2α-Methyl-3α-azidocholestane (15). 2α-Methylcholestan-3β-ol[29] was transformed in 77% yield into the azide, which exhibited mp 110–111°, $[\alpha]^{20}D$ +92°. *Anal.* Calcd for $C_{28}H_{49}N_3$: C, 78.62; H, 11.55; N, 9.83. Found: C, 78.41; H, 11.73; N, 9.72.

4α-Methyl-3α-azidocholestane (16). In an analogous manner, 4α-methylcholestan-3β-ol[29] yielded 63% of azide (mp 104–105°, $[\alpha]^{20}D$ −54°) accompanied by 15% of olefin and 5% of 4α-methylcholestan-3-one. *Anal.* Calcd for $C_{28}H_{49}N_3$: C, 78.62; H, 11.55; N, 9.83. Found: C, 78.35; H, 11.51; N, 9.83.

6β-Azidocholestane (27). Cholestan-6α-ol[30] was transformed in 40% yield into the azide, which crystallized in needles (mp 69–70°, $[\alpha]^{20}D$ −30°) from acetone. *Anal.* Calcd for $C_{27}H_{47}N_3$: C, 78.38; H, 11.46; N, 10.16. Found: C, 78.58; H, 11.47; N, 10.01.

7α-Azidocholestan-3β-ol Acetate (31). An over-all yield of 66% of azide (mp 68–69°, $[\alpha]^{20}D$ +35°, after recrystallization from acetone–methanol) was realized starting with cholestane-3β,7β-diol 3-acetate.[31] *Anal.* Calcd for $C_{29}H_{49}O_2N_3$: C, 73.84; H, 10.47; N, 8.91. Found: C, 73.80; H, 10.61; N, 8.86.

(29) Y. Mazur and F. Sondheimer, *J. Am. Chem. Soc.*, 80, 5220 (1958).
(30) R. Tschesche, *Ber.*, 65, 1842 (1932).
(31) O. Wintersteiner and M. Moore, *J. Am. Chem. Soc.*, 65, 1503 (1943).

Saponification of **31** with 5% methanolic potassium hydroxide solution (30-min reflux) and recrystallization from acetone–methanol provided 7α-azidocholestan-3β-ol mp 125–126°, $[\alpha]^{20}D$ +82°. *Anal.* Calcd for $C_{27}H_{47}ON_3$: C, 75.47; H, 11.03; N, 9.78. Found: C, 75.65; H, 10.93; N, 9.79.

Reduction of 0.1 g of the hydroxy azide with lithium aluminum hydride followed by acetylation in ether solution and recrystallization from methanol furnished colorless needles (0.085 g) of 7α-acetaminocholestan-3β-ol, mp 268–270°, $[\alpha]^{20}D$ −3° (lit.[27] mp 270–272°, $[\alpha]^{20}D$ −9°).

7β-Azidocholestan-3β-ol Acetate (34). Starting with cholestane-3β,7α-diol 3-acetate[31] there was obtained 34% of Δ^7-cholesten-3β-ol acetate and 50% of the azide **34**, which exhibited mp 110–111°, $[\alpha]^{20}D$ −50°, after recrystallization from acetone–methanol. *Anal.* Calcd for $C_{29}H_{49}O_2N_3$: C, 73.84; H, 10.47; N, 8.91. Found: C, 73.86; H, 10.66; N, 8.85.

Saponification in the above described manner led to 7β-azidocholestan-3β-ol, mp 158–159°, $[\alpha]^{20}D$ −40° (*Anal.* Calcd for $C_{28}H_{47}ON_3$: C, 75.47; H, 11.03; N, 9.78. Found: C, 75.68; H, 11.00; N, 9.69), which was reduced with lithium aluminum hydride and acetylated to yield, after recrystallization from methanol, 7β-acetaminocholestan-3β-ol, mp 253–255°, $[\alpha]^{20}D$ +60° (lit.[27] mp 255–259° $[\alpha]^{20}D$ +63°).

