Nuclear Magnetic Resonance Studies of Aziridines. Solvent Effect, Anisotropy Effect of the Nitrogen Atom, and Its Variation with Hydrogen Bond Formation

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Abstract: Nmr studies of ethylenimine (I), 1-aziridinepropionitrile (II), and methyl 1-aziridinepropionate (III) were undertaken in connection with the elucidation of the nature of an anisotropy effect (a magnetic anisotropy effect and an electric field effect) of the nitrogen atom and the effect of the hydrogen bond. The assignment of *syn* and *anti* aziridine proton signals in II and III was made on the basis of the intermolecular anisotropy effect of the three-membered ring; high-field peaks were assigned to *syn* and low-field peaks to *anti* protons. The theoretical assignment based on the magnetic anisotropy effect of the nitrogen atom is in accord with the above conclusion. It was also found that a downfield shift of the aziridine protons occurs on hydrogen bond formation between the nitrogen atom and chloroform-*d* or methanol-d_4. Furthermore the downfield shift of the *syn* proton is larger than that of the *anti* proton especially in methanol-d_4 solution. These downfield shifts may be interpreted in terms of the variation of the magnetic anisotropy effect and the effect of an additional electric field produced by the excess dipole moment due to the contribution of the charge-transfer structure in the hydrogen bond system: $N^+D\ CCl_3^-$. Consideration of these two effects strongly supports the above assignment.

In our previous papers, an anisotropy effect (a magnetic anisotropy effect and an electric field effect) of the lone pair electrons of a nitrogen atom in the hydroxyimino,[1] phenylimino,[2] and chloroimino[3] groups was studied in relation to the assignment of *syn* and *anti* proton signals. The substances which we have investigated[1-3] are suitable for the study of the anisotropy effect because the protons in question are magnetically or electrically nonequivalent, but are chemically (or electronically) equivalent, and we can minimize unknown factors such as a diamagnetic shielding term[4] due to the difference of electron densities. The separation of the chemical shift between *syn* and *anti* protons in the hydroxyimino and the chloroimino group is due to the magnetic anisotropy effect and to the electric field effect of the lone pair electrons of the nitrogen atom. It was noted that these effects displace neighboring proton signals in the opposite sense.[1b] The assignment of *syn* and *anti* proton signals is possible by the definite experimental results, since theoretical calculation remains semiquantitative. In order to determine which effect predominates, the experimental results are compared with the theoretical calculation in individual cases.

As will be described in detail in the following section, the methylene proton signals of aziridines, three-membered heterocyclic compounds containing a nitrogen atom, are also separated at lower temperature and this is another example of the nitrogen anisotropy effect. The separated signals coalesce at higher temperature because the rate of internal inversion increases[5] (Figure 1) and thus the anisotropy effect is averaged out. In this paper, we examine the nmr spectra of ethylenimime (I), 1-aziridinepropionitrile (II), and methyl 1-aziridinepropionate (III) in order to elucidate the nature of the anisotropy effect of the nitrogen atom in aziridine ring. Considering the assignment obtained by experiment and by theoretical calculations, it is concluded that the magnetic anisotropy effect of the nitrogen atom is the dominant cause of the separation of *syn* and *anti* proton signals in the aziridine ring. It was also found that the downfield shift of the proton signal in the aziridine ring was observed in a hydrogen bond between the nitrogen atom and chloroform-*d* or methanol-d_4. Theoretical consideration was attempted for the elucidation of the above observation which strongly supported the above assignment.

Experimental Section

Commercial ethylenimine was used after distillation. 1-Aziridinepropionitrile and methyl 1-aziridinepropionate were synthesized by a reaction of ethylenimine with acrylonitrile and methyl acrylate, respectively, in the presence of base.[6] Nmr spectra were taken with a Varian A-60 and a Varian HR-100 spectrometer in neat solutions and in carbon tetrachloride, chloroform-*d*, and methanol-d_4. Frequency calibration was made with the usual sideband method. TMS was used as an internal standard.

Results and Discussion

Solvent Effect and Variation with Temperature on Nmr Spectra of Ethylenimine. Separation of *syn* and *anti* proton signals of ethylenimine was not observed at room temperature and even at −70° and two types of singlet peaks, CH and NH, were observed. In dilute solution in carbon tetrachloride and chloroform-*d*, CH and NH signals were displaced to the downfield and the upfield, respectively, as compared with those of neat sample as shown in Figure 2. The upfield shift of the NH signal with dilution is interpreted as a cleavage of hydrogen bond such as NH···N between solute molecules. The downfield shift of the CH signal with dilution is partially due to the decrease of the intermolecular

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[1] (a) H. Saitô, K. Nukada, and M. Ohno, *Tetrahedron Letters*, 2124 (1964); (b) H. Saitô and K. Nukada, *J. Mol. Spectry.*, **18**, 1 (1965); (c) H. Saitô and K. Nukada, *ibid.*, **18**, 355 (1965); (d) H. Saitô and K. Nukada, *Tetrahedron Letters*, 2117 (1965).

[2] H. Saitô and K. Nukada, *Tetrahedron*, **22**, 3313 (1966).

[3] H. Saitô and K. Nukada, submitted for publication.

[4] J. A. Pople, *J. Chem. Phys.*, **37**, 53, 60 (1962).

