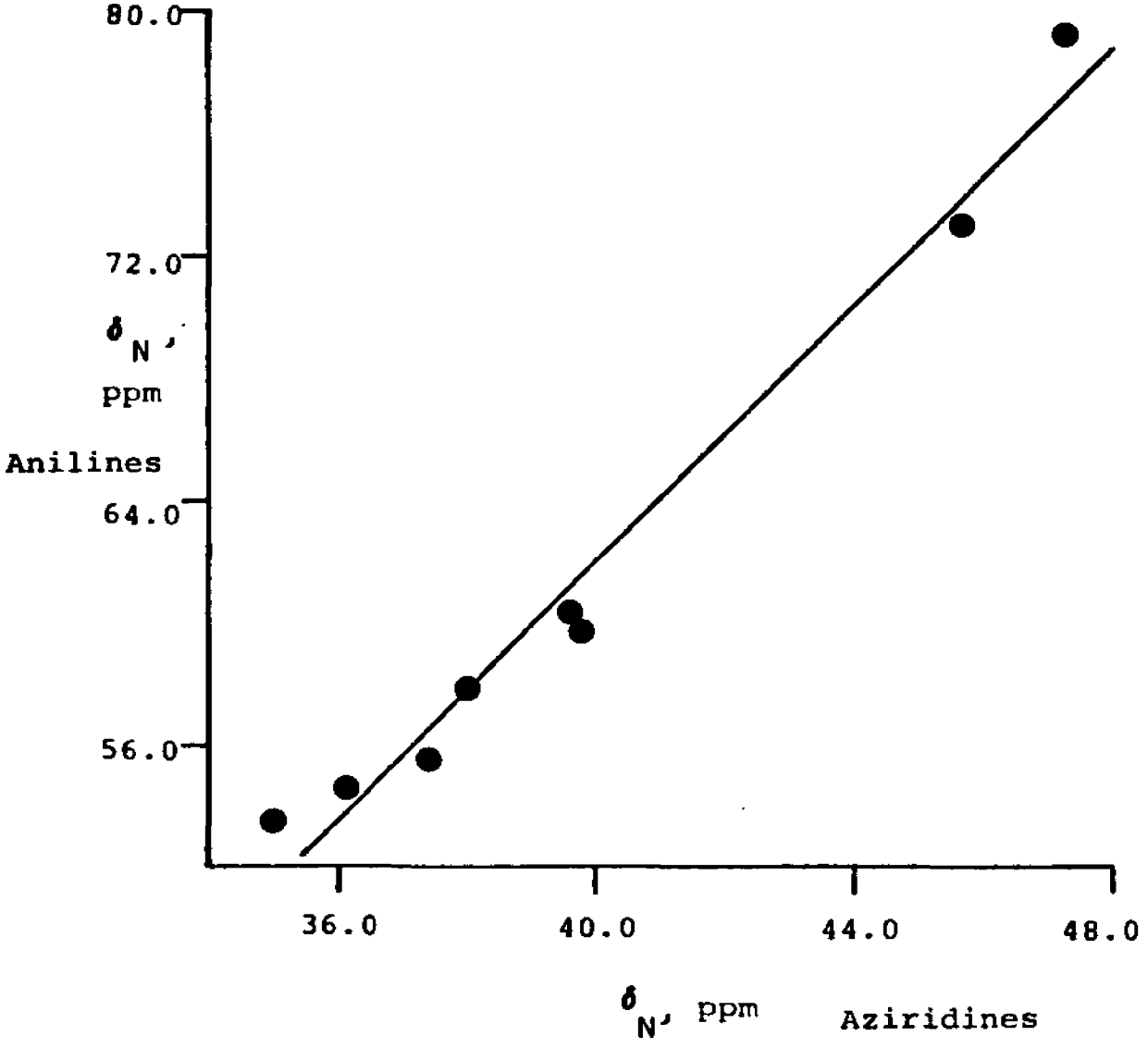


Figure 8. Correlation of δ_N values for N-arylaziridines with those of corresponding 4-substituted anilines.

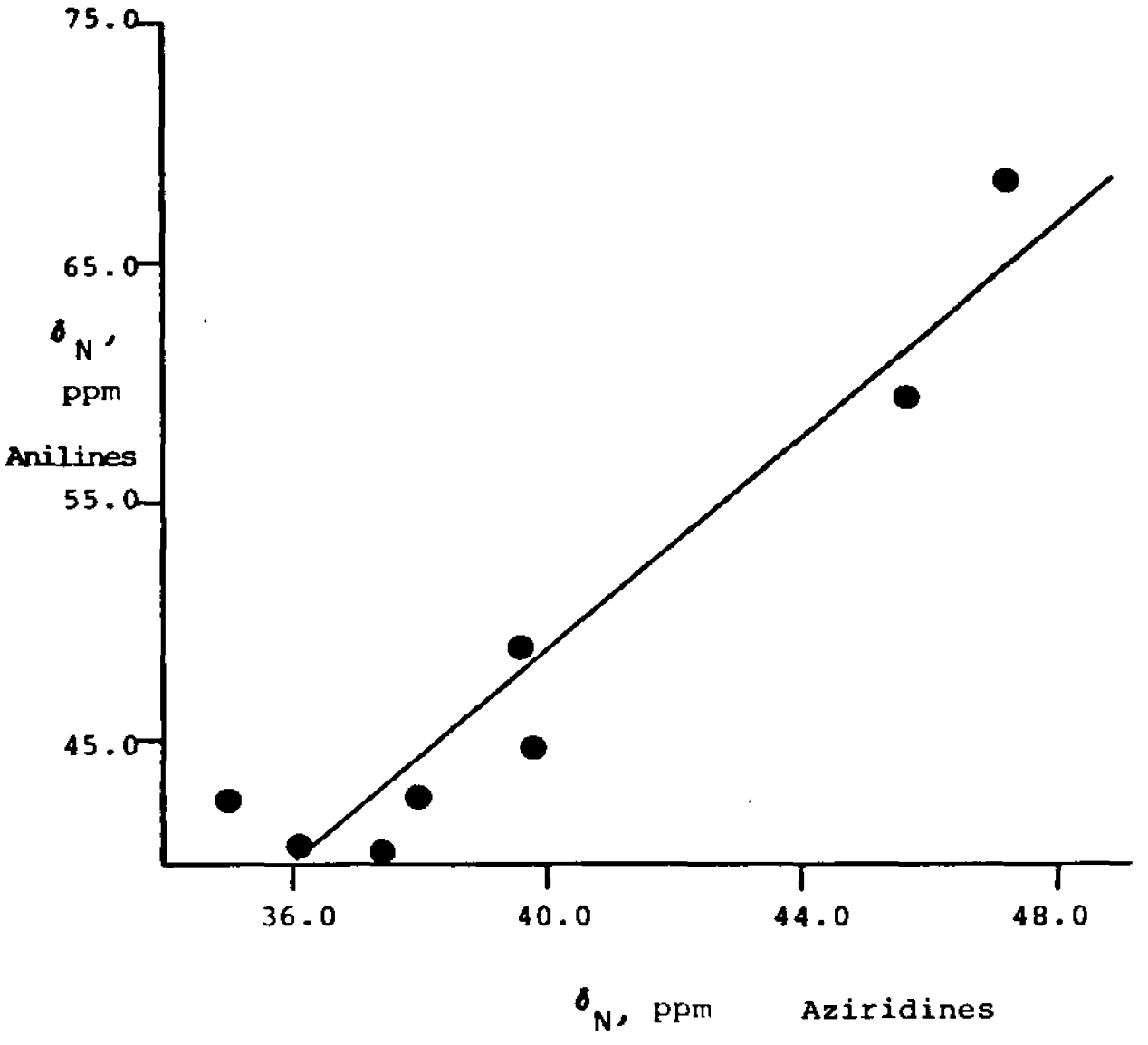


Figure 9. Correlation of δ_N values for N-arylaziridines with those of the corresponding 4-substituted N,N-dimethylanilines.