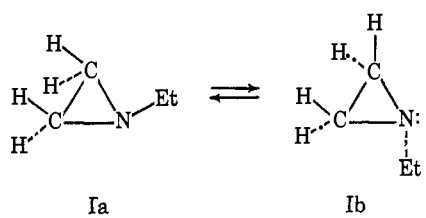
Nuclear Magnetic Resonance Spectra and Nitrogen Inversion in 1-Acylaziridines[1]

F. A. L. Anet and J. M. Osyany

Contribution No. 1888 from the Department of Chemistry, University of California, Los Angeles, California, and from the Department of Chemistry, University of Ottawa, Ottawa, Ontario. *Received August 17, 1966*

Abstract: The nmr spectra of several 1-acylaziridines were determined over a range of temperatures. Rates of nitrogen inversion were obtained for 1-methanesulfonyl, 1-(N,N-dimethylcarbamyl)-, and 1-carbomethoxyaziridine. A barrier to rotation about the carbon–nitrogen bond in the side chain of 1-(N,N-dimethylcarbamyl)-aziridine was also observed. The rates of nitrogen inversion in 1-acylaziridines were found to be much higher than those of 1-alkylaziridines.

The rates of nitrogen inversion in many derivatives of aziridine (ethylenimine) are of a suitable magnitude for study by nmr spectroscopy.[2,3] Thus, at room temperature the ring protons in 1-ethylaziridine (I) give[2] rise to an A_2B_2 pattern, showing that the rate constant (k, in units of sec^{-1}) for the nitrogen inversion process (Ia ⇄ Ib) is much less than the chemical shift, ν_{AB} (in units of cps). At higher temperatures the spectrum broadens and then collapses (at 108°) to a single band. At the coalescence temperature,[4] k is approximately equal to $\pi\nu_{AB}/\sqrt{2}$.



Ia Ib

Since the rate constants in many cases were obtained[2,3] only at the coalescence temperatures, a comparison of one compound with another is not simple. Table I shows some results calculated from literature data[5] and given in the form of the temperature at which k is ~60 sec^{-1}

A change of the group on nitrogen from ethyl to cyclohexyl produces only a small effect, but a *t*-butyl group apparently increases the rate of nitrogen inversion tremendously. This has been ascribed to steric repulsions of the *t*-butyl group with the ring hydrogen atoms. Such repulsions should be largely relieved in the transition state for nitrogen inversion. However, the effect of the *t*-butyl group cannot be regarded as firmly established because the ring protons still form a single band at the lowest temperature reached. There are in fact two possible explanations for this behavior:

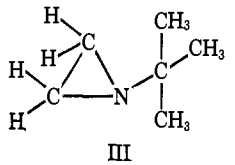
(1) Supported by the National Research Council of Canada and the National Science Foundation (Grant No. GP 3780).
(2) (a) A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, 78, 5126 (1956); 80, 5203 (1958); (b) A. Loewenstein, J. F. Neumer, and J. D. Roberts, *ibid.*, 82, 3599 (1960).
(3) H. S. Gutowsky, *Ann. N. Y. Acad. Sci.*, 70, 786 (1958); T. J. Burdos, C. Szantay, and C. K. Navada, *J. Am. Chem. Soc.*, 87, 5796 (1965).
(4) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, 25, 1228 (1956); J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book, Co., Inc., New York, N. Y., 1959, p 218.
(5) For compound V, a temperature coefficient for the rate constant similar to that found for compound IV was used in the calculation.

Table I. Nitrogen Inversion in Aziridine Derivatives

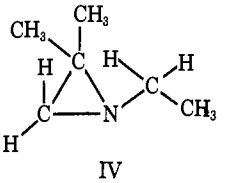
Compound	Substituent(s) on aziridine ring	Temp, °C, at which $k_{inv} \approx 60$ sec^{-1}	Ref
I	1-Ethyl	108	*a*
II	1-Cyclohexyl	95	*a*
III	1-*t*-Butyl	<-77	*a*
IV	1-Methyl-2,2-dimethyl	97	*b*
V	*trans*-1-Ethyl-2,3-dimethyl	~90	*a*
VI	1-Ethyl-2-methylene	-65 (-25[c])	*b*
VII	1-Phenyl	<-77 (-65[c])	*a*
VIII	1-Methanesulfonyl	<-37	*d*
IX	1-Trifluoromethyl-2,2-difluoro	-50	*e*

[a] Reference 2a. [b] Reference 2b. [c] In methanol solution. [d] Reference 8. [e] Reference 9.

