ETHYLENIMINE CHEMISTRY

VII.* PYRAMIDAL STABILITY OF N-AMINOETHYLENIMINE DERIVATIVES

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2-Methyl-N-aminoethylenimine was synthesized by the classic Wenker method and by amination of 2-methylethylenimine with hydroxylamine-O-sulfonic acid in alkaline media. NMR spectroscopy indicated the formation of exclusively the trans-inverted isomer, the pyramidal stability of the heteroatom of which, as in N-aminoethylenimine [3-5], is preserved over a broad range of temperatures. The hydrazones of N-aminoethylenimine are characterized by an appreciably lower pyramidal stability of the nitrogen than that associated with participation of its unshared electron pair in p,π conjugation with the π electrons of the C=N bond. The inversion barrier in the hydrazones decreases symbatically with an increase in the degree of the indicated interaction. However, the decrease is insufficient to freeze free rotation about the nitrogen-nitrogen bond up to −80°.

After the appearance of Roberts' [2] application of NMR spectroscopy to determine the rate of inversion of the nitrogen atom in ethylenimine derivatives this ring became the subject of intense investigations in this direction.

In 1966 we first detected the stable pyramidal structure of the nitrogen atom in the N-aminoethylenimine (I) molecule. The NMR spectrum of I, determined at 40 MHz for a 25% solution in CCl_4, contained a complex multiplet of the AA'BB' type for the protons of the ethylenimine ring, with an average position of the resonance absorption of the ring protons at 8.56 ppm. For clarity we will reproduce here the NMR spectrum of I (Fig. 1) which we obtained at that time and published in [3]. The constancy of this spectrum over a broad range of temperatures attested to the significant pyramidal stability of nitrogen in this molecule [4, 5].

After us, in 1967-1968 Kostyanovskii and Brois reported a similar phenomenon for N-chloroethylenimine [6], 2,2-dimethyl-N-chloroethylenimine [6, 8], 2,2,3,3-tetramethyl-N-chloroethylenimine [7], their corresponding bromo derivatives [6-8], and for N-aminoethylenimine and 2,2-dimethyl-N-aminoethylenimine [5].

Thus, the stable pyramidal structures for nitrogen, first established by us, were subsequently confirmed in the case of a number of other ethylenimine derivatives. In the process, Brois and Kostyanovskii were able to isolate individual cis and trans inversion isomers for 2-alkyl-N-haloethylenimines [6, 8, 9].

In 1969 Kostyanovskii [9, 10] reported the synthesis and isolation of optically active isomers of 2-methyl-N-haloethylenimine with an asymmetric pyramidal nitrogen and asymmetric C_2.

Continuing our systematic investigations of the chemistry of I [1, 3], we synthesized and isolated the stable trans inversion isomer of 1-amino-2-methylethylenimine.

*See [1] for communication VI.

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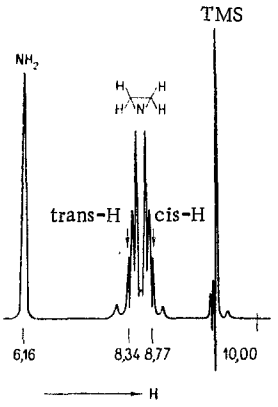


Fig. 1

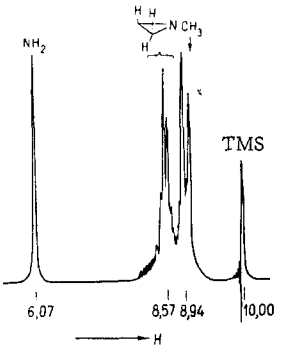
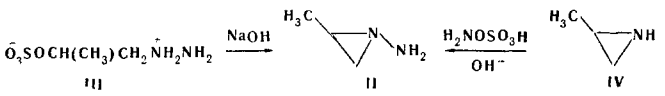


Fig. 2

Fig. 1. NMR spectrum of 1-aminoethylenimine.