[5] (a) A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 5126 (1956); (b) J. D. Roberts and A. T. Bottini, *ibid.*, **80**, 5203 (1958); (c) A. Loewenstein, J. F. Neumer, and J. D. Roberts, *ibid.*, **82**, 3599 (1960).

[6] (a) Bestian, H. von, *Ann.*, **566**, 210 (1950); (b) T. Yoshida and K. Naito, *Kogyo Kagaku Zasshi*, **55**, 455 (1952).

diamagnetic anisotropy effect[7] between solute molecules and partially due to the formation of a hydrogen bond between solute and solvent molecules. Because carbon tetrachloride is relatively weak as a proton acceptor, the downfield shift in carbon tetrachloride is mainly due to the former reason. Thus the amount of the former effect can be estimated from the difference of the CH shifts between infinite dilution in carbon tetrachloride and the neat state, as given in Table I.

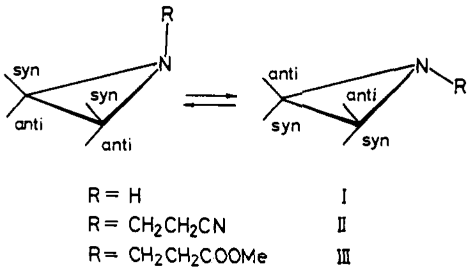


Figure 1. Inversion of aziridine molecules.

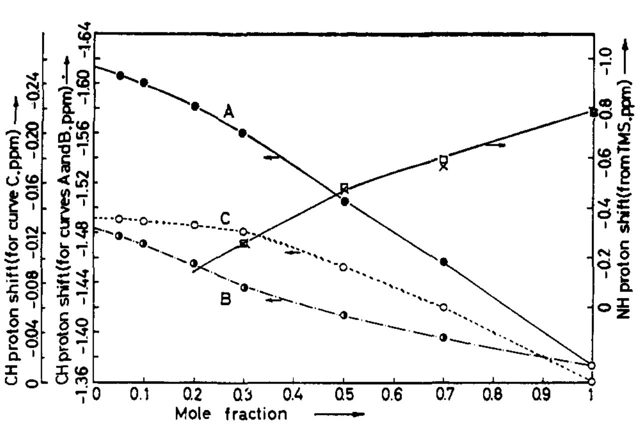


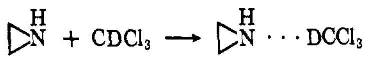
Figure 2. A plot of CH and NH proton signals of ethylenimine (I) against the concentration of solute. CH signal: ◑, in carbon tetrachloride; ●, in chloroform-*d*; ○, difference of CH signal in carbon tetrachloride and chloroform-*d*. NH signal: □, in chloroform-*d*; ×, in carbon tetrachloride.

Table I. Intermolecular Diamagnetic Anisotropy Effect (ppm) Due to the Neighboring Solute Molecules (Aziridine)

		$\delta_0{}^a$	$\delta_{\text{neat}}{}^b$	$\delta_{\text{neat}} - \delta_0{}^c$
Ethylenimine (I)		−1.48	−1.37	0.11
1-Aziridinepropionitrile (II)	High-field peak	−1.17	−1.16	0.01
	Low-field peak	−1.72	−1.65	0.07
Methyl 1-aziridinepropionate (III)	High-field peak	−1.04	−1.00	0.04
	Low-field peak	−1.61	−1.50	0.11

[a] Aziridine ring proton signal in carbon tetrachloride solution at the infinite dilution. [b] Aziridine ring proton signal at the neat state. [c] A measure of intermolecular diamagnetic anisotropy effect defined as the difference of δ_0 and δ_{neat}.

The effect of the intermolecular diamagnetic anisotropy by the three-membered ring compounds was recognized as a contribution of the ring current[8a,b] and investigated by many authors in cyclopropane,[8] epoxide,[9] and aziridine[10] derivatives. The downfield shift extrapolated to infinite dilution in chloroform-*d* is twice as large as the value in carbon tetrachloride as shown in Figure 2 and Table II. The excess downfield shift in chloroform-*d* is attributed to hydrogen bond formation between solute and solvent molecules. In a hydrogen bond system where a nitrogen atom acts as a proton acceptor, the variation of the nitrogen anisotropy effect was observed as an upfield shift of ^{14}N chemical shift[11] which is attributed to the contribution of charge-transfer structure: O^-HN^+. Because of the small degree of variation of chemical shift, few papers[12] concerning the chemical shift variation of a proton which is in an α-methylene (methyl) group with respect to the proton acceptor in a hydrogen bond have been published. In Figure 2 the dilution curve (B), which illustrates the variation of the intermolecular diamagnetic anisotropy effect, was subtracted from curve A and curve C was obtained. The hydrogen bond between solute molecules is formed equally in both solvents as the NH proton signal is observed at almost the same position above the 0.3 mole fraction as shown in Figure 2. Curve C then describes the variation of the chemical shift due to a hydrogen bond between a nitrogen atom in ethylenimine and chloroform-*d*. According to an experiment[13] carried out with the external standard method, however, the solvent effect on TMS need not be considered in the present case because the effects of chloroform, carbon tetrachloride, and methanol on TMS are almost equal. Curve C was analyzed by the method of Huggins and his co-workers.[14] The hydrogen bond system is expressed in eq 1; the equilibrium constant is expressed in eq 2, where X is the mole