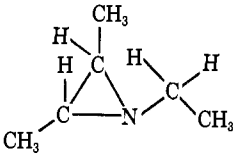
(a) if ν_{AB} has a "normal" value, than $k > \nu_{AB}$, or (b) if ν_{AB} is fairly small (say 0–3 cps), then as a result of coupling a single line will result no matter what the value of k may be. The chemical shift, ν_{AB}, may well be appreciably different in 1-*t*-butylaziridine (III) from that in I or in 1-cyclohexylaziridine (II) and conceivably could be quite small. That the second explanation may be the correct one is suggested by the data for the ring-methylated compounds IV and V, which have only slightly higher k's than I or II. Yet the steric repulsions are not very different in III, IV, and V, as shown by



III



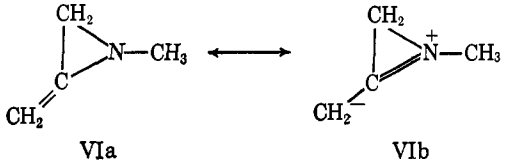
IV



V

molecular models, and it would therefore be expected that the rates of nitrogen inversion in these three compounds would be similar.[6]

The high rate of nitrogen inversion in the allenimine (VI) has been explained[2] in terms of a resonance interaction involving structures VIa and VIb.



VIa VIb

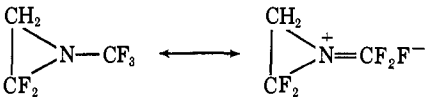
In 1-phenylaziridine (VII) it is possible that both steric and resonance effects are responsible for the high rate of nitrogen inversion.[2] However, the arguments previously applied to III also apply to VII, and thus the resonance effect is probably of major importance.

(6) The high rate of nitrogen inversion in 1-methyl-*trans*-2,3-dibenzoylaziridine [A. B. Turner, H. H. Heine, J. Irving, and J. B. Bush, Jr., *J. Am. Chem. Soc.*, 87, 1050 (1965)] is not easy to explain, except as a steric effect, as is also the fact that the *trans* isomer is less stable than the *cis* isomer in this series, as shown by equilibration.

Hydroxylic solvents greatly decrease the rate of nitrogen inversion in the derivatives of aziridine that have been studied.[2] Hydrogen bonding to the lone pair of electrons on the nitrogen atom offers[2] a satisfactory explanation for this fact. It is known[7] that complete protonation of simple amines essentially prevents the inversion from taking place.

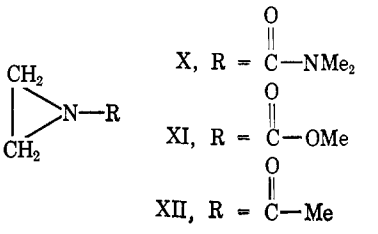
More recently, Traylor[8] has studied the 1-methanesulfonyl (VIII) and the 1-toluene-*p*-sulfonyl derivatives of aziridine. The aziridine ring protons remained unsplit down to $-37°$, the lowest temperature attained. As previously discussed in connection with III, this type of evidence for rapid nitrogen inversion is ambiguous.

The rate of nitrogen inversion in 1-(trifluoromethyl)-2,2-difluoroaziridine (IX) (Table I) has been reported very recently.[9] The rate is much higher than in I and may indicate a resonance interaction of the type[10] IXa ↔ IXb.



IXa IXb

We have reinvestigated the low temperature nmr spectra of VII and VIII at a frequency of 60 Mc/sec (the previous work was at 40 Mc/sec), and have also studied a number of 1-acylaziridines, X–XIII, to determine the nature of the barriers to internal motions in these molecules. The 1-substituent in each case has a π orbital (or, with VIII, d orbitals) which can interact with the electron pair of the aziridine nitrogen atom.



X, R = $-C(=O)-NMe_2$
XI, R = $-C(=O)-OMe$
XII, R = $-C(=O)-Me$

After completion of this paper, the work of Bystrov, *et al.*,[11] came to our attention. These authors studied the nmr spectra (at 20.5 Mc/sec) of many 1-substituted aziridines, including compound XII, but they did not obtain significant information on rates of inversion in compounds where there is a strong interaction between the nitrogen atom and the 1 substituent. As will be shown in the present paper, the relative chemical shifts, ν_{AB}, of such aziridine derivatives are much smaller than those of typical 1-alkylaziridines. This makes the observation of nitrogen inversion at the low spectrometer frequency of 20.5 Mc/sec virtually impossible.

