CHEMISTRY LETTERS, pp. 465-468, 1973. Published by the Chemical Society of Japan

THE PROTON MAGNETIC RESONANCE SPECTRUM OF ETHYLENIMINE

Hiroshi NAKANISHI and Osamu YAMAMOTO
National Chemical Laboratory for Industry
1-1-5, Honmachi, Shibuya-ku, Tokyo

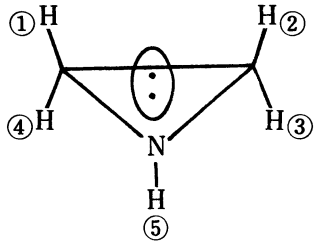
An NMR spectrum of completely dehydrated ethylenimine in liquid phase is found to show well resolved multiplets for the aziridine ring protons and the computer analysis is made to determine the NMR parameters. Temperature dependent NMR spectra show that the nitrogen inversion of ethylenimine does not occur at room temperature.

It is well known that the rate of nitrogen inversion in aziridine derivatives is much slower than that of ordinary amines. The temperature dependent NMR spectra of these compounds have been measured by many investigators[1] in order to obtain kinetic parameters of nitrogen inversion, and it has been shown that the rate of inversion is sufficiently low at room temperature for many aziridine compounds. Nevertheless, it has been reported[2-6] that ethylenimine, the most fundamental compound of this class, shows only one singlet peak for the four protons of the aziridine ring and a broad signal for an amino proton in several solvents. The singlet peak for the methylene protons has been reported[4] to be unchanged even after lowering the temperature to -70°C. This apparent difference in the nitrogen inversion rate between ethylenimine and the other aziridine derivatives may be attributed to (1) rapid intermolecular exchange between NH protons, or (2) the influence of water contained in an incompletely dried sample. Recently Carter et al.[7] observed the NMR spectrum of ethylenimine in gas phase taking account of the possibility of the first case, and found four very broad peaks for the ring protons. The second possibility was suggested by Bardos et al.[8] for 2,2,3,3-tetramethylaziridine.

In this paper, we report that the NMR spectrum of thoroughly dehydrated ethylenimine in liquid phase shows well resolved multiplets for the ring protons and that the nitrogen inversion does not occur at room temperature.

Ethylenimine of commercial source was distilled and was completely dried by

refluxing over sodium hydroxide for three hours. Decalin-d_{18} was used as a solvent, and this was also dried completely by heating with sodium for five hours. The sampling was made in a high vacuum system, and the sample was degassed and sealed.



NMR spectrum of thoroughly dried ethylenimine shows thirteen separate peaks for the ring protons and a very broad peak for the amino proton at room temperature. The line widths of the six higher field peaks for the ring protons are considerably broader than those of the lower field ones probably because of the incomplete washing out of the long range coupling with ^{14}N nucleus by the nitrogen quadrupole interaction. Therefore, the NMR spectrum with ^{14}N decoupling was measured in order to obtain the genuine line shape of this compound, which is shown in the upper figure. On the other hand, the sample which was not sealed showed a slightly broad singlet for the ring protons. 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. Furthermore, the amino proton also shows a clear multiplet structure by ^{14}N decoupling. 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 ethylenimine and the hydroxy proton of water contained in the sample is very fast.

The spectral analysis of this compound as an AA'BB'C spin system was made using a LAOCOON MBYH program. The chemical shifts and coupling constants obtained are given in the table, in which coupling constants in N-methylaziridine obtained by Yonezawa et al.[9,10] are also included for comparison. A calculated spectrum using these parameters is shown in the lower figure. The observed and the calculated spectra agree very well with each other. Although some reserchers have suggested[4, 9, 10] 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 aziridine compounds, we assign the chemical shift of the trans protons (H_1 and H_2) to the higher field peaks in ethylenimine for the following two reasons: (1) Yonezawa et al. reported[9] that in N-methylaziridine the cis vicinal coupling constant J_{12} between the two trans protons (H_1 and H_2) is smaller than another cis coupling constant J_{34} between the two cis protons (H_3 and H_4) as shown in the table. Since the coupling

constants in the two aziridine compounds can be considered not to change so drastically, a similar trend between these two cis vicinal coupling constants J_{12} and J_{34} can be also assumed in ethylenimine. This leads us to assign the higher field peaks of ethylenimine to the trans protons in the aziridine ring. (2) The line broadening due to the residual coupling with the nitrogen nucleus in the ^{14}N undecoupled ethylenimine spectrum occurs in the higher field peaks, while that in N-methylaziridine occurs in the lower field peaks which were assigned to the trans protons. Since the geometry of the molecule may probablly be little changed from N-methylaziridine to ethylenimine, (which is suggested by the small difference in the corresponding proton coupling constants for the two compounds), the broadening effect seems to indicate that in ethylenimine the higher field peaks belong to the trans protons (H_1 and H_2). Thus the chemical shifts of the trans and cis protons are reversed by substitution of methyl group on the amino hydrogen. This