(1)

$$K = \frac{X(C + B - X)}{(C - X)(B - X)} \tag{2}$$

fraction of species forming a hydrogen bond on the right-hand side of eq 1 and C and B are initial mole fractions of chloroform-*d* and ethylenimine, respectively. The proton nmr signal of the proton acceptor in an equilibrium, ν', is expressed in eq 3–5 in terms of the free proton shift[15] of ethylenimine, ν_B, and hydrogen bond

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[7] This is usually called a "solvent effect" and the solute–solute interaction due to the anisotropy effect is especially called an "intermolecular diamagnetic anisotropy effect" in this paper. The same effect of benzene is discussed by Buckingham and his co-workers: A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960). The intermolecular diamagnetic anisotropy effect of the three-membered ring can be considered to be the same as that of benzene qualitatively. Thus the downfield shift with dilution is expected in the present case.

[8] (a) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3218 (1963); (b) J. J. Burke and P. C. Lauterbur, *ibid.*, **86**, 1870 (1964); (c) S. Forsen and T. Norin, *Tetrahedron Letters*, 2845 (1964); (d) K. Tori and K. Kitahonoki, *J. Am. Chem. Soc.*, **87**, 386 (1965).

[9] (a) R. F. Jefferies, R. S. Rosich, and D. E. White, *Tetrahedron Letters*, 1853 (1963); (b) K. Tori, K. Kitahonoki, Y. Takano, and H. Tanida, *ibid.*, 559 (1964).

[10] (a) K. Tori, K. Kitahonoki, Y. Takano, H. Tanida, and T. Tsuji, *ibid.*, 869 (1965); (b) K. Tori, K. Aono, K. Kitahonoki, R. Muneyuki, Y. Takano, H. Tanida, and T. Tsuji, *ibid.*, 2921 (1966).

[11] (a) H. Saitô, K. Nukada, H. Kato, T. Yonezawa, and K. Fukui, *ibid.*, 111 (1965); (b) A. Loewenstein and Y. Margalit, *J. Phys. Chem.*, **69**, 4125 (1965).

[12] I. Morishima, T. Fujii, and T. Yonezawa, *Bull. Chem. Soc. Japan*, in press; Abstract of Symposium on Structural Chemistry, Nagoya, 1965.

[13] H. Sugawara, H. Saitô, and K. Nukada, unpublished work.

[14] C. M. Huggins, G. C. Pimentel, and J. N. Shoolery, *J. Chem. Phys.*, **23**, 1244 (1955).

[15] Free proton shift in this treatment means that in this shift the contribution of the hydrogen bond between nitrogen and chloroform-*d*

Table II. Chemical Shift of Aziridine Protons (ppm) at Infinite Dilution

Solute	Solvent	High-field peak (*syn* protons)	Low-field peak (*anti* protons)	Separation
Ethylenimine	CCl_4	-1.48^a (0)^b		...
	$CDCl_3$	−1.61 (−0.13)		...
1-Aziridinepropionitrile	CCl_4	−1.17 (0)	−1.72 (0)	0.55
	$CDCl_3$	−1.26 (−0.09)	−1.84 (−0.12)	0.58
	CD_3OD	−1.38 (−0.21)	−1.80 (−0.08)	0.42
Methyl 1-aziridinepropionate	CCl_4	−1.04 (0)	−1.60 (0)	0.56
	$CDCl_3$	−1.16 (−0.12)	−1.76 (−0.16)	0.60
	CD_3OD	−1.31 (−0.27)	−1.73 (−0.13)	0.42

[a] The separation between *syn* and *anti* proton signals is not observed. [b] The values in parentheses are chemical shifts relative to those in carbon tetrachloride solution in each peak. Thus the intermolecular anisotropy effect is eliminated in this value.

shift, ν_X, where $\nu_{B\rightarrow O}'$ and $\nu_{C\rightarrow O}'$ are chemical shifts at

$$\nu' = \frac{X}{B}\nu_X + \frac{B - X}{B}\nu_B \qquad (3)$$

$$\nu_X = \nu_{B\rightarrow O}' + \frac{1}{K}(\nu_{B\rightarrow O}' - \nu_{C\rightarrow O}') \qquad (4)$$

$$\nu_B = \nu_{C\rightarrow O}' \qquad (5)$$

infinite dilution and neat state, respectively. Adopting an appropriate value of *K* by trial and error, the dilution shift is calculated with eq 3–5. The best value of *K* from the experimental curve is 3 ± 1. The same procedure is applied to the experiment at 0 and −20° and the results are listed in Table III. A plot of *K* against inverse temperature gives a value of $\Delta H = 2.8 \pm 1.5$ kcal for the energy of hydrogen bond. This is reasonable compared with that obtained by Huggins, *et al.*,[14] $\Delta H = 4 \pm 1$ kcal, in triethylamine–chloroform system. The hydrogen bond shift (downfield shift), ν_X, is 0.18 ppm relative to the free (neat) proton signal.