In a 1-acylaziridine the ground state can be described as a resonance hybrid of XIIIa and XIIIb. If structure XIIIa is the main contributor to the resonance hybrid,

(7) M. Saunders and F. Yamada, *ibid.*, **85**, 1882 (1963).
(8) T. G. Traylor, *Chem. Ind.* (London), 649 (1963).
(9) A. L. Logothetis, *J. Org. Chem.*, **29**, 3049 (1964).
(10) J. D. Roberts, R. L. Webb, and E. A. McElhill, *J. Am. Chem. Soc.*, **72**, 408 (1950); S. Andreades, *ibid.*, **86**, 2003 (1964); however, W. A. Sheppard, *ibid.*, **87**, 2410 (1965), has brought forth arguments against negative hyperconjugation.
(11) V. F. Bystrov, R. G. Kostyanovskii, O. A. Panshin, A. U. Stepanyants, and O. A. Iuzhakova, *Opt. i. Spektroskopiya*, **19**, 217 (1965); *Opt. Spectry.* (USSR), **19**, 122 (1965).

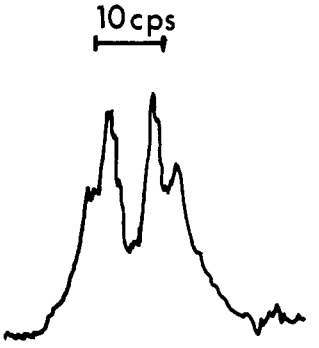
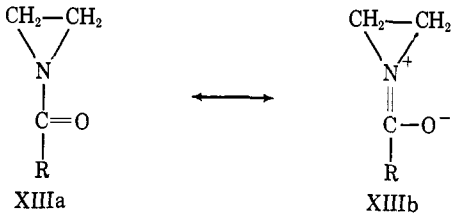


Figure 1. Nmr spectrum of the aziridine protons of X in furan solution at −97°.

the nitrogen atom will be strongly pyramidal. An appreciable barrier to nitrogen inversion, but only a small barrier to rotation, will then be expected. On the other hand, if structure XIIIb is the main contributor, the nitrogen atom will be almost planar, and therefore



XIIIa XIIIb

the barrier to inversion will be small, but that due to rotation will be high. In an intermediate situation, it is conceivable that both types of barrier may be reasonably large.

In simple amides, *e.g.*, formamide, the contributions from dipolar structures analogous to XIIIb are quite large. Thus,[4,12] these compounds show strongly hindered rotation about the N–CO bond. However, there is a conflict between the natural tendency of the nitrogen atom to be pyramidal, as in ammonia, and the conjugative interaction of the nitrogen atom with the carbonyl group, which tends to make the nitrogen atom planar. A compromise is reached, and formamide is almost, but not quite, planar.[13] The barrier to rotation in formamide is quite large (18 kcal/mole),[14] but the barrier to inversion is very small (1 kcal/mole),[13] as expected from the above arguments.

In the 1-acylaziridine series, structure XIIIb is not as highly favored as the corresponding structure in a simple amide, owing to the strain involved in having an sp^2-hybridized atom in a three-membered ring. Thus the compromise in this case should give rise to a more pyramidal nitrogen atom than is found in a simple amide.

It will be shown in the subsequent discussion that the process being observed by studying the nmr spectrum of the aziridine protons in X or XI is in fact nitrogen inversion and not restricted rotation. However, there is an observable restricted rotation in the side chain of X, similar to that which occurs in simple amides.

It appears that neither steric nor inductive effects are of major importance in determining rates of nitrogen inversion, at least in X or XI, although such effects may be important in other aziridine derivatives.

(12) M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962).
(13) C. C. Constain and J. M. Dowling, *J. Chem. Phys.*, **32**, 158 (1960).
(14) B. Sunners, L. H. Piette, and W. G. Schneider, *Can. J. Chem.*, **38**, 681 (1960).

Results

1-Phenylaziridine (VII). The single band (τ 8.07) given by the aziridine ring protons broadened at low temperatures and gave a typical A_2B_2 spectrum with ν_{AB} = 22 cps at or below about −60°. Further data are given in Table II.