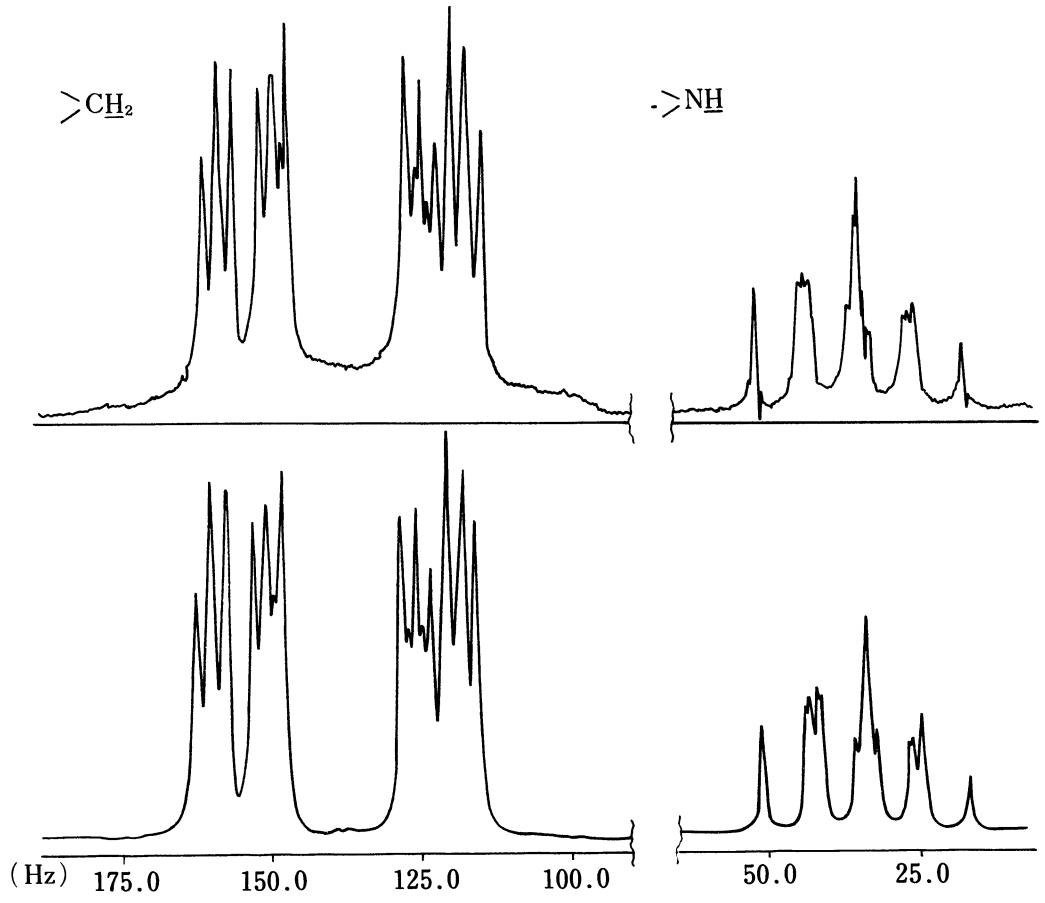


Figure: The observed ^{14}N decoupled (upper) and the calculated (bottom) PMR spectra of thoroughly dried ethylenimine. Refered to TMS.

Table: Chemical shifts* and coupling constants of aziridine compounds. (100MHz)

Compound	$\delta_1=\delta_2$	$\delta_3=\delta_4$	δ_5	J_{12}	J_{34}	$J_{13}=J_{24}$	$J_{14}=J_{23}$	$J_{15}=J_{25}$	$J_{35}=J_{45}$
N-H	121.8_3	154.8_6	34.4_9	5.2_1	6.3_4	3.8_4	1.0_6	7.6_3	9.6_7
N-Me**	157.0***	87.2***		5.3	7.0	3.8	1.0		

* The Chemical shifts refer to internal TMS. ** Reference 9. *** Reference 10.

assignment and the fitting of the observed and calculated spectra lead to one unique set of parameters, which is shown in the table, and the signs of these J values are all positive.

The spectrum of the completely dried ethylenimine solution does not change when the temperature is lowered, although the signal of the amino proton shifts to a somewhat lower field. This fact indicates that the nitrogen inversion in this compound is slow enough at room temperature. As the temperature is raised, the peaks of the ring protons become broad and the spectrum shows one broad unsymmetric signal at 76°C, and eventually a sharp doublet peak due to the coupling with NH proton at the temperature above 80°C. In order to obtain the kinetic parameters of the nitrogen inversion of ethylenimine it is necessary to make a complete line shape analysis in this AA'BB'C exchanging spin system by the density matrix method.

The authors express their hearty thanks to Dr. S.Sato of Nippon Electric Varian Co. Ltd. for measuring the ^{14}N decoupled spectrum with a Varian XL-100 spectrometer.

References

1) J.B.Lambert, "Topics in stereochemistry," Vol.6, Wiley-Interscience, New York (1971), p.19 and references therein.
2) F.S.Mortimer, J.Mol.Spectrosc., 5, 199 (1960).
3) Varian NMR Spectral Catalog. No. 372.
4) H.Saito, K.Nukada, T.Kobayashi, and K.Morita, J.Amer.Chem.Soc., 89, 6605(1967).
5) S.J.Brois, Tetrahedron, 26, 227 (1970).
6) M.Ueyama and K.Tori, Nippon Kagaku Zashi, 92, 741 (1971).
7) R.E.Carter and T.Drakenberg, Chem.Commun., 1972, 582.
8) T.J.Bardos, C.Szantay, and C.K.Navada, J.Amer.Chem.Soc., 87, 5796 (1965).
9) T.Yonezawa and I.Morishima, J.Mol.Spectrosc., 27, 210 (1968).
10) T.Yonezawa, I.Morishima, and K.Fukuta, Bull.Chem.Soc.Japan, 41, 2297 (1968).

(Received February 27, 1973)