Table III. Equilibrium Constant (*K*) of Hydrogen Bond between Ethylenimine and Chloroform-*d*

Temp, °C	*K*
38	3 ± 1
0	3.8 ± 1
−20	7 ± 2

The downfield shift of the proton acceptor due to the hydrogen bond may be interpreted as a contribution of the charge-transfer structure,[16] $N^+D\ CCl_3^-$, as shown in the following section. The contribution of the charge-transfer structure is estimated roughly by comparison of the hydrogen bond shift and the downfield shift of the completely protonate state. Although the hydrochloride of ethylenimine could give rise to an nmr spectrum of the completely protonated state, we failed in the measurement of nmr spectra because of its instability even in the presence of a trace of acid. The extent of the downfield shift of a number of amines in CF_3COOH solution relative to the neat state is in a range of 0.9–1.3 ppm.[17] Adopting these values as an estimation of the downfield shift of ethylenimine in a protonated state, the contribution of the charge-transfer structure is estimated as 14–20%. Though the value is somewhat large compared with the ordinary one[16] (2–6%), it is reasonable considering the error due to the estimation of the downfield shift in the completely protonated state.

Solvent Effect of Nmr Spectra of 1-Aziridinepropionitrile (II) and Methyl 1-Aziridinepropionate (III). Nmr spectra of II and III show an A_2X_2 pattern[18] for aziridine ring and an A_2B_2 pattern with equal AB coupling[18] for the dimethylene moiety at room temperature as illustrated in Figures 3A and 4. Coupling constants of the aziridine ring protons obtained from the analysis of the A_2X_2 spin system are listed in Table IV. The *cis* and *trans* coupling constants of II and III are small and the geminal coupling (absolute value) is extremely large compared with the values of other compounds[19] as given in Table IV.

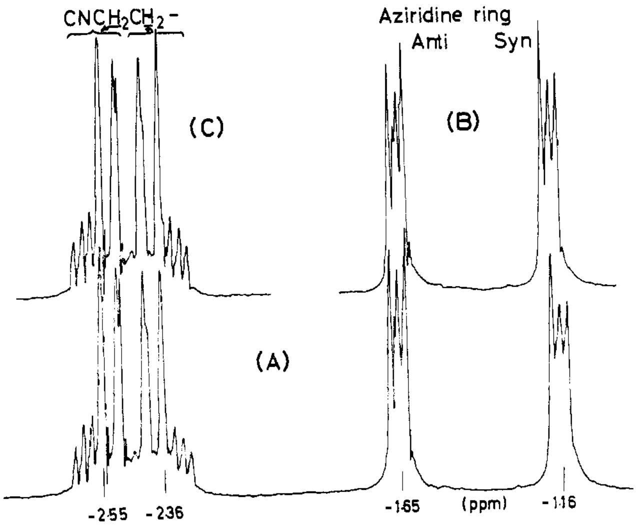

Figure 3. Nmr spectra (100 Mc) of 1-aziridinepropionitrile (II) (neat): A, normal; B, irradiated on a methylene proton signals (compare the *syn* aziridine signal with that of normal spectra); C, irradiated on *syn* aziridine signals (see the high-field half of the spectrum of the dimethylene moiety).

Variations of proton chemical shift of aziridine ring with concentration of solute in carbon tetrachloride,

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is not involved but contribution from the hydrogen bond between solute molecules is involved. Thus the hydrogen bond shift is defined relative to the shift at the neat state. (The correction of the intermolecular diamagnetic anisotropy effect is included.)

(16) C. A. Coulson and U. Danielsson, *Arkiv Fysik*, 8, 239, 245 (1954).

(17) Y. Kawazoe and M. Ohnishi, Abstract of the 2nd Nmr Symposium, Tokyo, 1962.

(18) 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.

(19) (a) F. S. Mortimer, *J. Mol. Spectry.*, 5, 199 (1960); (b) S. J. Brois and G. P. Beardsley, *Tetrahedron Letters*, 5113 (1966).

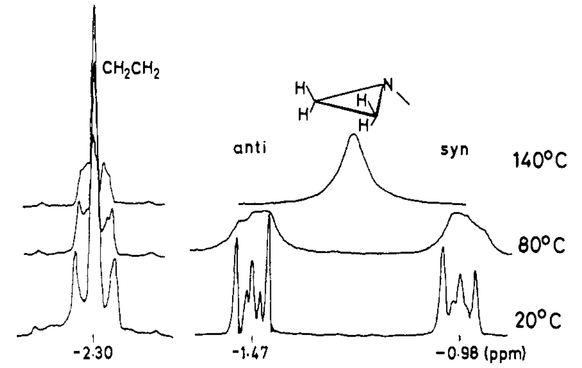


Figure 4. Nmr spectra (60 Mc) of methyl 1-aziridinepropionate (III) (neat). Methoxyl proton is not shown in this figure which resonates at −3.41 ppm.

