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NUCLEAR MAGNETIC RESONANCE STUDY OF EXCHANGING SYSTEMS—IV[1]

COMPLETE LINE SHAPE ANALYSIS OF NITROGEN INVERSION OF ETHYLENIMINE BY THE DENSITY MATRIX METHOD

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Abstract—An NMR spectrum of completely dehydrated ethylenimine **1** in liquid phase was found to show well resolved multiplets for the aziridine ring protons at room temperature. The computer analysis was made to determine the NMR parameters. Temperature dependent NMR spectra show that the nitrogen inversion of **1** is slow enough in the NMR time scale at room temperature. In order to obtain the kinetic parameters of this inversion, the complete line shape analysis for the NMR spectra of **1** as an AA'BB'C spin system was performed using the density matrix method, and fitting the calculated spectra with the observed at various temperatures. The activation parameters are obtained as follows:

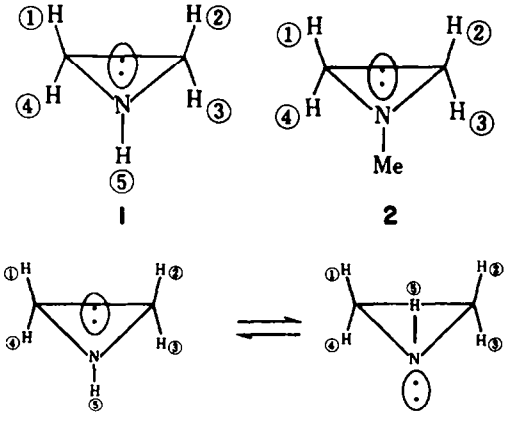
$$Ea = 15{\cdot}9 \pm 0{\cdot}4 \text{ Kcal/mole}$$
$$\Delta G^{\neq} = 17{\cdot}1 \pm 0{\cdot}8 \text{ Kcal/mole}$$
$$\Delta H^{\neq} = 15{\cdot}3 \pm 0{\cdot}4 \text{ Kcal/mole at } 25{\cdot}0°$$
$$\Delta S^{\neq} = -6{\cdot}2 \pm 1{\cdot}2 \text{ e.u.}$$

Some discussion is made about the activation parameters of the nitrogen inversion of various aziridines.

INTRODUCTION

It is well known from IR and micro-wave spectroscopies that the nitrogen inversion in ordinary amines occurs rapidly even at sufficiently low temperatures (for example, the activation energy for ammonia is 5·8 Kcal/mole[2] and that for dimethylamine is 4·4 Kcal/mole[3]). On the other hand, it has been shown from the NMR spectroscopy[4-6] that the rates of the nitrogen inversion of many aziridines are sufficiently low at room temperature (for example, the activation energy is 19·0 Kcal/mole for N-methylaziridine **2**[7]). Since ethylenimine is the most fundamental compound among aziridine derivatives, many investigators have measured the NMR spectra of **1** in liquid phase,[8-12] and have reported that its spectrum shows only one singlet peak for the four protons of the aziridine ring and a broad signal for the amino proton. The singlet peak for the ring protons has been reported[10] to be unchanged even at a temperature as low as −70°. Thus it has been concluded that the nitrogen inversion of **1** is very rapid even at low temperatures. This conclusion is very contrasting with the slow nitrogen inversion of other aziridines.

On the other hand, from the study of micro-wave spectra, the activation energy of the nitrogen inversion of **1** was reported[13-15] to be larger than 12·0 Kcal/mole in gas phase. Recently, theoretical interests have been concentrated in the calculation of the activation energy for the nitrogen inversion



1 **2**

Fig 1. The intramolecular nitrogen inversion of ethylenimine.

of 1 using various molecular orbital methods.[16-20] Although the values of the activation energy obtained from these calculations are different from one to another as described later, all values are larger than 13 Kcal/mole. Thus, taking into account of these results, we can expect that the activation energy of the nitrogen inversion of 1 is also as large as that of other aziridines. Then it seems that the singlet peak for the aziridine ring protons of 1 may be attributed to (1) rapid intermolecular exchange between NH protons, or (2) the influence of water in an incompletely dried sample. Recently Carter *et al.*[21] observed the NMR spectrum of 1 in gas phase taking account of the possibility of the first case, and found four very broad peaks for the aziridine ring protons. The second possibility was suggested by Bardos *et al.*[22] for 2, 2, 3, 3 - tetramethylaziridine.