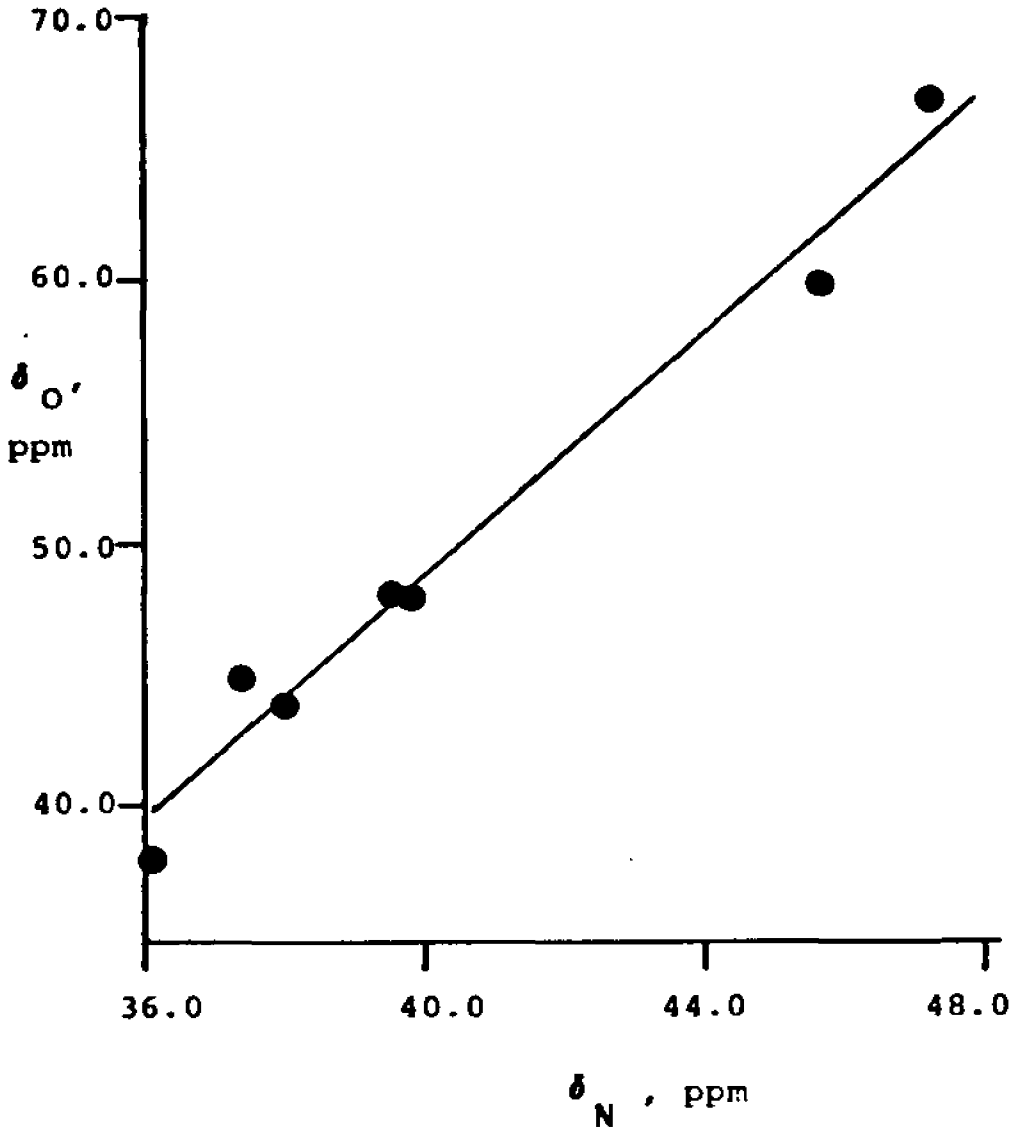
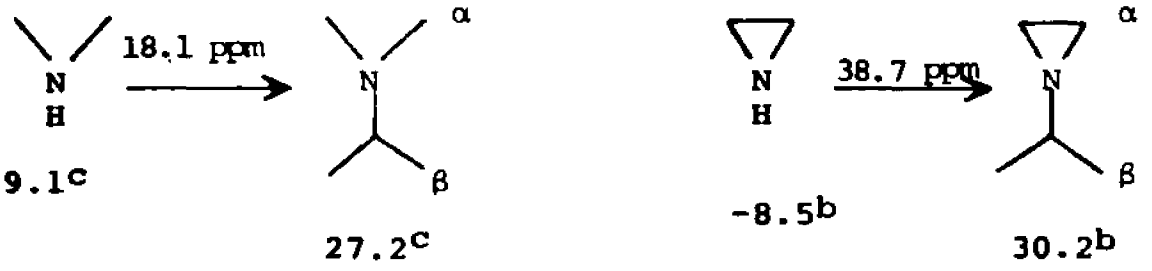


Figure 10. Correlation of δ_N values for N-arylaziridines with δ_O values for corresponding 4-substituted anisoles.

The larger deshielding effect for aziridine would appear to imply greater conjugative interaction in this system. However, even alkyl groups have a greater influence on aziridine resonance positions :



In the acyclic molecules, deshielding expected upon additional α and β substitution may be partly attenuated by a shielding, mutual "αβ " effect (43b). The contribution from this effect, which varies with geometry, might be expected to be smaller in the aziridines because the ring α carbons are constrained to be further away from the β carbons (see below).

The influence of 2-methyl substitution on the N-phenylaziridine chemical shift is an order of magnitude smaller than that in the N,N-dimethylanilines (48a). If n-π interaction in the aziridines is attenuated, then the effect of any steric perturbations would be expected to be smaller. Molecular models indicate that the large exocyclic bond angles of the aziridine ring cause the methylene ring carbons to be bent further away from the aryl ring plane than the N-methyl carbons of N,N-dimethylanilines. Furthermore, adoption of the bisected conformation induces

severe steric interactions with 2-substituents on the aryl ring. Thus, it is likely that there is little conformational change on 2-methyl substitution and that the observed changes in nitrogen chemical shift are largely inductive.

While the nitrogen shifts are consistent with reduced interactions between the aziridine and benzene rings, they do not alone reflect the nature of the interaction, especially in terms of the classical separation into inductive and conjugative effects. To assess the latter possibility, the 4-substituted N-arylaziridine chemical shifts have been subjected to a DSP analysis using values of σ_I and σ_R^-. The latter parameter is considered to be most appropriate for electron-rich aniline-type systems (61). The eight compounds under consideration fit the requirements for a minimum basis set of substituents as suggested by Taft (61). Values of ρ_I and ρ_R were derived from a multiple regression analysis of the experimental data fitted to equation [2]:

$$\Delta\delta_N = \rho_I \sigma_I + \rho_R \sigma_R^- \qquad [2]$$

Values of ρ_I = 4.31 and ρ_R = 10.98 were obtained from this treatment, with a correlation coefficient r = 0.993 and a Taft f value of 0.13 (61). Correlations are considered reasonable if f<0.2. Attempted correlations of the data with either σ_I or σ_R^- separately or with σ_p gave much

lower correlation coefficients. The ratio $\lambda = \rho_R/\rho_I = 2.55$ is higher than from any other set of data for aniline systems, including ^{15}N shifts of 4-substituted anilines, ionization constants of anilinium salts, and reaction rates of anilines as nucleophiles. This would appear to suggest that conjugative interactions are relatively more important than inductive interactions in the aziridines than in the anilines. At the same time the ρ values themselves are smaller than those derived for the aniline chemical shifts, again consistent with the suggestion that the extent of total substituent interaction is considerably smaller than in the anilines.

The possibility that the unexpectedly large λ value arises from inappropriate use of σ_R^- for the weakly interacting aziridinyl group suggested correlation of the data with σ_R^o. This parameter has been applied successfully to chemical shifts of the weakly donating ^{19}F substituent. Thus, multiple regression fitting of $\Delta\delta_N$ to equation [2] using σ_R^o in place of σ_R^- affords values of $\rho_I = 7.0$ and $\rho_R = 12.8$, with $r = 0.981$ and $f = 0.22$. Although the ratio $\lambda = 1.83$ is now lower, it is still larger than that for nitrogen chemical shifts of 4-substituted anilines. In addition, the f value indicates at best a marginal correlation, casting doubt on the significance of the ρ and λ values obtained.

In order to determine whether the results obtained using $\sigma_{\bar{R}}$ could be artifacts of a particular data set, several partial sets of substituent chemical shifts (SCS) were correlated with σ_I and $\sigma_{\bar{R}}$. Omission of the shift of the 4-$N(CH_3)_2$ compound, which displayed the largest deviation from the calculated shift, results in values of $\rho_I = 4.39$ and $\rho = 10.41$, with $f = 0.054$. This much improved fit of the data gives $\lambda = 2.37$, only slightly lower than for the whole data set, eliminating the possibility that insufficiently good fitting of the data produced the high λ value. Use of data sets lacking NO_2, CN, and $N(CH_3)_2$ or OCH_3 and $N(CH_3)_2$ produces values of $f<0.1$ and $\lambda>2$. It seems that the high λ value is a real result from this set of data, not merely an artifact.

Contributing to the unusually high λ value is the fact that DSP analyses of non-proton nmr shifts generally give high λ values (61) - as high as 4.35 for ^{19}F shifts of aryl fluorides. Probably, these values merely serve as a confirmation of the heavier dependence of shifts of second-row nuclei on π-electron density, which would be reflected in the resonance term, than on σ-electron density. Even so, this does not explain how the λ value for the aziridine SCS is so much higher than that for the aniline SCS. Fitting of inversion barriers in N-aryl-2,2-dimethylaziridines (68) to equation [2] also produces a high λ value (2.02), with $f = 0.105$. Since these inversion

barriers are dependent on n-π overlap, it is possible that λ can be characteristic of the property measured rather than the system, as with ^{19}F shifts. Alternatively, the geometry of the N-phenylaziridine molecule, which discourages twisting of the lone pair from the perpendicular conformation, maximizes n-π interaction and, thereby, the ratio of resonance to inductive contributions. A relevant example given by Taft (61) is the saponification of phthalide esters, which are constrained to coplanarity. The λ value of 1.10 is higher than values for benzoate esters, $\lambda < 1.0$, even though the ρ values for the phthalide esters are lower. Thus, a system with less total substituent interaction can have a higher contribution from conjugative interactions if the geometry consistent with maximum overlap is highly favored. While this picture seems to be consistent with the data for the N-arylaziridines, confidence in it is lessened by the possibility that σ_I and σ_R^- values derived for other systems may not accurately reflect substituent interactions in this system.