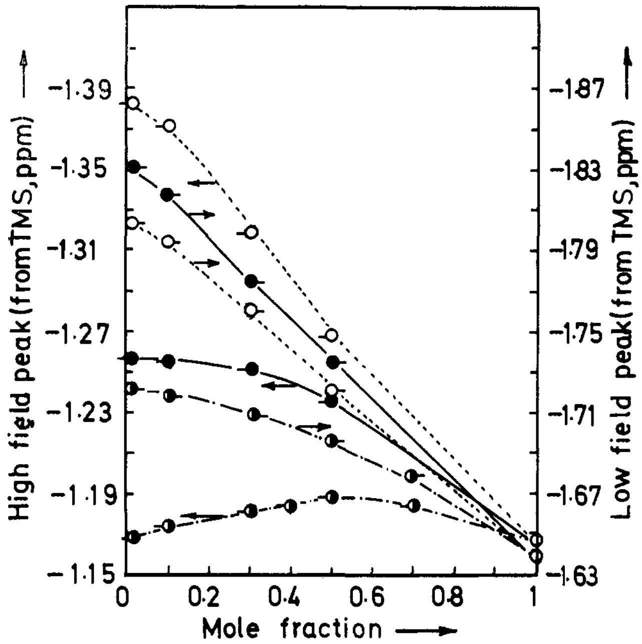


Figure 5. Variation of the aziridine proton signals of 1-aziridinepropionitrile with dilution. High-field peak (*syn* protons): —◑, in carbon tetrachloride; —●, in chloroform-*d*; —○, in methanol-d_4. Low-field peaks (*anti* protons): ◑—, in carbon tetrachloride; ●—, in chloroform-*d*; ○—, in methanol-d_4.

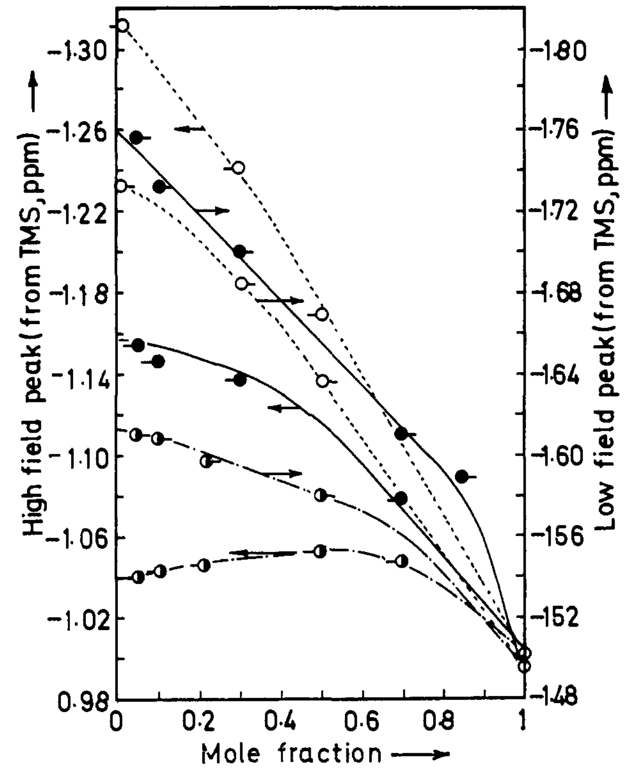


Figure 6. Variation of the aziridine proton signals of methyl 1-aziridinepropionate with dilution. The symbols are the same as used in Figure 5.

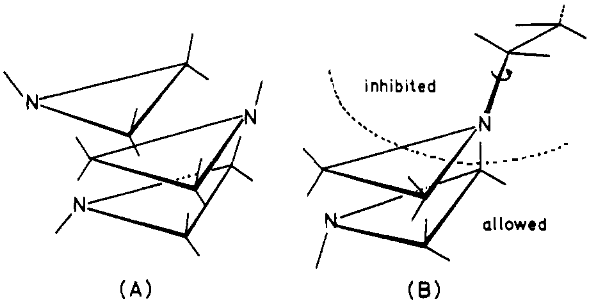
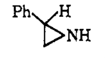


Figure 7. A model of interaction of aziridines in a concentrated or neat state: A, ethylenimine; B, 1-aziridinepropionitrile and methyl 1-aziridinepropionate.

Table IV. Coupling Constants (cps) of Aziridine Protons

	J_{cis}	J_{trans}	J_{gem}	Ref
▷NCH_2CH_2CN	3.5	1.0	6 ± 1	This work
▷NCH_2CH_2COOMe	3.4	1.3	6 ± 1	This work
▷NH	6.3	3.8	. . .	*a*
	6.1	3.3	0.9	*b*

[a] See ref 19a. [b] See ref 19b.

chloroform-*d*, and methanol-d_4 are given in Figures 5 and 6. The downfield shift with dilution by carbon tetrachloride, owing to the decrease of the intermolecular anisotropy effect of aziridine ring, appears in different ways in the high- and low-field peaks. The downfield shift of the low-field peaks of II and III in carbon tetrachloride are 0.07 and 0.11 ppm, respectively, as shown in Table I. On the other hand, the downfield shift of the high-field peaks are 0.01 and 0.04 ppm, respectively. Comparison of the downfield shift of ethylenimine, 0.11 ppm (Table I), with that of the high-field and low-field peaks of II and III revealed that the relation between the downfield shift of the high-field peaks with concentration was anomalous compared with those of the low-field peaks. This anomaly presumably arises from steric hindrance by substituents on the aziridine ring in the proximity of other aziridine rings. Because of the diamagnetic anisotropy effect of the molecular plane of the three-membered ring, the aziridine protons are shifted upfield when another aziridine ring approaches. The proximity of another aziridine ring to *syn* protons is interrupted by the steric hindrance of a bulky substituent as illustrated in Figure 7 whereas there is no such a hindrance on the *anti* sides. Thus the high-field signal, the shift of which is anomalous in a concentrated solution, is assigned to *syn* protons and the low-field peak, the shift of which is

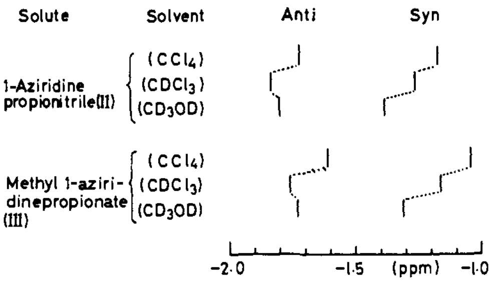


Figure 8. The effect of the hydrogen bond for the aziridine proton signals at infinite dilution (relative to TMS).