Recently we succeeded in obtaining the NMR spectrum of completely dehydrated ethylenimine in liquid phase,[1b] and found that its NMR spectrum consists of many well resolved peaks for the ring protons at room temperature. This fact led us to a conclusion that the rate of the nitrogen inversion of 1 is also slow enough at room temperature on the NMR time scale as in the other aziridines. Based on this fact, we have attempted to obtain the kinetic parameters for the inversion process of 1 from the complete line shape analysis of its temperature dependent spectra. Here we should use the density matrix method to make the exact line shape analysis for the complex spin system such as AA'BB'C that ethylenimine shows. As we have successfully used this method to determine the kinetic parameters of the pivot bond rotation in 9,10-dihydro-4,5-dimethylphenanthrene, which has an AA'BB' spin system, in a previous paper, [1a] the extension of this method from AA'BB' to AA'BB'C spin system will be straightforward.

In this paper, we report the NMR spectrum of completely dehydrated ethylenimine in liquid phase. The spectral analysis is performed and some discussion will be made about the obtained NMR parameters. Further, we report the results of the complete line shape analysis of the temperature dependent NMR spectra of 1 by the density matrix method, and present the kinetic parameters of the intramolecular inversion process of 1. We will discuss about the activation parameters of the nitrogen inversion by comparing with those reported for some other aziridines.

RESULTS AND DISCUSSION

The NMR spectra of ethylenimine (1)

The NMR spectrum of thoroughly dehydrated ethylenimine in decalin-d_{18} at room temperature is shown in Fig 2. The undecoupled spectrum (Fig 2a) shows thirteen separate peaks for the four

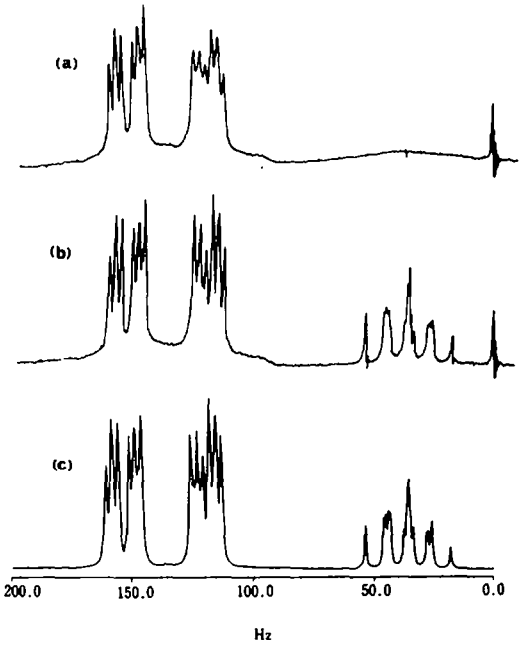


Fig 2. The observed and calculated NMR spectra of ethylenimine at room temperature. (a) An ^{14}N-undecoupled spectrum (b) An ^{14}N-decoupled spectrum (c) A calculated spectrum.