Photoelectron Spectroscopy

The photoelectron spectra of aniline systems are characterized by three low-energy bands. The first (lowest IP , π_4) and third (π_2) energy levels arise from interaction of the nitrogen lone pair with the degenerate highest occupied benzene orbitals. Furthermore, analysis

of overlap populations suggests that π_2 has somewhat greater lone-pair character than π_4 (69). The second (π_3) level is localized on the benzene ring and has no lone-pair character. The difference, $\pi_2 - \pi_4$ decreases when delocalization of the lone pair decreases (48a,70). In N,N-dimethylanilines this difference is 2.4 eV, less than the 2.8 eV value for the more extensively delocalized primary aniline. The $\pi_2 - \pi_4$ difference in N-phenylaziridine was found to be 2.2 eV (Table VII), confirming the decrease in n-π interaction inferred from the ^{15}N shifts and other studies. The probable reason for this small interaction is the lower lone-pair energy of aziridine (47) relative to $(CH_3)_2NH$ (Figure 11). However, $\pi_2 - \pi_4$ remains very close to this value throughout much of the series, despite the variable lone-pair delocalization which is manifested in the chemical shifts. These data closely parallel those for N,N-dimethylanilines (71) with the sole exception of the 2,6-dimethyl compound. Since this substitution seems to have much less effect on delocalization in N-arylaziridines (see ^{15}N nmr discussion) than in dimethylanilines, it is not surprising that $\pi_2 - \pi_4$ is nearly the same as for the unsubstituted N-phenylaziridine.

Attempts to correlate δ_N with the IP of the orbitals resulting from lone-pair-π interaction were fruitless. A general trend in which lower IP coresponds to an increase in ^{15}N shielding is indicated in the π_4 vs. δ_N comparison, but

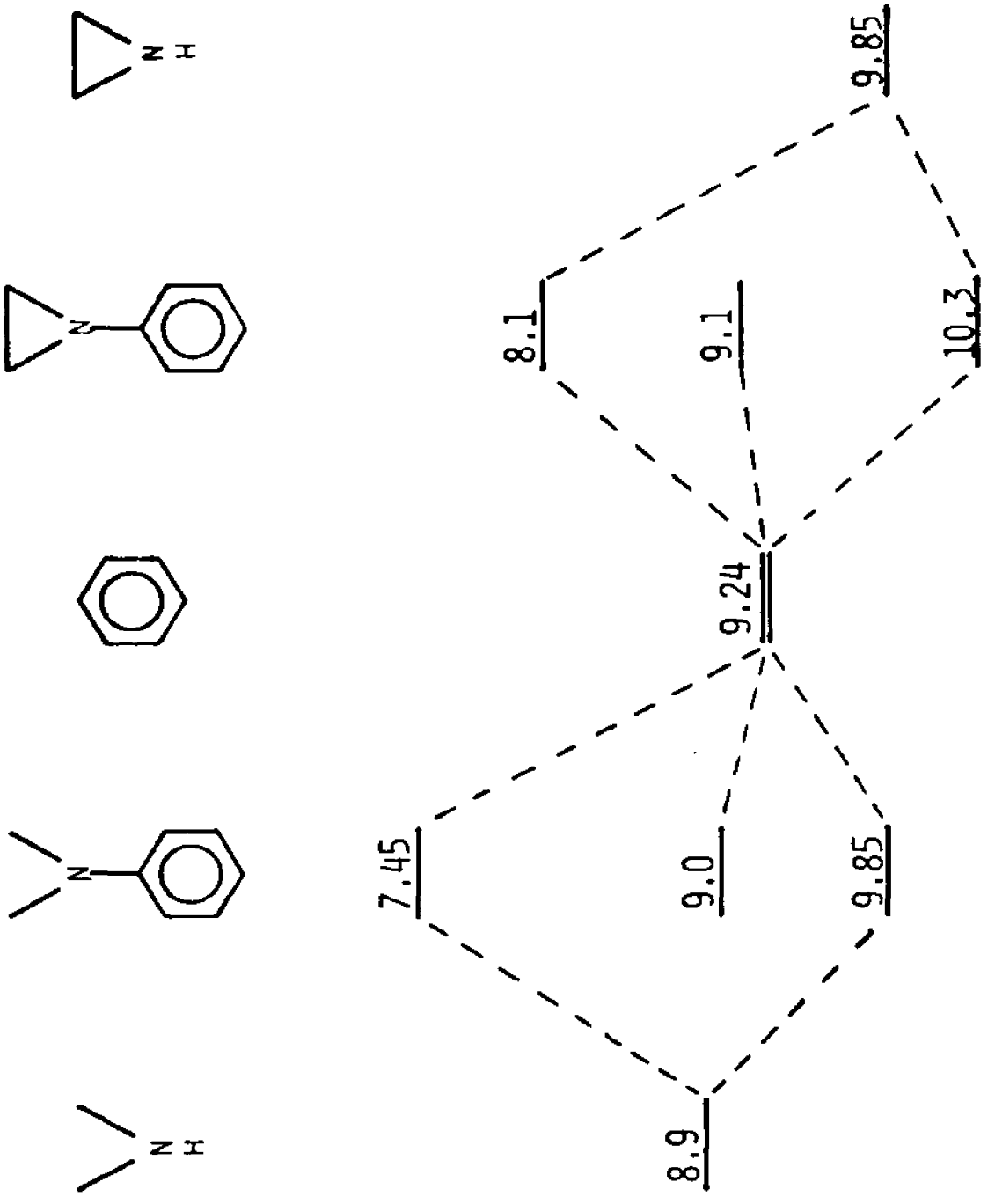


Figure 11. Interaction of aziridine and dimethylamine lone-pair orbitals with the highest occupied benzene π orbital.

this is not statistically significant ($r = 0.883$). Moreover, π_2, the orbital considered to have greater lone-pair character, shows not even a trend with the δ_N values.

The constancy of $\pi_2 - \pi_4$ and lack of correlation of the ^{15}N shifts with π_2 or π_4 separately result from direct interaction of the 4-substituent with these orbitals. The correlations are good in the case of 2,6-dialkyl-N,N-dimethylanilines where inductive effects of differing alkyl substituents on π_2 and π_4 are fairly constant. Thus, sterically induced reduction in delocalization dominates $\pi_2 - \pi_4$ and the ^{15}N shifts. However, with a variety of functional groups as substituents, the situation is more complicated. The strong resonance donors OCH_3 and $N(CH_3)_2$ interact with π_4 to decrease its IP, thereby increasing $\pi_2 - \pi_4$. This overcomes any decrease associated with lessened lone-pair delocalization. On the other hand, CN and NO_2 lower the IPs of all orbitals. This lowering is likely to be greater for π_4 than for π_2 because of the close proximity of the former to the NO_2 antibonding orbitals (70). Thus, $\pi_2 - \pi_4$ will be decreased, and in this way compensate for any increase owing to enhanced $n-\pi$ interaction. These direct substituent effects on π_2 and π_4 are not likely to affect ^{15}N resonance positions in the same way and will thereby make a correlation between δ_N and $\pi_2 - \pi_4$ less likely.

In several series of disubstituted benzenes, the IP of

the highest occupied orbital has been correlated with the corresponding ionization from the monosubstituted benzene (66). When benzene is substituted by an electron-donating group and a series of 4-substituents, the slope of the correlation line is less than unity. This slope decreases as $\pi_3 - \pi_4$, the displacement of the highest occupied orbital, π_4, from the relatively unperturbed π_3 orbital increases. The quantity $\pi_3 - \pi_4$ is not strictly a measure of electron donation to the phenyl group by the substituent. For N-phenylaziridine, $\pi_3 - \pi_4 = 1.0$ eV, which falls between the values of 0.83 and 1.16 observed for anisole and aniline, respectively. The slope of 0.678 (r = 0.978, standard deviation = 0.11 eV, Figure 12) for 4-substituted N-phenylaziridines is similar to the values of 0.7 and 0.67 found for substituted anisoles and anilines. Thus, the slope of this plot is a rough measure of the interaction between 4-substituents and the π_4 orbital, and so may be useful in confirming assignments of PES bands in similar systems (66).