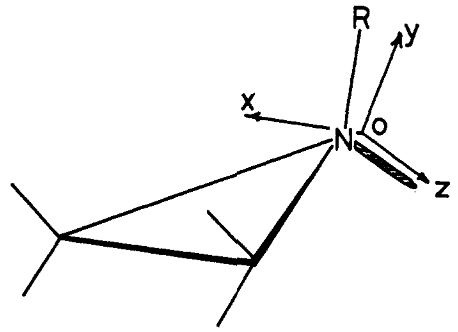


Figure 9. The coordinate system employed.

normal even in a concentrated solution, is assigned to *anti* protons.

The chemical shift of ring protons in chloroform-*d* and methanol-d_4 solutions appears at lower field than that in carbon tetrachloride solution (Figures 5 and 6). The downfield shifts at infinite dilution in both solvents are given in Table II and illustrated in Figure 8. The shift of the *syn* aziridine protons of II and III in methanol-d_4 solution is about twice as great as that in chloroform-*d*, whereas the value of the *anti* aziridine proton signals in the former solvent is smaller than that in the latter solvent. Their observation is due to the presence of the hydrogen bond between the nitrogen atom of the solute molecule and solvents.[20] The hydrogen bond shift of II and III is approximately regarded as the difference of the chemical shifts between infinite dilution in proton acceptor and that in carbon tetrachloride as listed in Table II. This approximation[21] is applicable when K is large enough to satisfy the conditions $K \gg \nu_{B \rightarrow 0'} - \nu_{C \rightarrow 0'}$ in eq 4.

The equal AB coupling constant of 6.5 cps, which does not vary with increasing temperature, for the dimethylene moiety of II indicates that free rotation occurs around the CH_2CH_2 single bond.[22] An A_2X_2 pattern of aziridine ring protons of II and III coalesces at about 80° and becomes a singlet peak at about 120° owing to the rapid internal inversion (Figure 4).

The aziridine protons on the *syn* side (the high-field peak) give rise to broader peaks than those on the *anti* side (the low-field peak), presumably owing to an additional long-range coupling[23] with either of the methylene protons of the dimethylene moiety. The coupling constant is 0.5 cps. The coupling constant across four single bond was reported in the case of N,N-dimethylformamide to be 0.3 cps (*cis*) and 0.65 cps (*trans*).[24] It is thus concluded that the long-range coupling is due to the interaction between the *syn* proton of the aziridine ring and methylene protons (the nearer methylene to the nitrogen atom of aziridine). The higher field part of spectrum of dimethylene protons is assigned to the α-methylene protons because it is broader than the other half of the spectrum. In order to confirm the existence of the long-range coupling, decoupling was performed between these two types of proton signals. The *syn* proton signals become sharp with the irradiation of the α-methylene protons as shown in Figure 3B. In Figure 3C, the variation of the spectrum is shown when *syn* proton signals are irradiated. Contrary to the case of the amides, the long-range coupling of the *cis* (*syn*) pair is larger than that of the *trans* (*anti*) pair. The same is true also in the case of III.

The Magnetic and the Electric Anisotropy Effects of Nitrogen Atom and Its Variation with Hydrogen Bonding. In this section the magnetic and the electric anisotropy effects of the nitrogen atom in the aziridine ring are discussed semiquantitatively. First the effect of the magnetic anisotropy is discussed in detail. Goldstein and his co-workers[25] found a good correlation between ^{13}C–H coupling constant and the s nature of the hybridized orbitals calculated by the method of maximum overlap orbitals.[26] For the calculation of the magnetic anisotropy effect of the nitrogen atom, the hybridized orbitals of Goldstein, *et al.*, were used after transforming the orbitals to the coordinate system illustrated in Figure 9. A Z axis is chosen along lone pair electrons of the nitrogen atom and an X axis lies in a plane of the three-membered ring and perpendicular to a plane given with R and Z. The hybridized orbitals transformed in this way are given in Table V. The atomic magnetic susceptibility of the nitrogen atom calculated by Pople's method[4] using the above orbitals are given by

$$\chi_{xx}^{N} = \frac{Ne^2\hbar^2}{m^2c^2}\left(\frac{0.5269}{\epsilon_{n \rightarrow \sigma^*}} + \frac{0.1151}{\epsilon_{\sigma \rightarrow \sigma^*}}\right)$$

$$\chi_{yy}^{N} = \frac{Ne^2\hbar^2}{m^2c^2}\left(\frac{0.4750}{\epsilon_{n \rightarrow \sigma^*}} + \frac{0.1574}{\epsilon_{\sigma \rightarrow \sigma^*}}\right) \qquad (6)$$

$$\chi_{zz}^{N} = \frac{Ne^2\hbar^2}{m^2c^2}\left(\frac{0.6159}{\epsilon_{\sigma \rightarrow \sigma^*}}\right)$$

Table V. Hybridized Atomic Orbitals of the Nitrogen Atom[a,b]

$\psi_n = 0.5158S + 0.8571P_z$
$\psi_{NR} = 0.5158S + 0.7992P_y - 0.3102P_z$
$\psi_{CN} = 0.4836S \pm 0.8041P_x - 0.3962P_y - 0.2713P_z$

[a] S, P_x, P_y, and P_z denote the 2S, $2P_x$, $2P_y$, and $2P_z$ atomic orbitals of the nitrogen atom, respectively. [b] Subscripts *n*, NR, and CN express the orbitals directed toward lone pair electrons and NR and CN bonds, respectively.