methylene protons of the azirine ring and a very broad peak for the amino proton. The line widths of the six higher peaks for the ring protons are considerably broader than those of the peaks at the lower field. This may be attributed to the incomplete washing out of the spin coupling with ^{14}N nucleus by the nitrogen quadrupole interaction.[23] In order to obtain the genuine line shape of 1, the ^{14}N decoupled spectrum was measured as shown in Fig 2b. The higher field peaks for the ring protons become sharp and the fine structure appears. Furthermore, the amino proton also shows a clear multiplet by ^{14}N decoupling. On the other hand, the sample which was not sealed showed a slightly broad singlet for the ring protons at room temperature. Now it is evident that even a trace of water contained in the sample makes the multiplet signals of the methylene protons to collapse into one singlet peak in this compound. These facts indicate that the second possibility described above is the actual case, and that the rate of the proton exchange between the amino proton of 1 and the OH proton of water contained in the sample is very fast in the NMR time scale.

In order to determine the chemical shifts and the coupling constants, the spectral analysis of 1 as an AA'BB'C spin system was performed using a LAOCOON MBYH program.* The NMR parameters obtained are shown in Table 1, in which coupling constants of 2 obtained by Yonezawa *et al.*[24,25] are also included for comparison. The assignment de-

*LAOCOON II by Castellano and Bothner-By[26] was modified by the authors.

Table 1. Chemical shifts[a] and coupling constants aziridines 1 and 2. (100 MHz)

Compound	1	2[b]
$\delta_1 = \delta_2$	$121{\cdot}8_3$(Hz)	$157{\cdot}0$[c](Hz)
$\delta_3 = \delta_4$	$154{\cdot}8_6$	$87{\cdot}2$[c]
δ_5	$34{\cdot}4_9$	
J_{12}	$5{\cdot}2_1$	5·3
J_{34}	$6{\cdot}3_4$	7·0
$J_{13} = J_{24}$	$3{\cdot}8_4$	3·8
$J_{14} = J_{23}$	$1{\cdot}0_6$	1·0
$J_{15} = J_{25}$	$7{\cdot}6_3$	
$J_{35} = J_{45}$	$9{\cdot}6_7$	

[a]The chemical shifts refer to internal TMS.
[b]Ref 24.
[c]Ref 25.

scribed below and the fitting of the calculated spectrum with the observed lead to one unique set of parameters, which is given in Table 1. The signs of these coupling constants are all positive, and the coupling constants with the opposite signs gave a different spectrum from the observed. A calculated spectrum using these parameters is shown in Fig 2c. The rms-error obtained is about 0·1 Hz. The observed and the calculated spectra agree very well with each other. Although some researchers have suggested[10,24,25] that the chemical shift of the ring protons *cis* to the N-alkyl group is at a higher field than that of the *trans* protons in aziridines, we assign the chemical shift of the *trans* protons (H_1 and H_2) to the higher field peaks in 1 for the following reasons: (1) It is reported[24] that in 2 the *cis* vicinal coupling constant J_{12} between the two *trans* protons in 2 is smaller than another *cis* coupling constant J_{34} between the two *cis* protons as shown in Table 1. Since the coupling constants in the two aziridines (1 and 2) can be considered not to change so dramatically, a similar trend between these two *cis* vicinal coupling constants J_{12} and J_{34} can be assumed in 1. This leads us to assign the higher field peaks of 1 to the *trans* protons in the aziridine ring. (2) The line broadening due to the residual coupling with the nitrogen in the ^{14}N undecoupled ethylenimine spectrum occurs in the higher field peaks, while that in 2 occurs in the lower field peaks which were assigned to the *trans* protons.[24,25] Since the geometry of the molecule is reported to be little changed from 2 to 1 from micro-wave studies,[27,28] (which is also suggested by the small difference in the corresponding proton coupling constants for these two compounds), the broadening effect seems to indicate that the higher field peaks belong to the *trans* protons (H_1 and H_2) in 1. In addition, we wish to point out that this assignment is certainly reasonable from the following reason: the dihedral angle between the H_1–C and H_5–N bonds and that between the H_4–C and H_5–N bonds can be calculated to be about 128° and 11°, respectively, from the molecular geometry obtained by a micro-wave study.[27] Taking account of Kaplus[29] and other[30] equations about the dihedral angles and the spin coupling constants, it is suggested from this fact that the coupling constant J_{15} is smaller than J_{45} in 1. This inference is in good agreement with the assignment described above. Thus the chemical shifts of the *trans* and the *cis* protons are reversed by substitution of Me group on the amino hydrogen. In comparison with the two chemical shifts between compounds 1 and 2, it is evident that the chemical shift of the *trans* protons (H_1 and H_2) moves to a lower field by the Me substitution at N atom, while that of the *cis* protons (H_3 and H_4) moves to a higher field. This tendency of the change in the chemical shifts by the substitution of a Me group in 1 is consistent with those in other 3-membered hetero compounds.[12] The reverse chemical shifts of the *trans* and *cis* protons in 1 in comparison with 2 may be explained by a larger substitution effect in 1 than other analogous compounds.