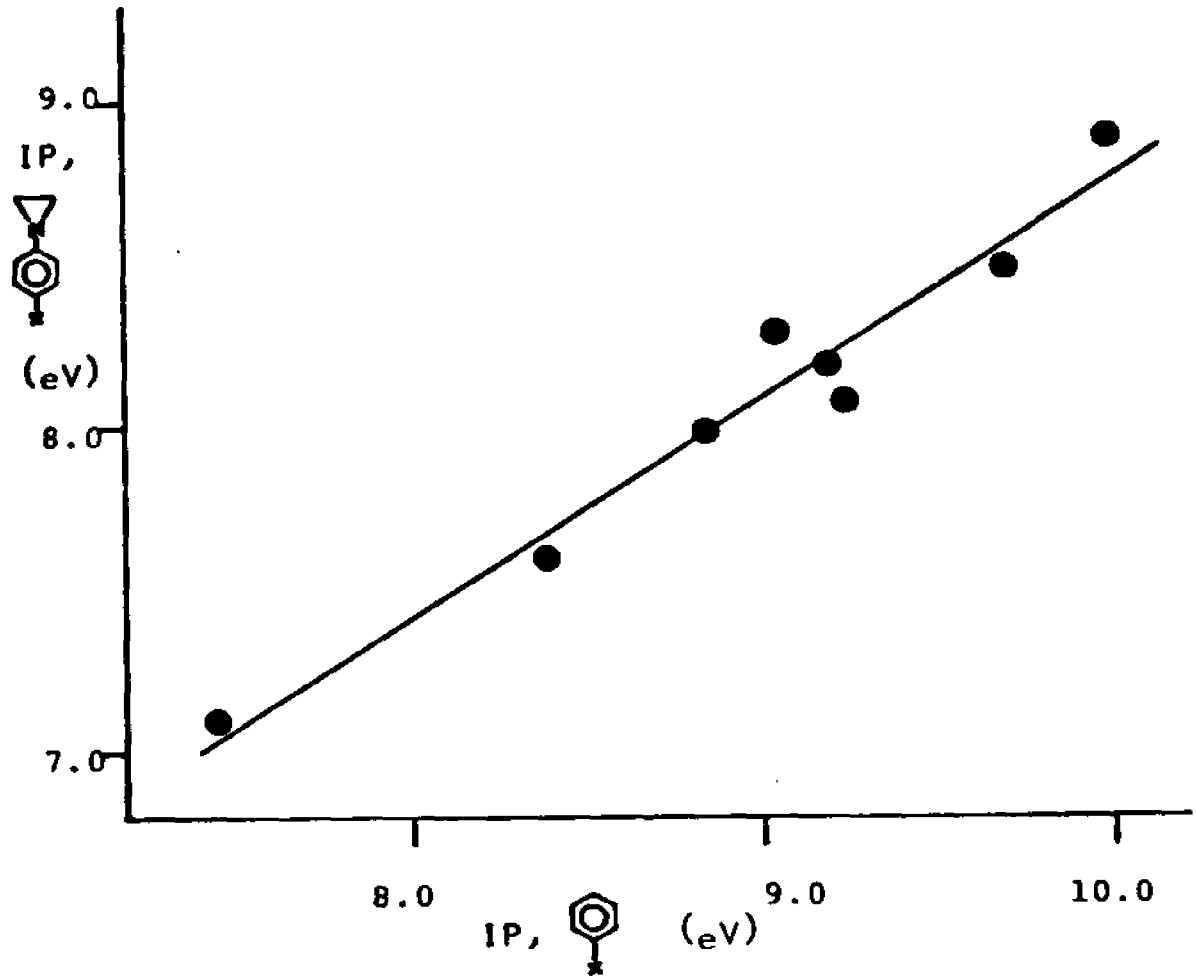


Figure 12. Correlation of the lowest IP of N-arylaziridines with that of the corresponding monosubstituted benzene.

CHAPTER IV

^{15}N CHEMICAL SHIFTS AND IONIZATION POTENTIALS OF AZIRINES

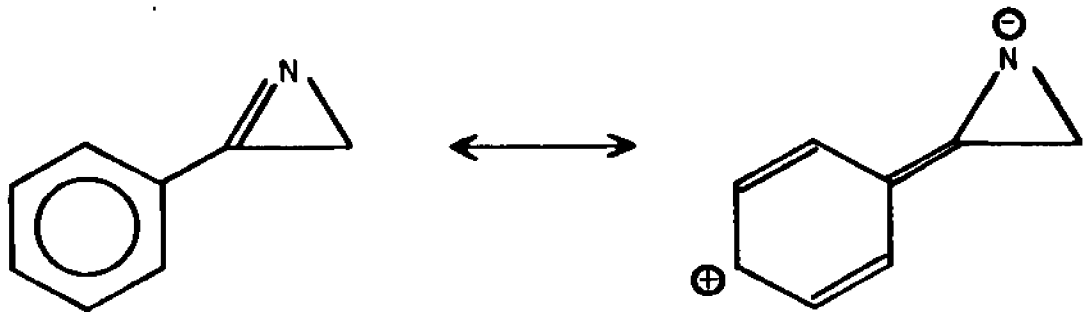
Introduction

The 1-azirine ring system (I) has been the subject of

I

many studies over the past decade. Reviews have appeared on the synthesis (72) and reactions (73) of azirines. However, there are very few studies of azirines or their carbocyclic analogs, cyclopropenes, using nmr spectroscopy. Both systems exhibit the unusual bonding characteristic of three-membered rings (see Chapter II). In addition, they have properties associated with the inclusion of a double bond into a small ring. Just as the endocyclic single bonds of three-membered rings have partial double-bond character, a double bond will have some triple-bond character (21). This is manifested in the large value of the one-bond C1-H coupling constant in cyclopropene (74) and in 3-phenylazirine (75) and in the shielding of the methyl carbon of 1-methylcyclopropene (74). The shielding of the ipso-phenyl carbon of 2-phenylazirine (II) has also been attributed to the triple-bond character of the C-N double

bond (75); the ipso carbon of benzonitrile is shielded relative to benzene. However, the para-carbon of II is deshielded, indicating contribution from resonance structure III :



II III

The fact that the deshielding is greater than that observed in acyclic imines has been rationalized by suggesting a greater contribution from III because of reduced ring strain (75).

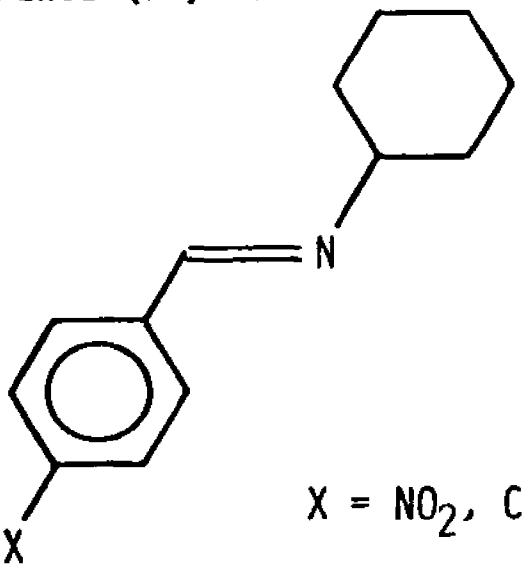
The ^{13}C chemical shifts of vinyl ring carbons in cycloalkenes (74,76) vary with ring size in a manner similar to that of cycloalkane shifts (36) with the exception of cyclobutene, which is slightly deshielded (6.4 ppm) relative to cyclopentene. Comparison of ^{15}N shifts of cyclic imines of different ring sizes would be of interest. Unfortunately, stable azirines and azetines with little or no substitution have not been reported and differences in effects of substituents on imines of differing ring size

would need to be separated from shift changes owing to ring size effects alone.

Substituent parameters for ^{13}C chemical shifts in the cyclopropenes were derived from shifts of a series of methylcyclopropenes (77) and found to be analogous to those for acyclic alkenes (76). The β substituent effect through the double bond (i.e. the effect on C2 of the methyl group in 1-methylcyclopropene) is -9.9 ppm, slightly larger than the corresponding value for the acyclic alkenes, -7.9 ppm. It has been suggested that the methyl group is also a γ substituent if the positions are labelled with the CH_2 carbon as the α carbon; the additional shielding of -2.0 ppm in the ring system is a reasonable value for a γ effect. Correction terms for interactions between pairs of substituents were also calculated in this study.

^{15}N chemical shift data for acyclic imines without an aryl substituent on nitrogen are sparse. Only a few aliphatic imines have been examined (78) and substituent parameters were not determined. It can be inferred from these data that the β effect of a methyl group through the imine bond on the ^{15}N shift is similar to that observed on the ^{13}C shift in cyclopropenes. Replacement of an isopropyl group on the imine carbon by phenyl results in a deshielding of +8.3 ppm, possibly the result of more facile $n \longrightarrow \pi^*$ transitions in the conjugated imine. Determination of ^{15}N

chemical shifts for a series of N-(arylmethylidene)-cyclohexylamines (IV) revealed a shift range of 23.8 ppm



IV

X = NO_2, Cl, H, CH_3, OCH_3

in $CHCl_3$ (79), nearly as large as that for 4-substituted anilines. Apparently, substituent-induced electronic changes are effectively transmitted through the imine bond to the nitrogen. The trifluoroacetate salts of this series are greatly shielded relative to the free bases, as expected on protonation of sp^2 lone pairs, but the shift range is nearly identical (79,80). This implies that substituent effects on the $n \longrightarrow \pi^*$ transition are not important contributors to shift changes. Unfortunately, azirines are not stable in acidic media, making protonation studies unlikely. Alkyl substituent effects in N-(phenylmethylidene)alkylamines were found to parallel those in alkylamines (79).

From photoelectron spectra, the larger cycloalkenes have π IPs near those of acyclic alkenes (9.1 eV) (81), while four- and three-membered rings show successive increases in

IP up to the value of 9.8 eV for cyclopropene (82). While no adequate explanation has been offered, the change may be associated with the additional π-type overlap and partial triple-bond character of small-ring double bonds. The ionization potential of the C-N π bond in aliphatic acyclic imines is in the range 10.3 - 10.66 eV (83), which is between typical values for C-C and C-O π bonds. The sp^2 lone pair IP is in the range 9.25 - 9.5 eV, near the value for pyridine, 9.59 eV (84). The photoelectron spectrum of N-(phenylmethylidene)methylamine (85) shows that there is an interaction between C-N and phenyl π orbitals (Figure 13) comparable in extent to that observed in the spectrum of 1-phenylpropene (86). The IPs are higher for the imine because the IP of the C-N double bond is higher than that of the C-C double bond, but the π_2 - π_4 splittings, which are characteristic of the conjugative interaction, are similar. In the triply-bonded analogs the situation is quite different. Phenylacetylene seems to be as conjugated as styrene, but in benzonitrile (70), the low-lying C-N π orbitals (12.21 eV in acetonitrile) do not interact strongly with the benzene π orbitals. The effect of nitrile substitution on benzene is to lower the energies of both benzene π orbitals to 9.72 and 10.14 eV.