Table II. Coalescence Temperature (T_c), Rate Constants (k), and Free Energy of Activation (ΔF^*) for Nitrogen Inversion

Compound	Solvent	T_c, °C	k,[a] sec^{-1}	ΔF^* at T_c, kcal/mole
VII	CS_2	−40	50	12.8
VIII	$CDCl_3$	−25	25	14.0
X	CH_2=CHCl	−86	*Ca.* 10	10.8
XI[b]	CH_2=CHCl	−138	*Ca.* 10	7.6

[a] Calculated from the expression $k = \pi\nu/\sqrt{2}$. Since the spectra at low temperatures are actually AA'BB' systems, this expression is not strictly valid, but the order of magnitude should be correct. [b] The value of T_c(−85°) for XI, quoted from our unpublished work in D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, p 82, is in error and should be corrected to that shown above.

1-Methanesulfonylaziridine (VIII). The methyl band occurred at τ 6.88 and the ring protons at τ 7.59, in approximate agreement with the results of Traylor.[8] The band of the ring protons broadened below 0° and became a typical A_2B_2 spectrum with ν_{AB} = 11 cps at −60°. Further data are found in Table II.

1-(N,N-Dimethylcarbamyl)aziridine (X). The nmr spectrum (carbon tetrachloride solution) at room temperature showed a sharp band at τ 7.99 for the ring methylene protons and two broad bands at τ 6.92 and 7.08 for the methyl groups. The methyl bands became quite sharp below room temperature and coalesced to a single broad band above 37°. In vinyl chloride solution at −90°, the ring methylene protons were a barely resolved A_2B_2 multiplet centered at τ 7.97 and the methyl bands occurred at τ 7.00 and 7.17. Rate constants for nitrogen inversion are given in Table II.

In chlorodifluoromethane solution the methylene protons gave only a slightly broadened line down to −130°. In aromatic solvents, *e.g.*, furan, the methylene protons gave two well-separated peaks at low temperatures (Figure 1).

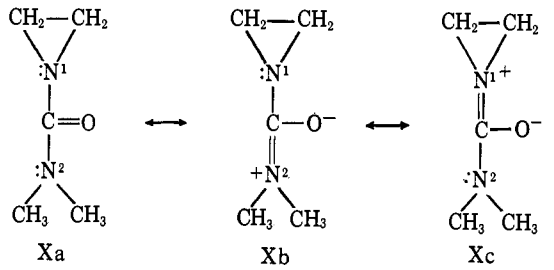
1-Carbomethoxyaziridine (XI). At room temperature and in carbon tetrachloride solution the methylene and methyl protons occurred at τ 7.87 and 6.33, respectively. In vinyl chloride solution at −90° these chemical shifts changed to 7.86 and 6.38. At −148°, the methylene protons formed a poorly resolved A_2B_2 system, with two main peaks separated by 4 cps, and centered on τ 7.81. The methyl band was unsplit (line width ≈ 2.5 cps) at τ 6.37. Further data are given in Table II.

1-Acetylaziridine. In vinyl chloride solution at *ca.* −60°, the chemical shifts of the methylene and methyl proton were τ 7.85 and 7.92, respectively. Below −120° both bands broadened appreciably, but the ring proton band was much broader than the

methyl band. No splitting was observed down to −160°.

Discussion

1-(N,N-Dimethylcarbamyl)aziridine (X). Three structures, Xa, Xb, and Xc, can be considered to contribute to the resonance hybrid of the urea X. The fact that two different methyl bands can be observed for X at room temperature or below means that rotation about the N^2–CO bond is highly hindered, and therefore that

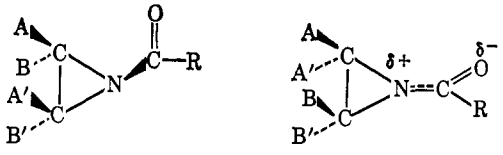


Xa Xb Xc

structure Xb contributes substantially to the resonance hybrid. At the coalescence temperature (+37°), ΔF^* for rotation can be calculated to be 16 4 kcal/mole, comparable to that of other amides.[12] Since X has a cross-conjugated system, this evidence also implies that Xc does not contribute greatly to the resonance hybrid.

The A_2B_2 pattern observed for the ring protons of X below −90° is consistent with either slow nitrogen (N^1) inversion or slow rotation about the N^1–CO bond at these temperatures. Slow rotation implies a large contribution from structure Xc, but from the argument developed above this is unlikely. That slow inversion is actually the process observed can be seen by an analysis of the spectrum of the ring protons at low temperatures.

The nonequivalent protons, A, A′, B, and B′ of the aziridine ring of X are shown for the two possibilities below.



