CHEMISTRY OF ETHYLENIMINE

I. N-Aminoethylenimine

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The most important physicochemical characteristics (IR, NMR, and mass spectra, dipole moment, dissociation constant) of N-aminoethylenimine (I) were studied. It was shown that in the molecule of (I) a pπ-interaction between the unshared electron pair of the amino-group nitrogen and the electron system of the ethylenimine ring takes place.

Inasmuch as two sp-hybrid atomic orbitals cannot form between them an angle of less than 90°, the structure of three-member heterocycles has a unique character [1]. The corresponding linked orbitals are not directly oriented to each other, as is the case in heterocycles with a larger number of carbon atoms; but forms bent, so-called "banana" linkages with a relatively more pronounced p-character of the endo-orbitals, in distinction to the greater s-character of the exo-linkages. Due to the peculiar character of the bent linkage, there is a better overlapping with the neighboring p-orbitals of the substituents, if these are distributed parallel to the heterocycle plane and symmetrically with respect to the bent linkages of the ring.

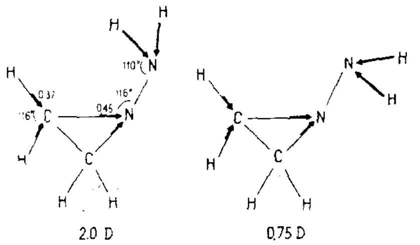


Fig. 1. Vector diagram of the dipole moments of cis and trans isomers of N-aminoethylenimine.

Such a type of bond between a substituent containing, for instance, an unshared electron pair and a three-member heterocycle had not been investigated until now among ethylenimine derivatives. In order to study the magnitude of such an interaction, we synthesized the N- and the C-amino substituted aziridines.

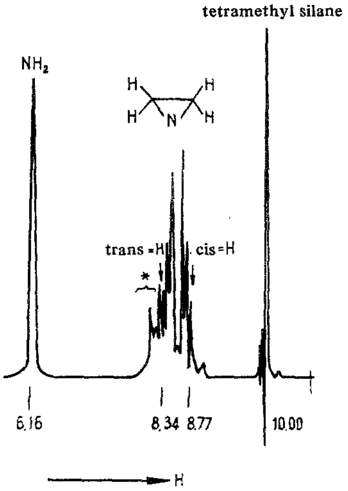


Fig. 2. PMR spectrum of N-aminoethylenimine.

This paper presents the results of our investigation of N-amino-ethylenimine (I).

To establish the pπ-interaction between the amino-group nitrogen and the aziridine ring, we determined the magnitude of the dipole moment, dissociation constant, as well as the IR and mass spectra, and the NMR spectra of N-amino ethylenimine.

The magnitude of the molecular exaltation of (I) was exceptionally high. (Found: MR_D: 17.40. Calculated MR_D 16.6). This phenomenon, as well as the 26° increase in the boiling point when compared with ethylenimine, testify to the presence of a definite linkage

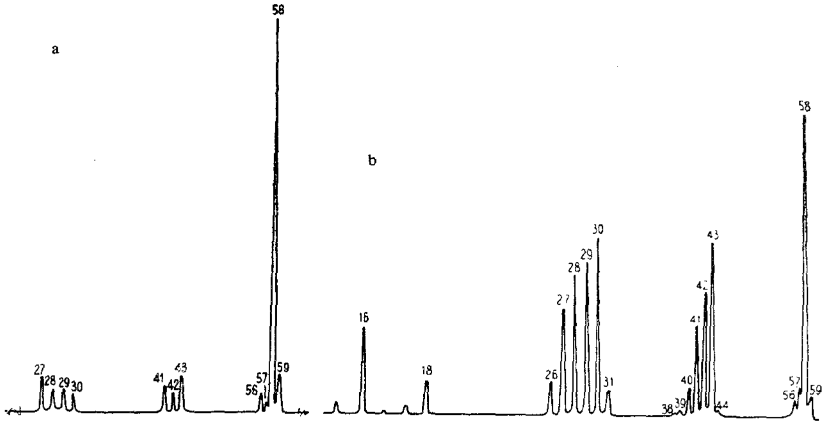


Fig. 3. Mass spectrum of N-aminoethylenimine.

between the unshared electron pair of the amino group with the unsaturated aziridine ring. However, here is evident a marked intermolecular influence of the donating properties of the amino group of one molecule on the aziridine ring of the other, and also the possible formation of an intermolecular hydrogen bond.