In the remainder of this chapter, ^{15}N chemical shifts and IPs of 1-azirines are presented and discussed. However, there are few cases in which any comparison is made between

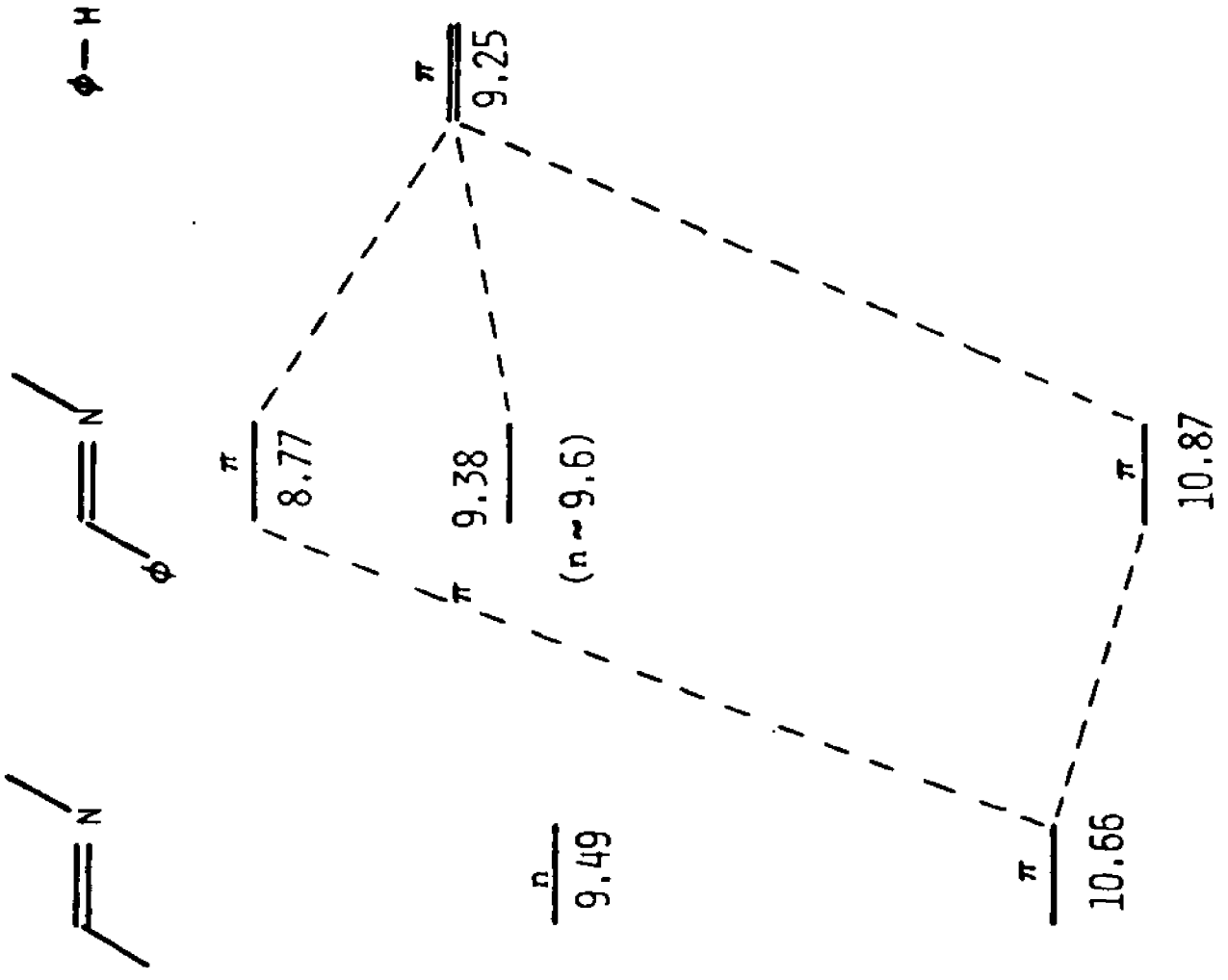


Figure 13. π - π Orbital interactions in phenyl-substituted acyclic imines.

nmr and PES data. IPs of the nitrogen lone pair and imine π orbitals display small and nonsystematic changes in the compounds examined, eliminating the possibility of a general correlation with the chemical shifts.

Results

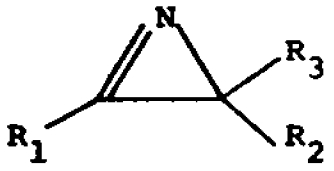
^{15}N chemical shifts of azirines 7a-j are listed in Table VIII. Photoelectron spectroscopic ionization potentials for 7a-i are presented in a correlation diagram (Figure 14) with data for some acyclic imines obtained from literature references cited in the introduction to this chapter.

Discussion

^{15}N Chemical Shifts

In accord with the commonly observed trend for ^{13}C and ^{15}N shifts, the ^{15}N shifts of azirines 7a-c are at higher shielding compared with those for the acyclic imines (79) derived by formal breaking of the C-C bond. Differing β substituent effects in the two series are responsible for variation in the magnitude of this shielding ring-closure shift from 45.5 ppm for 7c to 56.4 ppm for 7a. The 21.4 ppm deshielding resulting from introduction of a β-methyl group in 7b is unusually large. It was noted in Chapter II that the effect of ring β-methyl substituents on the ^{15}N shift is larger than that for β-substituents in an N-alkyl group. In the acyclic imines, the introduction of a β substituent in N-(phenylmethylidene)ethylamine causes a deshielding of 15.3 ppm relative to N-(phenylmethylidene)methylamine. A second β substituent results in a deshielding of 12.1 ppm for the

Table VIII ^{15}N Chemical Shifts of Azirines[a]



Compound	R_1	R_2	R_3	$\delta_N(CDCl_3)$	δ_N(DMSO)
7a	C_6H_5	H	H	261.7	264.7[b]
7b	C_6H_5	CH_3	H	283.1	
7c	C_6H_5	CH_3	CH_3	300.1	
7d	C_6H_5	$CH(OCH_3)_2$	H	268.5	
7e	C_6H_5	C_6H_5	H		279.2
7f	4-$CH_3C_6H_4$	H	H	257.0	
7g	4-$CH_3OC_6H_4$	H	H	253.1	
7h	$(CH_3)_2N$	CH_3	CH_3	207.5[c]	
7i	CH_3	$CO_2C_2H_5$	H	266.2	
7j	$-(CH_2)_6-$		H	247.8	

a. As in Table III.

b. The solvent shift of +3.0 ppm in DMSO relative to $CDCl_3$ is consistent with that observed for pyridine in the same solvents (+5.2 ppm) (87).

c. $\delta_{N(CH_3)_2}$ = 53.6

Figure 14. PES ionization potentials (in eV) of azirines and imines (83,85).

isopropyl compound relative to the ethyl compound. The decrease in β substituent effect with increasing substitution - the "saturation effect" - is well documented and is discussed in Chapter II. In the azirines, the second β-methyl group induces an additional 17.0 ppm deshielding of 7c relative to 7b. Thus, 7c displays a deviation from substituent chemical shift additivity of -4.4 ppm. The deviations for geminal methyl substitution in aziridines (Chapter II) and cyclopropenes (77) are lower : -0.9 ppm and -1.5 ppm, respectively. However, in both cases, the absence of a phenyl substituent on the adjacent carbon would eliminate interaction between phenyl and methyl substituents and hence, lessen the deviation.

Replacement of two methyl hydrogens of 7b with methoxy groups shields the nitrogen by -14.6 ppm ($\delta_{7g} - \delta_{7b}$), the sum of the γ substituent effects of the oxygens and δ effects of the methyls. Effects of δ substituents are usually very small, but the effect on the ^{15}N shift of an oxygen situated at the γ position is known to be quite large : -8.4 ppm for acyclics and -7.2 ppm if both atoms are incorporated into a six-membered ring (88). Thus, γ heteroatom substitution brings about chemical shift changes of the usual magnitude in the azirine system.

A phenyl group at C3 should deshield the nitrogen by interaction with the Walsh orbitals of the three-membered

ring. For aziridine, this deshielding is 26.7 ppm for one phenyl group and 25.2 ppm for a second phenyl trans to the first. In the 2-phenylazirine system, a phenyl substituent at C3 deshields the nitrogen by 14.5 ppm ($\delta_{7e}-\delta_{7a}$). The lower value for the azirine agrees with the inference from ^{13}C chemical shifts of the para phenyl carbons (75) that this interaction is smaller for azirines than for aziridines.

Indications of the effect of electron-donating para substituents on the azirine nitrogen chemical shift of 2-phenylazirines were obtained from spectra of 7f and 7g. In the corresponding benzylidene imines (79), methyl and methoxy groups produced shieldings of -3.7 and -8.3 ppm, respectively. The data in Table VIII show that the response of the azirine nitrogen is comparable, although slightly larger : -4.7 and -8.6 ppm. The behavior of azirine ^{15}N shifts in this respect is clearly in the normal range for doubly-bonded nitrogens. In fact, if triple-bond character in the C-N double bond were evident here, the SCS would be expected to decrease rather than increasing slightly. The corresponding 4-substituted benzonitriles (89) display much smaller shieldings : -0.3 and -2.7 ppm. If ^{15}N spectra could be obtained for the less stable 4-nitro and 4-chloro compounds, DSP analysis of these data and the imine data might provide more insight into the relative electronic structure of the two systems.