X_{inv} X_{rot}

The systems belong to the AA′BB′ subtype of the A_2B_2 classification, because A and A′ have different coupling constants to, say, B. Such spectra[15] are dependent on the values of the chemical shift, ν_{AB}, and of the four coupling constants: J_{AB}, $J_{AB'}$, $J_{AA'}$, and $J_{BB'}$ ($J_{A'B} = J_{AB'}$ and $J_{A'B'} = J_{AB}$ by symmetry). An AA′BB′ spectrum does not change if the values of J_{AB} and $J_{AB'}$ are interchanged, but it is very dependent on the magnitudes of J_{AB} and $J_{A'B}$.

From the known[16] coupling constants in aziridine, 1-methylaziridine, and 2-phenylaziridine and the general angular dependence[17] of vicinal coupling constants, it can be estimated that the ring coupling constants in X_{inv} and X_{rot} should be as shown in Table III.

(15) K. B. Wiberg and B. J. Nist, "Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962, p 309; D. M. Grant, *Ann. Rev. Phys. Chem.*, **15**, 492 (1964).

(16) S. J. Brois, *J. Org. Chem.*, **27**, 3532 (1962); P. S. Mortimer, *J. Mol. Spectry.*, **5**, 199 (1960).

(17) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

Table III. Expected Coupling Constants in Cps

	X_{inv}	X_{rot}
$J_{AA'} (= J_{BB'})$	6–7	1–2
$J_{AB} (= J_{A'B'})$	1–2	6–7
$J_{AB'} (= J_{A'B})$	3–4	3–4
$(J^2_{AB} + J^2_{AB'})^{1/2}$	3.2–4.5	6.7–8.0

Unfortunately, it is not easy to carry out an analysis of the ring proton spectra of X at low temperatures because of the small number of lines resolved. An alternative approach, based on spectral moment analysis,[18] was therefore employed. Although not all the parameters can be obtained easily, the chemical shift ν_{AB} is simply given by the expression $\nu_{AB} = 2\sqrt{M_2}$, where M_2 is the reduced second moment, a quantity which is easily obtainable from the spectrum. A second relationship is $J^2_{AB} + J^2_{AB'} = 2(M_4 - M_2)/M_2$, where M_4 is the reduced fourth moment.

Measurements of the fourth moment may lead to errors because of the neglect of weak peaks on the fringes of the band and the general difficulty of obtaining correct intensities. Measurements of M_2 and M_4 were made on solutions of X in (a) vinyl chloride, (b) a vinyl chloride–toluene mixture, (c) furan. Whereas there may be large changes in ν_{AB}, the coupling constants are not expected to vary appreciably as the solvent is changed. The results of the moment analysis are given in Table IV. Even though the chemical shift ν_{AB} changes by a factor of two, the value of $(J^2_{AB} + J^2_{AB'})^{1/2}$ remains essentially constant and is much closer to that expected for X_{inv} than for X_{rot}.

Table IV. Moment Analysis of the Ring-Proton Bands of X at Low Temperatures

Solvent	ν_{AB}, cps	$(J^2_{AB} + J^2_{AB'})^{1/2}$, cps
a	5.1	3.7
a	5.9	4.3
b	10.4	3.9
b	10.4	3.9
c	7.4	4.4
c	7.5	4.2
c	7.8	6.3
c	8.1	4.3
		Mean[d] = 4.4 ± 0.5

[a] Vinyl chloride. [b] Vinyl chloride–toluene mixture of undetermined composition. [c] Furan. [d] The mean is 4.1 ± 0.3 cps if the 6.3-cps entry is left out of the calculation.

Calculations[15] of A_2B_2 spectra also show that X_{inv} gives a better fit to the spectrum than X_{rot}. Finally, the results obtained with XI and XII, to be discussed below, support the contention that the process being observed with X is nitrogen inversion.

The relative chemical shift, ν_{AB}, of the ring protons of X is much less than that of a typical 1-alkylaziridine, where ν_{AB} is about 30 cps at 60 Mc/sec. For X, ν_{AB} is nearly zero for a solution in chlorodifluoromethane, a solvent not unlike chloroform or carbon tetrachloride. The biggest value of ν_{AB} occurs for aromatic solvents, but even here ν_{AB} is only about 8 cps. These

(18) W. A. Anderson and H. M. McConnell, *ibid.*, **26**, 1496 (1957); F. A. L. Anet, *Can. J. Chem.*, **39**, 2316 (1961).

observations show that it is dangerous to assume that the lack of a splitting in the band of the ring protons in an aziridine derivative indicates rapid nitrogen inversion, especially if the spectrum has been observed in only one solvent.