In order to determine the kinetic parameters of the intramolecular nitrogen inversion of 1, its NMR spectra were measured in the temperature range between −10° and 100°. The line shape for the ring protons remains unchanged at the temperature below 20°, although the amino proton signal moves somewhat to a lower field as the temperature is lowered. This fact indicates that the nitrogen inversion of 1 is low enough below 20°. As the temperature is raised, the line widths of the ring protons become broader; at 44°, the signal for the methylene protons consists of four broad peaks, and at 77°, the lines coalesce into a very broad unsymmetrical signal. At the temperature above 80°, the spectrum begins to show a sharp doublet-like peaks due to the spin coupling with the amino proton. Unfortunately, a good spectrum could not be obtained at the temperatures above 95°, because at that temperature 1 begins to boil violently in the sample tube. Nevertheless, a careful observation shows that the line widths of the doublet-like peaks become sharper with increasing temperature, and that the higher field peak becomes larger in the peak height than the lower field one.

For the analysis of the temperature dependent line shapes of 1, we used the coupling constants shown in the Table 1. The chemical shifts of the aziridine ring protons change as the temperature is raised, i.e., both two ring proton signals (*trans* and *cis* to the amino hydrogen) move to lower fields. However, the difference between the two chemical shifts remains almost unchanged at all temperatures. This means that the change in these chemical shifts with temperature make little effect on the line shape of this compound, because the latter depends only on the chemical shift difference and not on the absolute value of each chemical shift. On the other hand, the amino proton signal shifts to a higher field with increasing temperature. The relationship be-

tween the chemical shift of the amino proton and the temperature was found to be linear. This high field shift may be due to the change in the extent of intermolecular hydrogen bonding through the amino proton.

The evaluation of the nitrogen inversion rate of ethylenimine

As described before, in an ^{14}N-undecoupled spectrum of 1, the line widths of the six higher field peaks for the ring protons are apparently broader than those of the lower field ones. Therefore, in the line shape analysis, we must specify, in the density matrix equations, three kinds of "natural" line widths T_2^{cis}, T_2^{trans}, and T_2^{amino} for the *cis* and *trans* protons of the ring, and the amino proton, respectively. In the density matrix, these "natural" line width terms are included in the diagonal elements of the real part. In the limit of no spin coupling, we can determine which spins are flipped for a particular transition, and thus we may use the line width of each spin for a "pure" transition. For a "mixed" transition we may use a simple average of line widths in the first approximation. In practise, these different "natural" line widths (T_2^{cis} and T_2^{trans}) were determined by the trial and error method in the process of the fitting of the calculated spectrum with the observed one.

The line width of the amino proton T_2^{amino} does not influence the line shape of the AA'BB' part in this system because the amino proton resonance is considerably far from those of the ring protons.