In the unusual dimethylamino compound 7h, the interaction between the dimethylamino nitrogen lone pair and the azirine double bond can be assessed through the ^{15}N chemical shifts. Delocalization of a nitrogen lone pair into a π system deshields the nitrogen nucleus (see references cited in Chapter III). Not surprisingly, the pyridine nitrogen of aminopyridines (90) is shielded when the amino group is in the 2 or 4 position. The azirine nitrogen of 7h is significantly shielded relative to other azirine nitrogens. In addition, the dimethylamino nitrogen is deshielded relative to most tertiary amine nitrogens and to N,N-dimethylaniline. The value is close to that (58.1 ppm) found for the dimethylamino nitrogen of 2-dimethylamino-pyridine (91). However, tertiary amides are considerably further deshielded to 95-130 ppm (92). The intermediate position of the $N(CH_3)_2$ group in 7h appears to suggest an intermediate extent of delocalization. ^{15}N chemical shift data for amidines would be useful for comparison with those for 7h, but none have been published. Still, the upfield resonance position of the azirine nitrogen indicates considerable n-π interaction.

The influence of an ester group at C3 can be inferred from the ^{15}N shifts of 7i and 7j. Carbonyl and phenyl substituents have an unusually large effect on the carbon shift of cyclopropane (93,46). This may be attributed to overlap of substituent π orbitals with small-ring Walsh

orbitals, as discussed earlier. The bulk of the 18.4 ppm deshielding of 7i relative to 7j probably arises from such an interaction between the azirine ring bonds and the ester π bonds. If this is indeed true, a 3-$CO_2CH_2CH_3$ group interacts more strongly than a 3-C_6H_5 group. Possible explanations could be the greater electronegativity of the ester and better orbital energy matching with the ester. Comparison of 7j with 7b shows that the deshielding effect of the phenyl group at C2 is considerable if the long-range effects of the cyclooctyl methylenes on the nitrogen shift of 7j are small. This result contrasts with the small (8.3 ppm) deshielding observed in acyclic imines (78) on replacement of an isopropyl group on the imine carbon with phenyl.

Photoelectron Spectroscopy

The most striking characteristic of the spectra of 2-phenylazirines 7a-d is the lack of any ionization potentials below 9 eV. As discussed in the introduction to this chapter, the interaction of a benzene π orbital with that of an acyclic imine produces a lower-energy orbital at 8.77 eV (see Figure 12). A similar interaction between the azirine double bond and the benzene π orbitals would be expected to give a similarly low IP. Apparently, the triple bond character of the azirine double bond is significant in determining its energy. Like benzonitrile, the 2-phenylazirines display only a small (probably inductive) interaction between the benzene orbitals and the low-lying carbon-nitrogen multiple bond. This interaction leads to a small stabilization of the interacting benzene orbital and a small destabilization of the imine orbital; in 7a, the stabilized benzene π orbital is at 9.8 eV. In order to better characterize the interaction here, we need to know the energy of an "isolated" azirine double bond. This may be inferred from the IPs of 7i, in which the 2-substituent is not capable of strong conjugative interaction. Of the four IPs detected, two can be assigned to orbitals localized on the ester group. The highest occupied orbitals of ethyl acetate, at 10.39 and 10.99 eV, have been assigned to the carbonyl oxygen lone pair (n_b) and a combination of n and C=O π orbitals which is localized on the alkoxy oxygen (π_2),

respectively (94). Varying the substitution on the carbonyl carbon will affect the energy of n_O more than that of π_2; the corresponding IPs for ethyl formate are 10.96 and 11.28 eV. If the 3-(2-methyl)-1-azirinyl group is more electron donating to an ester than methyl, which seems likely in view of the higher polarizibility of the former, the IPs of the ester group in 7i should be lower than those of ethyl acetate. Thus, it is reasonable to assign the bands at 10.1 or 10.15 eV and 10.8 eV to the ester group, leaving 10.1 or 10.15 for the azirine nitrogen lone pair and 11.3 eV for the imine π bond. The lower energy of the imine π bond in azirines relative to that of acyclic imines (10.3-10.66 eV, reference 83) may be responsible for the small π-π interaction with the benzene ring. All of the azirines, except 7i have an IP in the range 10.75-11.0 which may be assigned to the imine orbital, slightly destabilized by electron donation from the phenyl group. The peak due to the interactive benzene orbital in 7a and 7b is lowered to 9.7-9.8 eV, where it coincides with the nitrogen lone pair ionization. The small decrease in IP of the lone pair in these compounds and in 7d (9.6 eV), 7e (9.8 eV), 7f (9.75 eV), and 7g (9.9 eV) probably stems from the same inductive interaction that lowers the IP of the carbon-nitrogen double bond. In 7c, the lone-pair-π degeneracy is lifted, and IPs of 9.05, 9.25, and 9.65 eV are observed. Probably, the 9.25 eV band can be assigned to the non-interactive benzene π orbital. However, it is impossible to determine from these

data alone whether the lone pair or the π orbital was raised in energy by 0.65 eV in 7c relative to 7b. The nitrogen chemical shifts in the series 7a → 7b → 7c do not display this sort of discontinuity.

In 7e, overlap of Walsh-type orbitals with the 3-phenyl substituent lowers the IP to 8.65 eV, a value identical to the lowest IP of phenylcyclopropane (31). This is puzzling in view of the fact that both ^{13}C (75) and ^{15}N (see above) shifts suggest that this interaction is weaker in azirines than in cyclopropanes. In phenyloxirane, where the small-ring delocalization into the benzene ring is even less, the lowest IP is 9.07 eV (95). In the PES spectrum of 7e, the band at 9.35 eV can be assigned to one or both unperturbed benzene π orbitals, and the one at 9.8 eV to the lone pair. The ionization at 10.35 eV could be either a drastically lowered benzene π orbital or a raised imine π orbital. If the IP of 11.0 eV is due to the imine π orbital, the 10.35 eV band must be a benzene π orbital, possibly arising from a through-space overlap of the two benzene rings, as suggested for cis-2,3-diphenylaziridine (Chapter II).

The 4-substituents in 7f and 7g lower the first IPs to 8.9 and 8.8 eV, respectively. These values are comparable to those for the corresponding acetophenones (70,71), 9.12 and 8.62 eV. The noninteractive benzene π orbital undergoes a slight stabilization and can be assigned to the band

occurring at 9.6 eV in both 7f and 7g. Ionizations from the nitrogen lone-pair and imine π orbitals are in the usual ranges, as discussed above.

Assignment of IPs in 7d is complicated by overlap of ionizations from orbitals discussed up to this point with those arising from interaction between the methoxy lone pairs. Cyclic acetals dioxolane and dioxane both have a lowest IP of 10.1 eV; the second IPs are at 10.65 and 10.35, respectively (96). Bands at 9.3 and 11.1 eV in 7d can reliably be assigned to the unperturbed benzene π and imine π orbitals, respectively. This leaves IPs at 9.6, 9.95, 10.35, and 10.65 eV to be assigned to the nitrogen lone pair, two oxygen lone-pair orbitals, and the other benzene π orbital. It is possible, in fact, that the oxygen lone pairs, which interact through the acetal C-H bond, could overlap with the Walsh orbitals in the azirine ring. More information is needed in order to assign the IPs.

The photoelectron spectrum of 7h, containing only three bands below 11 eV, is readily interpreted. The azirine lone pair appears at 9.05 eV; this value, being lower than that for the other azirines, is consistent with the increase in electron density at this nitrogen which was inferred from its chemical shift. The bands at 8.3 and 10.75 eV are typical for tertiary sp^3 nitrogens and azirine double bonds, respectively; the highest IP of trimethylamine occurs at

8.44 eV (97). The higher energy of the lone pair in 7h could result from a larger inductive destabilization in the azirine, or, more likely in view of the ^{15}N shifts, n-π overlap with the double bond. The azirine double-bond energy is slightly higher than in 7i; it is not clear why both the dimethylamino lone pair and the azirine double bond move to higher energy upon interaction with each other.

CHAPTER V

EXPERIMENTAL METHODS

NMR Spectra : Natural-abundance ^{13}C and ^{15}N spectra of $CDCl_3$ solutions (see concentrations below) 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 or 6.25 kHz over 8K data points was used, with pulse angles of ~20° and a repetition time of 1-2 s. Chemical shifts were measured with respect to internal $(CH_3)_4Si$ (0.0 ppm) or $CDCl_3$ (76.9 ppm). ^{15}N spectra were obtained with a 4 or 5 kHz spectral width, 8K data points, and 20° pulse angles. For secondary amines a repetition time of 1-3 s was used. Tertiary amines and imines 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. For some aziridines, pulse angles of 30-50° and a repetition time of 5 s were found to produce spectra readily. The effect of $Cr(acac)_3$ on the shifts is expected to be <0.5 ppm (98a). The combined effects of solvent, relaxation reagent, and bulk susceptibility are expected to introduce an uncertainty of <1 ppm (98b,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 (98d) :

Concentrations of 1-5 were in the range 4-8 M except for 4f, which was 1.8 M. For 6a-f,i-j, the concentration was 4 M, while 6g,h were 2.2 M. Concentrations of 7a-d,f-j were 2.9-4.9 M, while 7e was 1.4 M.

^{1}H nmr spectra were obtained in $CDCl_3$ at 60 MHz on either a Perkin-Elmer R-24A or a Varian A-60A spectrometer. Shifts are measured with respect to internal $(CH_3)_4Si$.