1-Carbomethoxyaziridine (XI). The ring protons of XI show changes with temperature which are similar to those of X, except that the coalescence temperature is much lower than in the latter compound. In particular, the A_2B_2 spectrum of XI shows great resemblance to that of X, indicating that the process being observed here, as in X, is nitrogen inversion. This is also consistent with the much lower ΔF^* (Table II) found for XI as compared to X. The methoxy group is less efficient than the dimethylamino group in its conjugative ability and therefore the carbonyl group conjugates better with the aziridine nitrogen atom in the urethan (XI) than in the urea (X). Although there is probably an appreciable restriction to rotation about the MeO–CO bond in XI, it is very likely that, as in simple esters, only one form exists to an appreciable extent. If this is so, the nmr spectrum will not depend on the rate of the restricted rotation and so this process cannot be studied by the present method.

1-Acetylaziridine (XII). The lack of splitting of the ring proton band of XII, even at −160°, may be a result of slow nitrogen inversion together with a small value for ν_{AB}. However, the facts are compatible with fast inversion at −160°, and it is likely that this is so considering that the acetyl group should be a much better conjugative group than a carbomethoxy group. There is no sign of restricted rotation of the N′–CO bond in XII, or for that matter in XI or X. Here again there could be appreciable barriers to rotation if the chemical shifts involved accidentally happened to be very small. It is also true that the free energy of activation for restricted rotation would have to be at least 6 kcal/mole for an effect to be seen in the temperature range used.

It is interesting that 1-acylaziridines have abnormally high carbonyl stretching frequencies, *e.g.*, 1730 cm^{-1} for 1-propionylaziridine.[19] This fact supports nonplanar amide structures for such compounds but is not inconsistent with rapid nitrogen inversion. The greater broadening observed at −160° for the ring protons as compared to the methyl protons of XII indicates that some process is becoming slow. It is likely that these two groups of protons have different T_1's, which are relatively short at these temperatures, and which therefore control the line widths. Only the methyl protons can undergo rapid internal rotation, thus giving a longer T_1 and hence a narrower line than is given by the aziridine protons.

1-Phenylaziridine (VII) and 1-Methanesulfonylaziridine (VIII). The coalescence temperature observed for VII is considerably higher than might have been anticipated on the basis of previous work[3] at 40 Mc/sec, but the reason for this is not clear. Nevertheless, the rate constant for nitrogen inversion in VII is much higher than that of a typical 1-alkylaziridine, as expected.

In the case of VIII, our results are in agreement with the conclusion of Traylor[8] that nitrogen inversion is much faster than in 1-alkylaziridines. Further discussion of this compound is deferred to another paper,[20] in which the results on sulfur and phosphorus derivatives of aziridine will be presented.

Conclusion

The barriers to nitrogen inversion in 1-acylaziridines are mainly controlled by the conjugative interaction of the acyl group with the aziridine nitrogen atom. The greater the interaction the lower the barrier becomes. No evidence was obtained to suggest the presence of appreciable (>6 kcal/mole) barriers to internal rotation about the aziridine nitrogen–acyl bonds of the type found in simple amides.

Experimental Section

Preparation of 1-Substituted Aziridines. 1-Phenylaziridine,[3] 1-methanesulfonylaziridine,[8,21] 1-(N,N-dimethylcarbamyl)aziridine,[21] 1-carbomethoxyaziridine,[21] and 1-acetylaziridine[21] were prepared as described in the literature. All compounds were purified by vacuum bulb-to-bulb distillation. The nmr spectra showed no bands that could not be assigned.

Nmr Spectra. The spectra were obtained on a Varian HR60 (60 Mc/sec) spectrometer equipped with a low temperature probe as described previously.[22]

(19) H. C. Brown and A. Tsukamoto, *J. Am. Chem. Soc.*, **83**, 4549 (1961).

(20) F. A. L. Anet, R. D. Trepka, and D. J. Cram, *ibid.*, **89**, 357 (1967).

(21) H. Bestian, *Ann. Chem.*, **566**, 210 (1950).

(22) F. A. L. Anet, *J. Am. Chem. Soc.*, **86**, 458 (1960).