The theoretical spectrum of 1 was calculated using the density matrix equations which were described in the previous paper.[1a] In the AA'BB'C five spin system, we have 110 linear equations of the density matrix. By taking into account the selection rule $\Delta M = 1$, and that the transitions occur only between symmetric states and between antisymmetric states, the coefficient matrix of the density operator equations of the total 110×110 dimension decomposes into eight diagonal blocks [two of 3×3 dimension, two of 18×18 dimension, and one of 36×36 dimension (symmetric part), and two of 8×8 dimension and one of 16×16 dimension (antisymmetric part)]. A computer program named INVERS EX2 was written along this line. The rate of the nitrogen inversion of 1 at each temperature was determined by the visual fitting of the experimental and theoretical spectra.

In order to reduce the computation time, it may be convenient to calculate the spectrum of 1 regarding as an AA'BB'X spin system, because the chemical shift of the amino proton is considerably smaller than those of the ring protons ($J_{35}/(\delta_3-\delta_5) = 0.08$). Then, the total density matrix is divided into twelve blocks [four of 2×2 dimension and four of 8×8 dimension (symmetric part) and four of 4×4 dimension (antisymmetric part)], by neglecting the off-diagonal elements of the imaginary parts of the density matrices, which are corresponding to the mix transitions between the energy levels of the ring protons and the amino proton. Although the computation time in the calculation of the spectrum of the AA'BB'X spin system is reduced by a factor of about 15, as is expected, the intensities of the higher field peaks of the aziridine ring protons are somewhat different from those of the AA'BB'C spin system, while the line shape in the lower field is almost the same in both cases. When the temperature is raised and the line shape becomes very much broader, the difference in the line shapes of the calculated spectra between the two spin systems becomes negligibly small. Therefore, it may be expected that the activation parameters from the AA'BB'X spin system calculation are not so different from those obtained in the exact calculation of the AA'BB'C spin system in the ethylenimine case. Indeed, the differences in the two calculations are 0·2 Kcal/mole in Ea, 0·3 Kcal/mole in $\Delta G^{\neq}$, 0·1 Kcal/mole in $\Delta H^{\neq}$, and 1·0 e.u. in $\Delta S^{\neq}$, which are within the experimental errors.

The kinetic parameters of the nitrogen inversion of ethylen-imine

Some typical examples of the experimental and the theoretical spectra of 1 at various temperatures are shown in Fig 3. The agreement between the observed and the calculated spectra is excellent at all temperatures. The lifetime τ obtained by visual fitting of the observed and calculated spectra is plotted as log τ vs 1/T in Fig 4, which shows a good linear relationship. The activation parameters of the nitrogen inversion of 1 were calculated from the slope and the intercept of the plotted line by using

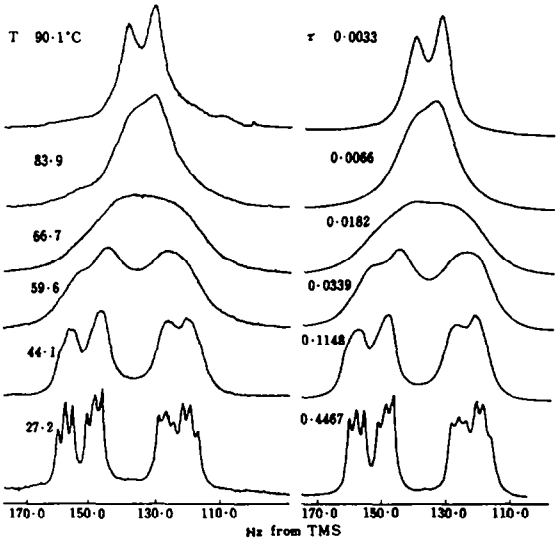


Fig 3. The observed (left) and the calculated (right) NMR spectra of ethylenimine at several temperatures.

Fig 4. Arrhenius plot of the nitrogen inversion of ethylenimine.