Photoelectron Spectra : PES ionization potentials of vaporized samples were determined using a modified (99) Perkin-Elmer PS-16 photoelectron spectrometer. The modifications mostly concerned repositioning of components for easier maintenance and improvements in vacuum. Improvement in temperature control of the probe by installation of a Lauda MGW temperature bath facilitated the present study. Control of the bath temperature and coolant flow determines the extent to which the UV light source heats the sample; constant probe temperatures of 40-275°C can be attained. Solid compounds and liquids boiling above 250°C/760 mm were placed in the probe and heated to 40-65°C, while more volatile samples were introduced from a flask connected via a glass stopcock to the probe inlet. The argon (15.75) or nitrogen (15.58) ionization was used for

calibration.

Materials : Pyrrolidine, N-methylpyrrolidine, piperidine, N-methylpiperidine, and perhydroazepine were purchased from Aldrich Chemical Co. 2-Methylaziridine (2a) was purchased from Interchemical Co. N-Methylazetidine (5b) was obtained from Professor A. T. Bottini. N-Methylperhydroazepine was obtained by methylation of perhydroazepine with formaldehyde and formic acid. 1-Azirines 7a-f,h-i were obtained from Professor A. Hassner and used as received. 7j was distilled from polymeric material. The vinyl azide precursor to 7g was converted to the azirine by thermolysis in toluene (100,101) and distilled. Structures of all compounds mentioned above were confirmed by some combination of boiling point comparisons, ^{1}H, and ^{13}C nmr spectra. All other compounds were synthesized and characterized as described below.

Aziridines and Azetidines (Chapter II)

Aziridines 1a-c, 2b-c, 3a,b,d were synthesized from commercially available amino alcohols (except for 3b (102)) via the sulfate esters by the "Wenker procedure" (103). Experimentally determined boiling points and nmr spectra along with literature values for each compound follow.

Aziridine [1a] : bp 53-55.5°C [lit. (104) bp 56.7°C]; ^{1}H nmr δ 1.5 (4H, s), 0.4 (1H, s). [lit. (105) ^{1}H nmr δ 1.52, 0.0-1.5].

N-Methylaziridine [1b] : bp 25.5°C [lit. (104) bp 23.5°C]; ^{1}H nmr δ 1.6 (3H, s), 0.35-1.1 (4H, m); ^{13}C nmr δ 48.1, 27.9 [lit. (37) ^{13}C nmr δ 48.0, 28.5].

N-Ethylaziridine [1c] : bp 49.5-50.0°C [lit. (104) bp 52°C]; ^{1}H nmr δ 2.15 (2H, q, J = 7 Hz), 1.10 (3H, t, J = 7 Hz), 1.0-1.6 (4H, m); ^{13}C nmr δ 56.3, 26.9, 14.5.

2-Ethylaziridine [2b] : bp 86.5-88.0°C [lit. (104) bp 89°C].

2-Isopropylaziridine [2c] : bp 100-101°C [lit. (106) bp 100-103°C]; ^{13}C nmr δ 37.0, 33.2, 24.1, 20.1 [lit. (34) ^{13}C nmr δ 37.2, 32.8, 24.0, 20.6, 19.9].

2,2-Dimethylaziridine [3a] : bp 69.5-70°C [lit. (104) bp 70°C]; ^{1}H nmr δ 1.5 (2H, s), 1.2 (6H, s).

1,2-Dimethylaziridine [3b] : bp 41-42°C [lit. (104) bp 43°C]; ^{13}C nmr δ 47.8, 35.7, 35.5, 18.3.

cis-2,3-Dimethylaziridine [3d] : This compound was synthesized from racemic 2-amino-3-butanol. The product

contained cis and trans isomers; it had two ^{15}N peaks, at 25.0 and 30.6 ppm (pure trans isomer, 3c, δ_N = 30.7 ppm). Its ^{13}C spectrum also contained peaks for both isomers : ^{13}C nmr δ 33.5, 29.2, 19.2, 13.6 [lit. (34) ^{13}C nmr δ 29.2, 13.6].

Compounds 1d-g, 5c-f were synthesized from amino alcohols obtained from amines and 2-chloroethanol (107). Experimental and literature data for the final products are reported below.

N-Propylaziridine [1d] : bp 74-75.5°C; ^{13}C nmr δ 64.2, 27.1, 23.3, 12.0.

N-Isopropylaziridine [1e] : bp 64-65°C [lit. (108) bp 66-68°C]; ^{13}C nmr δ 61.9, 26.4, 22.2.

N-Butylaziridine [1f] : bp 104.5-107°C [lit. (109) bp 104-108°C]; ^{13}C nmr δ 62.3, 32.4, 27.2, 21.0, 14.3.

N-(tert-Butyl)aziridine [1g] : bp 88-89°C [lit. (107) bp 91-92°C]; ^{1}H nmr δ 1.4 (4H, m), 0.9 (9H, s); ^{13}C nmr δ 50.2, 24.1, 17.8.

N-Ethylazetidine [5c] : bp 72-73°C [lit. (107) bp 74-75°C]; ^{13}C nmr δ 55.0, 53.9, 17.7, 12.5.

N-Propylazetidine [5d] : bp 76-80 °C; ^{13}C nmr δ 60.4, 53.6, 19.3, 16.0, 10.1.

N-Isopropylazetidine [5e] : bp 91-92 °C [lit. (110) bp 94-96 °C]; ^{13}C nmr δ 58.7, 53.7, 19.6, 16.5.

N-(tert-Butyl)azetidine [5f] : bp 115-117 °C [lit. (107) bp 116.5-117.3 °C]; ^{1}H nmr δ 3.8 (4H, t, J = 7 Hz), 2-3 (2H, m), 1.55 (9H, s); ^{13}C nmr δ 51.8, 46.7, 24.0, 15.8.

Azetidine [5a] was synthesized according to the procedure of Wadsworth (111). Its physical properties are : bp 62 °C [lit. (111) bp 62 °C]; ^{1}H nmr δ 3.65 (4H, t, J = 7.5 Hz), 2.85 (1H, s), 2.35 (2H, p, J = 7.5 Hz) [lit. (112) ^{1}H nmr δ 3.5 (4H, t, J = 7 Hz), 2.3 (2H, p, J = 7 Hz)]; ^{13}C nmr δ 45.3, 19.3.

Compounds 2d, 3c, 4a-b,d-f were synthesized by addition of IN_3 to the corresponding alkenes, followed by reduction with $LiAlH_4$ (100, 113). The products had the following properties :

2-(tert-Butyl)aziridine [2d] : ^{13}C nmr δ 38.9, 29.5, 25.9, 20.6 [lit. (34) ^{13}C nmr δ 39.7, 30.1, 26.5, 21.4].

trans-2,3-Dimethylaziridine [3c] : ^{13}C nmr δ 33.7, 19.3

[lit. (34) ^{13}C nmr δ 33.5, 19.3].

2-Phenylaziridine [4g] : bp 90-94 °C/11 mm [lit. (113) bp 90-94 °C/11 mm]; ^{13}C nmr δ 140.8, 128.2, 126.7, 125.6, 31.6, 29.3 [lit. (34) ^{13}C nmr δ 140.7, 128.2, 126.7, 125.6, 31.6, 29.2].

2-Methyl-2-phenylaziridine [4b] : ^{13}C nmr δ 143.7, 128.0, 125.8, 36.2, 34.9, 24.7 [lit. (34) ^{13}C nmr δ 143.9, 128.2, 126.5, 126.0, 36.3, 35.0, 24.8].

trans-2-Methyl-3-phenylaziridine [4d] : ^{1}H nmr δ 7.1 (5H, s), 2.4 (1H, d, J = 4 Hz), 1.85 (1H, m), 1.2 (3H, d, J = 6 Hz), 1.0 (1H, brd s) [lit. (113) ^{1}H nmr δ 7.1 (5H, s), 2.44 (1H, d, J = 2.8 Hz), 1.83 (1H, m), 1.3 (1H, s), 1.2 (3H, d, J = 5.3 Hz)]; ^{13}C nmr δ 140.7, 128.2, 126.6, 125.5, 40.0, 37.0, 19.4 [lit. (34) ^{13}C nmr δ 140.8, 128.6, 127.0, 125.8, 40.4, 37.0, 19.5].

2,2-Diphenylaziridine [4e] : In the synthesis of 4e, some 2-amino-1,1-diphenylethanol is produced by hydrolysis of 4e (113). The ^{13}C nmr of this product mixture exhibits peaks which may be attributed to the amino alcohol as well as all of the peaks characteristic of the aziridine : ^{13}C nmr δ 142.2, 140.5 128.2, 127.6, 127.0, 70.9, 43.8, 35.2 [lit. (34) ^{13}C nmr δ 142.7, 128.3, 127.8, 127.1, 43.9, 35.3]. Of the two ^{15}N peaks at 36.1 and 44.4 ppm, the latter peak at

lower shielding may be assigned to the acyclic amine.

cis-2,3-Diphenylaziridine [4f] : mp 81.5-83.0°C [lit. (113) mp 81-82°C]; ^{13}C nmr δ 136.3, 127.5, 127.2, 126.1, 39.4 [lit. (34) ^{13}C nmr δ 136.9, 128.1, 127.8, 126.8, 39.9].

cis-2-Methyl-3-phenylaziridine [4c] was produced by reduction of phenyl vinyl ketoxime with $LiAlH_4$. The ketoxime was synthesized in three steps from 3-dimethylaminopropiophenone as described in reference 114. The product had bp 62°C/3.5 mm [lit. (114) bp 85°C/8 mm]; ^{13}C nmr δ 136.7, 126.8, 125.5, 35.9, 31.1, 12.5 [lit. (34) ^{13}C nmr δ 138.1, 128.1, 126.8, 37.1, 32.1, 13.6].

trans-2,3-Diphenylaziridine [4g] was synthesized by reaction of triphenylphosphine with the azidoalcohol resulting from reaction of sodium azide with trans-stilbene oxide (115). Triphenylphosphine oxide did not precipitate completely and had to be removed by chromatography of the product on silica gel with benzene. The final product had ^{1}H nmr δ 7.1 (10H, s), 2.9 (2H, s), 1.25 (1H, brd s) [lit. (113) ^{1}H nmr δ 7.15 (10H, s), 2.85 (2H, s), 1.23 (1H, brd s)]; ^{13}C nmr δ 139.6, 128.4, 127.1, 125.4, 43.6 [lit. (34) ^{13}C nmr δ 139.9, 128.6, 127.2, 125.6, 43.7].

trans-2,3-Dimethyl-2-phenylaziridine [4h] was synthesized by

addition of methylmagnesium iodide to propiophenone oxime (116). It had ^{13}C nmr δ 154.3, 141.5, 127.9, 126.4, 42.3, 38.1, 27.8, 15.8 [lit. (34) ^{13}C nmr δ 154.3, 141.7, 128.1, 126.5, 42.2, 39.0, 28.0, 15.5].