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(20) The equilibrium of the system in these cases is more complicated than that in the case of ethylenimine because there are other solute–solvent hydrogen bonds such as those between solvent and nitrile or carbonyl groups in II and III. The influence on the chemical shift of aziridine ring protons is negligible.

(21) This approximation is proved to be reasonable if we consider the following case. The difference of the chemical shift between chloroform-*d* and carbon tetrachloride solution, both at infinite dilution, is 0.13 ppm for ethylenimine (Table II). The valid hydrogen bond shift calculated from eq 4 is 0.18 ppm and this value is likely to the former one.

(22) This is the case in which populations in *trans* and in two *gauche* forms are the same: see R. J. Abraham and K. G. R. Pachler, *Mol. Phys.*, **7**, 165 (1964).

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Table VI. Distance R and Direction Cosines

Direction cosine	Ring proton	
	syn	*anti*
$\cos \theta_x$	0.530	0.530
$\cos \theta_y$	−0.382	−0.844
$\cos \theta_z$	−0.751	−0.077
R = 2.252 A		

Table VII. The Magnetic Anisotropy Effect (ppm) of the Nitrogen Atom[a]

Ring proton	Case 1				Case 2			
	σ_x	σ_y	σ_z	Total	σ_x	σ_y	σ_z	Total
syn	0.109	0.336	−0.282	0.163	0.095	0.301	−0.282	0.114
anti	0.109	−0.680	0.381	−0.190	0.095	−0.607	0.381	−0.131
Δ(*syn*–*anti*)				+0.353				+0.245

[a] Case 1, $\epsilon_{n \rightarrow \sigma^*}$ = 6 ev, $\epsilon_{\sigma \rightarrow \sigma^*}$ = 10 ev; case 2, $\epsilon_{n \rightarrow \sigma^*}$ = 7 ev, $\epsilon_{\sigma \rightarrow \sigma^*}$ = 10 ev.

where $\epsilon_{n \rightarrow \sigma^*}$ and $\epsilon_{\sigma \rightarrow \sigma^*}$ are the mean excitation energy from the lone pair electrons to the antibonding orbitals of NC and NR bonds and the mean excitation energy from the bonding orbitals of NC and NR bonds to the antibonding orbitals of NR and NC bonds, respectively. N, e, m, $\hbar$, and c are Avogadro's number, a charge of an electron, mass of an electron, Planck's constant divided by 2π, and the velocity of light, respectively. Unless $\chi_{xx}^N = \chi_{yy}^N = \chi_{zz}^N$, the nitrogen atom influences the magnetic anisotropy effect on the neighboring atoms. The magnetic anisotropy effect expressed for the Z component is

$$\sigma_z = \frac{\chi_{zz}^N(1 - 3\cos^2\theta_z)}{3NR^3} \tag{7}$$

where R is a distance between nitrogen atom and the proton in question and θ_z is an angle between vector R and the Z axis. X and Y components are obtained exchanging suffixes of eq 7 into X and Y, respectively. The values R, θ_x, θ_y, and θ_z obtained from those of ethylenimine[27] are used in the present calculation (Table VI). σ_x, σ_y, and σ_z are calculated using values of $\epsilon_{\sigma \rightarrow \sigma^*}$ = 10 ev[4] and $\epsilon_{n \rightarrow \sigma^*}$ = 6 ev[28] or 7 ev as shown in Table VII. Table VII shows that the calculated separation between *syn* and *anti* chemical shifts in both cases is rather reasonable compared with the observed value (0.55 ppm see Table II). Thus if it is considered that the magnetic anisotropy is the main effect to separate the chemical shift of *syn* and *anti* protons, the high-field peaks of aziridine ring protons are assigned to the *syn* protons and the low-field one to *anti* protons. This is consistent with the results obtained experimentally.

There are some cases such as those of oximes[1b] and amides[29] where the chemical shift cannot be interpreted in terms of the magnetic anisotropy effect of the neighboring functional groups. In the case of a hydroxyimino group it was concluded that the electric dipolar field effect of the lone pair electrons of the nitrogen atom is a dominant cause of the separation of *syn* and *anti* proton signals.[1b] Thus such an effect should also be investigated in the present case. The electric field **E** produced by the electric dipole moment of a nitrogen atom $\boldsymbol{\mu}$ at the point **R**, the distance from which to the nitrogen atom being R, is expressed by [30]

$$\mathbf{E} = -\frac{\boldsymbol{\mu}}{R^3} + \frac{3(\boldsymbol{\mu}\mathbf{R})\mathbf{R}}{R^5} \tag{8}$$