Table 1

Data of the Determination of the Dipole Moment

No. of measurement	f	ε	α
1	0.012190	2.3088	1.2545
2	0.010553	2.3088	1.4502
3	0.012078	2.3088	1.2671
4	0.0054105	2.9992	1.2355

The peculiarities of (I), as already indicated, are due to the presence of a nitrogen-nitrogen bond, in which each atom possesses an unshared electron pair capable of $p\pi$-interaction and of entering into a coordination bond. In fact the bonding of the unshared electron pair of the amino-group nitrogen atom with the electron system of the heterocycle brings forth only a relatively small rise in the basicity of the latter in comparison with ethylenimine [2, 5], as is evident from the character of potentiometric titration curves of a 0.1 N aqueous solution of (I) with 0.1 N HCl (at 20° in a nitrogen atmosphere), in which (I) behaves as an ordinary weak base. From the data it follows that the pK_a of the (I)-ion is numerically 8.22. An increase in the electron density in the ethylenimine ring at the expense of the already mentioned interaction leads also to an insignificant change in the dipole moment (μ = 1.49 D) when compared with ethylenimine [6]. The latter was determined by measuring the dielectric constants of dilute solutions of (I) in benzene at 20° in a nitrogen medium. Table I presents the data employed in the calculation of the dipole moment of (I).

The average value of the dipole moment obtained with the help of a vectorial diagram amounts to 1.37 D, confirming the experimentally found value of μ for I.

The proton magnetic resonance spectrum at a frequency of 40 Mc at room temperature is a AA'BB' type multiplet of the protons of the ethylinimine ring, characteristic of N-substituted ethylenimines with a slow inversion frequency of the heteroatom and also a slight broadening of the singlet of the amino-group protons.

The average position of the resonance absorption of the ring protons in (I) (8.56 ppm) testifies to a definite lowering of the electron density of the ring when compared with that of the unsubstituted ethylenimine, which is bound with a greater J-effect of the NH_2-group when compared with the hydrogen atom.

Nevertheless, the slow inversion of the nitrogen atom in (I) shows that the delocalization of the unshared pair and the consequent formation of a plane transitional state that would facilitate the inversion transition of the nitrogen does not take place. This process is rendered difficult by the preferential shift of the p-electrons of the amino-group nitrogen atom toward the ethylenimine ring. The chemical shift of the amino-group protons in (I) (τ = 6.16) is somewhat smaller than in the phenylhydrazine molecule, and this indirectly confirms the lowering of the electron density of the amino-group nitrogen atom.

As suggested by Kohlrausch and Reitz, and afterward by Thompson, Harris, and Cave [7–10], the deviation of the oscillatory spectra of ethylenimine from the oscillation types allows some comparisons with the results of our investigations of the IR-spectra and the combination dispersion spectra of (I), as well as a selection of the characteristic frequencies corresponding to these oscillations.

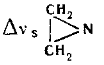
The presence of increased frequencies of the CH-valence vibrations 3005, 3080 cm^{-1}, when compared with those at 2800–2980 cm^{-1} in aliphatic amines, shows the strained condition of the ring of (I), which also characterizes other three-member rings. The deformation vibrations of the ring of (I) in the 1230 and the 825 cm^{-1} regions are somewhat higher when compared with those of ethylenimine (1210, 857 cm^{-1}). If the shift $\Delta\nu_s$  $\overset{CH_2}{\underset{CH_2}{|}}\!\!>\!N$ in the vibrational spectra of N-alkyl substituted ethylenimines testifies to a significant change in the hybridization of the electron clouds of nitrogen due to the steric effects of the alkyl groups [11], such an insignificant shift of the mentioned frequencies may be explained by the participation in the union of the unshared electron pair of the amino-group nitrogen with the electron system of the heterocycle.

Table 2

Fundamental Frequencies in the Oscillatory Spectrum of N-Aminoethylenimine

Oscillation type	cm^{-1}
CH-valence	3005 3080
CH_2-deformation	1455
CH_2-bending	1120
Ring deformation	1230 825
CH_2-twisting	1032
NH_2-valence	3320
symmetrical	3750
antisymmetrical	3180
NH_2-deformation	1608
–N–N-valence	1120 1070
$N_{tertiary}$-valence	925

Supplementary conclusions as to the structure of (I) may be drawn from mass spectroscopy. Measurements made at various potentials clearly illustrate the relative content of the main positive ions in the mass spectrum of (I). The greatest interest is attached to $C_2H_7N_2^+$, $C_2H_6N_2^+$, $C_2H_5N_2^+$ (m/e = 59, 58, 57), which retain the cyclic structure of (I), as well as to the ions $C_2H_5N^+$, $C_2H_4^+$ (m/e = 43, 42). Their presence indicates the ease with which ethylenimine ions are formed by the elimination of the NH_2 group.

In a following paper we shall publish the results of the most important chemical conversions of (I).

EXPERIMENTAL

N-Aminoethylenimine (I). Obtained by a method modified by us [12]. The synthesis will be described later on. (I) was separated in a PGK-3 preparative chromatograph. It is a colorless liquid with a characteristic ammoniacal odor. Bp. 82–83°; n_4^{20} 1.45453; n_C^{20} 1.45178; n_F^{20} 1.46120; d_4^{20} 0.9030. Found, %: C 41.30; N 48.00; H 10.55. Calculated for $C_2H_6N_2$, %: C 41.50; N 48.10; H 10.3.

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