Arrhenius' and Eyring' equations. The results are as follows:

$$Ea = 15{\cdot}9 \pm 0{\cdot}4 \text{ Kcal/mole}$$
$$\Delta G^{\neq} = 17{\cdot}1 \pm 0{\cdot}8 \text{ Kcal/mole}$$
$$\Delta H^{\neq} = 15{\cdot}3 \pm 0{\cdot}4 \text{ Kcal/mole} \quad \text{at } 25{\cdot}0°C$$
$$\Delta S^{\neq} = -6{\cdot}2 \pm 1{\cdot}2 \text{ e.u.}$$

One may point out a possibility that the temperature dependence of the line shape does not come from the intramolecular nitrogen inversion of **1**, but is due to the intermolecular exchange of the amino protons with different molecules. If it were so, when the temperature is high enough for the rate of the intermolecular exchange to be fast, the line shape of **1** should consist only of a singlet peak for the ring protons, just as is shown in the spectrum of *wet* ethylenimine, where the intermolecular exchange between the amino proton of **1** and the protons of water contained in the sample is very rapid. Moreover, in that case, the signal for the amino proton must become sharper when the temperature is raised. This is not the case, however. Indeed, the proton spectrum of **1** shows two sharp peaks for the ring protons and a very broad signal for the amino proton at high temperature. Thus, the activation parameters obtained in this study are attributed to the kinetic process of the intramolecular nitrogen inversion of **1**.

The activation parameters of the nitrogen inversion of many aziridines are known already. In Table 2, some of them are listed. The activation energies of N-alkyl substituted aziridines (**2**, **3**, **4**) are considerably larger than that of **1**. But compound **5** whose nitrogen is substituted by a bulky t-Bu group, has almost the same energy barrier as **1**. In general, it may be said that the larger the N-alkyl group of an aziridine compound is, the smaller the energy barrier of the nitrogen inversion. Considering this tendency of the energy barrier, it is very much interesting that **1**, whose nitrogen is substituted by the smallest hydrogen atom, has the smallest activation energy value as shown in this study. On the other hand, compound **7**, whose aziridine ring is substituted by four Me groups, has also much smaller

Table 2. Activation parameters for the nitrogen inversion of aziridine compounds. ▷N—R

	Compound R	Ea (Kcal/mole)	ΔG≠ (Kcal/mole)	ΔH≠ (Kcal/mole)	ΔS≠ (e.u.)	Solvent	Method	Ref
1	H	15·9	17·1 (25·0°C)	15·3	−6·2	decalin-d_{18}	CLS	This work
			17·3 (68)			gas	CT	21
		>12				gas	M.W.	13
		>11·6				gas	M.W.	14, 15
2	Me		19·0 (108)			c-C_6H_{12}	CT	7
		19·0				neat	CT	31
3	Et		19·4 (108)			neat	CT	32
4	c-C_6H_{11}		18·8 (95)			neat	CT	32
5	t-Bu		17·0 (52)			neat	CT	33, 34
6	C_6H_5		11·7 (−40)			CS_2	CT	35
7	Me_2 / Me_2 ▷NH	11·0				CCl_4	ALS	22

CLS: Complete Line Shape Method, CT: Coalescence Temperature Method, } NMR
ALS; Approximate Line Shape Method,
M.W.; Micro-wave spectroscopy.

energy barrier. In this case, the steric effect is probably a predominant factor. In compound **6**, which has an N-Ph group, the energy is also much smaller than **1** because of an electronic effect.

There may be three main factors which make the activation energy of **1** different from those of N-alkyl aziridines; (1) the intermolecular H-bonding effect, (2) the tunnelling effect, and (3) the different conformations of aziridine compounds.

It is certain that in **1** the intermolecular H-bonds $\left(\rangle N—H\cdots N\right)$ are formed in the NMR sample concentration and that the intermolecular interaction in N-alkyl aziridines is much less than that in **1**. At the present time, we cannot say exactly extent that this intermolecular H-bonding makes the influence on the process of the intramolecular nitrogen inversion of **1** in solution. However, the H-bonding effect on the barrier of the inversion seems small, because the free energy of activation of **1** in gas phase was reported[21] to be almost the same as our value obtained in liquid state within the experimental error, although the reported values were based on the analysis by the coalescence temperature method in the AA'BB'C spin system.