The chemical shift caused by the electric field is given as[31]

$$\sigma_{\mathrm{E}} = -2 \times 10^{-12}\mathbf{E}_{\mathrm{Z}} - 10^{-18}\mathbf{E}^2 \tag{9}$$

where $\mathbf{E}_{\mathrm{Z}}$ is a component of an electric field **E** along the C–H axis. The electric fields at the *syn* and *anti* proton of aziridines are calculated with eq 8 and listed in Table VIII. The chemical shift due to the electric field was calculated by using as values of effective lone pair dipole moment 3,[32] 2, and 1 D.[33] as listed in Table IX. It is shown that the electric field effect makes the *syn* proton shift to lower field than the *anti* proton contrary to the assignment obtained by the experiment. In aziridines, therefore, the electric field effect does not exceed the magnetic anisotropy effect. Although the smallest value of the dipole moment μ = 1 D. is adopted, the algebraic sum of both effects can only account for half of the observed value. The calculated value, however, will approach the observed value when either the magnetic anisotropy effect is made larger by adopting more appropriate excitation energies than those in Table VII or the electric field is estimated to be smaller than

Table VIII. The Electric Field at Aziridines Protons (esu)

Ring proton	$\mathbf{E}_{\mathrm{Z}}$, μ	$\mathbf{E}^2$, μ^2
syn	0.082×10^{24}	0.026×10^{30}
anti	0.060×10^{24}	0.0078×10^{30}

Table IX. Downfield Shift Due to the Electric Field Effect (ppm)

μ, D.	*syn*		*anti*		Δ(*syn*–*anti*)	Algebraic sum[a]
1	−0.190		−0.129		−0.061	0.292
		−0.242		−0.143		
2	−0.432		−0.272		−0.160	0.193
		−0.294		−0.160		
3	−0.726		−0.432		−0.294	0.059

[a] This is an algebraic sum of two contributions, the magnetic field effect (case 1) and the electric field effect.

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that appearing in Table IX. In Figure 10A is represented schematically how the separation of *syn* and *anti* proton signal is interpreted in terms of the magnetic anisotropy effect and the electric field effect of the nitrogen atom.

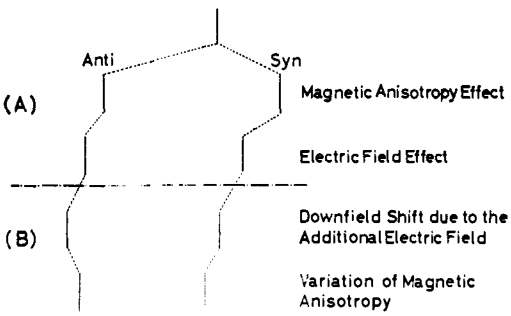

Figure 10. Schematic representation of the anisotropy effect of the nitrogen atom: A, separation of *syn* and *anti* proton signals due to the presence of the magnetic anisotropy effect and the electric field effect of the nitrogen atom; B, the downfield shift of *syn* and *anti* proton signals due to the additional electric field effect produced by the excess dipole moment and the variation of the magnetic anisotropy effect caused by the hydrogen bond.

The downfield shift of aziridine ring proton signals in hydrogen bond formation between a nitrogen atom and chloroform-*d* or methanol-d_4 is next discussed from a theoretical point of view. The energy of $n \rightarrow \sigma^*$ transition is expected to become larger by hydrogen bond formation, as $n \rightarrow \sigma^*$ transition of amines was shown to undergo marked blue shift in prototropic solvents.[34] Moreover, in hydrogen bonds it is expected that the charge transfer from proton acceptor to donor occurs[35] as is the case of triethylamine–phenol system, where the excess dipole moment due to the hydrogen bond was estimated to be about 1 D. The former effect causes the variation of the magnetic anisotropy effect of the nitrogen atom and the latter induces an additional electric field effect owing to the presence of the excess dipole moment in the charge-transfer structure. The formation of the hydrogen bond increases $\epsilon_{n \rightarrow \sigma^*}$ of the denominator of eq 6 and Table VII shows that it makes the *syn* proton signal shift to the downfield and the *anti* to the upfield. Assuming the excess dipole moment due to the hydrogen bond to be 1 D. for simplicity, the downfield shifts of *syn* and *anti* proton signals are estimated from Table IX to be $-0.24 \sim -0.29$ ppm and $-0.14 \sim 0.16$ ppm, respectively. Both the effects for the hydrogen bond are illustrated in Figure 10B. Because the downfield shift is observed for both *syn* and *anti* proton signals in the hydrogen bond formation, as shown in Table II and Figure 8, the former effect does not contribute predominantly to the downfield shift especially for chloroform-*d* solution (weak hydrogen bond case). Then it is proved that the additional electric field effect is predominant in the downfield shift in the hydrogen bond formation. In a stronger hydrogen bond case such as in methanol-d_4 solution, however, the former effect should, although not predominant, exist as shown below. The upfield shift of *anti* proton signal in methanol-d_4 solution relative to the value in chloroform-*d*, contrary to the fact that the downfield shift of the *syn* protons in the former solvent is larger than in the latter solvent, is not interpreted without consideration of the variation of the magnetic anisotropy effect in addition to the electric field effect (see Figure 10B). Therefore, in the case of methanol-d_4 solution, the magnetic anisotropy effect is not negligible in the hydrogen bond. Moreover if both the effects are considered, the separation between *syn* and *anti* proton signal is expected to be smaller than that in the absence of the hydrogen bond. This expectation was also proved true in the hydrogen bond in methanol-d_4 solution.

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