N-Arylaziridines (Chapter III)

N-Phenylaziridine [6a] was synthesized by the action of NaOH in ethanol/water on N-(2-bromoethyl)aniline hydrobromide (mp 137.5-139°C [lit. (117) mp 138-139°C]), which was obtained from the reaction of 48% HBr with commercially available 2-(N-phenyl)aminoethanol (117). The final product, 6a, had bp 67-75°C/12 mm [lit. (117) bp 70- 70.5°C/13 mm]; ^{13}C nmr δ 155.2, 128.9, 122.3, 121.0, 27.5 [lit. (58) ^{13}C nmr δ 155.4, 128.1, 120.7, 25.0].

N-Arylaziridines 6c-d,g-j were produced by ring closure of appropriate precursors with NaH/DMSO (118). Details and properties for each follow.

N-(4-Methoxyphenyl)aziridine [6c] was synthesized from N-(2-chlcroethyl)-4-methoxyaniline hydrochloride (mp 156-162°C [lit. (118) mp 157-160°C]), which was obtained in two steps from the aniline via 2-[N-(4-methoxyphenyl)]-aminoethanol (bp 102-106°C/.03 mm [lit. (118) bp 150-152°C/0.15 mm]) (118). The final product, 6c, had bp

57-58°C/0.1 mm [lit. (118) bp 63-63.5°C/0.42 mm]; ^{13}C nmr δ 154.6, 148.1, 121.3, 113.8, 55.0, 27.4; ^{1}H nmr δ 6.25-6.9 (4H, m), 3.55 (3H, s), 1.9 (4H, s).

N-(4-Methylphenyl)aziridine [6d] was synthesized by the route given for 6c. Intermediates which were purified had the following properties : 2-[N-(4-methylphenyl)]amino-ethanol : bp 83-85°C/0.1 mm [lit. (117) bp 155-157°C/8 mm]; 6d : bp 92-96°C/15 mm [lit. (119) bp 76-77°C/8 mm]; ^{13}C nmr δ 152.0, 130.2, 128.4, 119.8, 26.4, 19.7 [lit. (120) ^{13}C nmr δ 152.3, 129.0, 125.8, 120.3, 27.0, 20.2].

N-(4-Cyanophenyl)aziridine [6g] was synthesized from N-(2-tosyloxyethyl)-4-cyanoaniline (mp 93-105°C [lit. (118) mp 104.5-106°C]), which was prepared from 2-[N-(4-cyanophenyl)] aminoethanol (mp 90-93°C [lit. (118) mp 91-92°C]; ^{13}C nmr δ 152.6, 133.6, 120.9, 112.0, 95.8, 59.6, 45.1) by the procedure given in reference 118. The amino alcohol was synthesized by reduction of 3-(4-cyanophenyl)-2- oxazolidinone (mp 149-152°C; ^{13}C nmr δ 154.7, 142.6, 133.2, 119.0, 117.9, 105.2, 61.9, 44.6) with $LiBH_4$. Reduction was incomplete even under more drastic conditions (refluxing THF, 2 days vs. 0°C, 3 h) than those given for the methoxy compound. The amino alcohol was extracted with dilute HCl and the remaining oxazolidinone reused. The oxazolidinone was produced by NaH/acetone-induced ring closure of N-(2-chloroethoxycarbonyl)-4-

cyanoaniline (mp 104.5-107°C), which was synthesized by the reaction of 4-cyanoaniline with 2-chloroethylchloroformate in refluxing $CHCl_3$, following the procedure of reference 121. This sequence was used (118) for the 4-methoxy compound as far as the amino alcohol, but was never reported for the 4-cyano substitution. The final product, 6g, had mp 76.5-82°C [lit. (118) mp 84-85°C]; ^{13}C nmr δ 158.5, 132.4, 120.9, 118.6, 104.3, 27.2.

N-(4-Nitrophenyl)aziridine [6h] was synthesized from N-(2-tosyloxyethyl)-4-nitroaniline (mp 128.5-131°C [lit. (118) mp 128.5-130.5°C]), which in turn was prepared from 2-[N-(4-nitrophenyl)]aminoethanol (mp 106-108°C [lit. (118) mp 109-110°C]). The amino alcohol was prepared from 2-aminoethanol and 4-chloronitrobenzene (118).

N-(2-Methylphenyl)aziridine [6i] was synthesized from N-(2-bromoethyl)-2-methylaniline hydrobromide (mp 162-167°C [lit. (119) mp 210-213°C; this must be in error-it is inconsistent with other melting points reported in reference 119]), which was prepared by the procedure used for 6a (117) from the amino alcohol 2-[N-(2-methylphenyl)]aminoethanol : bp 88.5-89.5°C/0.1 mm [lit. (119) bp 144-146°C/7 mm]. The final product, 6i, was found to be a mixture of 6i and unreacted bromide as determined by ^{13}C nmr. In order to establish that the ^{15}N shift observed for the mixture was that of 6i, the ^{15}N spectrum of the bromide was determined.

Spectral data for both compounds are as follows. 6j : bp 95 °C/15 mm [lit. (119) bp 73-75 °C/8 mm]; ^{13}C nmr δ 151.9, 130.6, 130.0, 126.3, 122.1, 119.2, 27.7, 17.7. N-(2-bromoethyl)-2-methylaniline : ^{13}C nmr δ 146.0, 130.2, 127.1, 122.6, 117.5, 110.2, 60.8, 45.9, 17.4; ^{15}N nmr δ 58.9.

N-(2,6-Dimethylphenyl)aziridine [6j], a new compound, was synthesized in the manner described for 6i. Properties of the intermediates and the final product are as follows. 2-[N-(2,6-Dimethylphenyl)]aminoethanol : bp 80-83 °C/0.05 mm N-(2-bromoethyl)-2,6-dimethylaniline : mp 198-200 °C dec. (ethanol). 6j : bp 105-106 °C/11 mm; ^{1}H nmr δ 6.9 (3H, s), 2.35 (6H, s), 2.1 (4H, s); ^{13}C nmr δ 150.9, 128.8, 128.7, 121.8, 29.8, 18.6; Anal. Calcd for $C_{10}H_{13}N$: C, 81.63; H, 8.84; N, 9.52. Found : C, 81.74; H, 9.03; N, 9.55.

N-Arylaziridines 6b,e-f were synthesized directly from amino alcohols by treatment with triphenylphosphine, carbon tetrachloride, and triethylamine in acetonitrile (122). Properties of the aziridines and amino alcohol intermediates are given below.

N-(4-Dimethylaminophenyl)aziridine [6b], a new compound, was synthesized as described above. The amino alcohol was produced by the procedure of reference 123, except that the

hydrochloride salt formed on reaction of N,N-dimethyl-4-phenylenediamine with 2-chloroethylchloroformate (1:1 mole ratio) was hydrolyzed to the amino alcohol without purification. 2-[N-(4-dimethylaminophenyl)]aminoethanol : bp 134-136 °C/0.1 mm. 6b : bp 63 °C/0.05 mm; ^{13}C nmr δ 146.5, 145.7, 121.3, 113.6, 41.0, 27.4; Anal. Calcd for $C_{10}H_{14}N_2$: C, 74.07; H, 8.64; N, 17.28. Found : C, 73.78; H, 8.48; N, 17.09.

N-(4-Fluorophenyl)aziridine [6e] was synthesized as described above. The amino alcohol was synthesized from the aniline and 2-chloroethanol (117). 2-[N-(4-fluorophenyl)]aminoethanol : bp 82-83 °C/0.05 mm [lit. (116) bp 117-119 °C/0.15 mm]. 6e : bp 71-73 °C/11 mm [lit. (118) bp 85-86 °C/18 mm]; ^{13}C nmr δ 157.5, 150.7, 121.2, 114.6, 26.8 [lit. (120) ^{13}C nmr δ 157.8, 150.9, 121.4, 114.8, 27.1].

N-(4-chlorophenyl)aziridine [6f] was synthesized as described above. The amino alcohol was obtained by the procedure in reference 126. 2-[N-(4-chlorophenyl)]-aminoethanol : mp 76-77 °C [lit. (118) mp 76-77 °C]. 6f : bp 40 °C/0.05 mm [lit. (118) bp 63.5-64 °C/0.28 mm]; ^{13}C nmr δ 154.0, 128.8, 126.9, 122.2, 27.6 [lit. (120) ^{13}C nmr δ 153.5, 128.5, 126.8, 121.8, 27.3].

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