It is well known that the tunnelling effect exists in the nitrogen inversion in ammonia. But it has been also reported that this effect becomes much smaller for the nitrogen inversion as the molecule becomes larger,[5] and Kemp *et al.* reported[14] that the tunnelling effect in **1** is negligible. Thus the second possibility has been ruled out.

Then, the smaller activation energy of **1** may be attributed to the conformational difference in aziridine compounds. It will be considered that, in the transition state, the N–H or the N–R bond may probably be in the aziridine ring plane in the intramolecular nitrogen inversion process, and then, it may be supposed that the nearer the N–R bond is to the ring plane in the ground state, the smaller its activation energy becomes. Compound **5** has a smaller activation energy than compounds **2** and **3**. This may be explained along this line, because the t-Bu group in **5** may be nearer to the ring plane due to the larger steric repulsion against the aziridine ring than the Me group in **2** and **3** in the ground state. Compound **6** has the smallest activation energy among **1–6**. This fact also may be explained from the above consideration, because in **6** the benzene plane is near to the aziridine ring plane due to the resonance effect between the pheny and the aziridine rings. If a similar consideration could be adopted to **1**, its smaller energy barrier would be attributed to the N–H bond in the neighbourhood of the aziridine ring plane in the ground state. Actually, however, the angular relationship is reverse between **1** and **2**, i.e., it was reported[27,28] from microwave spectroscopy that the angle between the aziridine ring plane and the N–H bond of **1** is 70°, and the corresponding angle of **2** is 63°. Therefore, the simple steric consideration described above cannot be adopted to compare the barriers between **1** and N-alkylaziridines. The difference in the angles seems to indicate that the electronic hybridization at the nitrogen atom in **1** is somewhat different from that in **2**, because the former compound has a nitrogen atom in the N–H bond, while the latter in the N–C bond. Probably the difference in the electronic hybridization between these compounds may cause the smaller activation energy of **1** in comparison with N-alkylaziridines.

As described before briefly, the activation energy of the nitrogen inversion of **1** has been calculated theoretically using various molecular orbital methods. The results are given in Table 3. The calculated energy values are clearly different from each other. We do not know the errors of the activation energies calculated by these methods. But we would like to point out that the value from *ab initio* method is the closest to our experimentally obtained activation energy value.

Table 3. Calculated activation energy values of the nitrogen inversion of ethylenimine

Ea (Kcal/mole)	Method	Ref
13·8	MINDO	18
15·5	*ab initio*	17, 36
18·3	LCAO MO SCF	16
20·9	Extended Hückel	19
21·4	CNDO/2	20
34	Valence Force Field	37

EXPERIMENTAL

Sample. Ethylenimine used in this study was a commercial source. It was distilled (b.p. 57°) and thoroughly dried by refluxing over NaOH for many h. The purity was checked by the gas-chromatograph method (99·99%). As a solvent, decalin-d_{18} was used, which was also dried completely by heating with Na for 5 h at about 100°. The sampling was made in a high vacuum system under a completely dried condition and the sample was degassed and sealed.

Measurement. The NMR spectra were recorded at a temp range between −10° and 100° using a Varian HA-100D spectrometer. The sample temp was determined by use of the temp dependent chemical shift of the OH proton of methanol or ethylene glycol.[38] A ^{14}N-decoupled spectrum at room temp was recorded by a Varian XL-100 spectrometer by Dr. S. Satoh of Nippon Electric Varian Ltd.

Spectral analysis. The analysis of the NMR spectra at slow exchange limit and the calculations of the theoretical line shape were made using a FACOM 270/30 computer.

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