Fig. 2. NMR spectrum of 2-methyl-1-aminoethylenimine.

1-Amino-2-methylethylenimine (II) was synthesized via both the classic Wenker method, i.e., cyclization of the sulfate ester of 1-hydrazino-2-propanol (III), and by amination of 2-methylethylenimine (IV) with hydroxylamine-O-sulfonic acid in alkaline media:

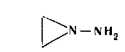
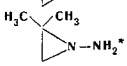
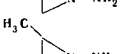
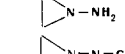
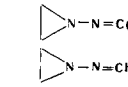
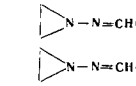
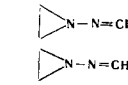


III II IV

Pure II was isolated by preparative gas-liquid chromatography.

The NMR spectrum of II (Fig. 2) contains a single doublet from the methyl protons ($\tau = 8.94$ ppm), a singlet from the amino group protons ($\tau = 6.07$ ppm), and a characteristic multiplet from the ring protons of the ethylenimine ring (centered at 8.6 ppm), and no changes whatsoever in the character and position of the resonance signals from the methyl protons and the heteroring protons are observed from 25 to 135°. Consequently, the substance that we isolated is not a mixture of the two expected cis and trans inversion isomers but has the structure of only one of them. The most likely structure should of course be the trans

TABLE 1. NMR Spectral Parameters of N-Aminoethylenimine and Its Derivatives

Compound	Chemical shifts (τ, ppm)					Coalescence temp., °C	ΔG, kcal/mole (± 0.5)
	cis and trans protons of the hetero ring	CH_3—C	CH_3C=	HC=	aromatic protons		
	8,77; 8,34	—	—	—	—	>150	>22
	8,90; 8,37	8,94; 8,73	—	—	—	>150	>22
	8,6	8,94	—	—	—	—	>22
	8,43; 8,16	—	8,24; 8,05	—	—	135	21
	8,38; 8,12	—	8,23	2,15	—	101	20
	8,11; 7,95	—	—	1,54	2—2,8	64	18
	7,90; 7,74†	—	—	1,58	1,68; 2,48	30	16

*Data of [5].

†At −20°.

form. The chemical shifts for the CH_3 protons in the spectra of the substance isolated by us, which coincide with those for the protons of the more shielded methyl group of 2,2-dimethyl-N-aminoethylenimine [5], are in agreement with this. Moreover, one should bear in mind that great shielding of the CH_3 protons in the trans isomers is known for 2-methyl-N-haloethylenimines [8, 9].

As recently shown by quantum-chemical calculations, the pyramidal stability of the nitrogen atom in I is mainly due to mutual repulsion of the unshared electron pairs of the two nitrogen atoms [11]. The increased rate of inversion of nitrogen in the bisaziridine molecule [12] can be explained from these positions, since the energy of mutual repulsion of the unshared electron pairs of the nitrogen atoms in this case is depressed because of conjugation of the latter with the electron system of the heteroring.

On the basis of what has been stated, a study of the pyramidal stability of the nitrogen atom in the hydrazones of I, which contain an exocyclic, sp^2-hybridized nitrogen atom [1, 13, 14], is of considerable interest.

We have found that, in contrast to I, its hydrazones are characterized by an appreciably lower pyramidal stability of the heteroatom. Table 1 shows that, in this respect, the hydrazones of a given series have coalescence temperatures from 30 to 135°, depending on the substituents on the carbon atom. Table 1 also contains the free enthalpies of inversion (ΔG), calculated by us according to the method in [15], and the NMR spectral parameters.

The pyramidal stability of the nitrogen atom in the hydrazones of I apparently depends on two mutually competitive effects. As already stated, mutual repulsion of the unshared electron pairs of adjacent atoms has a stabilizing effect. The reverse effect should be expected from participation of the unshared electron pair of the nitrogen atom in p, π conjugation with the π electrons of the C=N bond. It is apparently precisely this effect which is primarily responsible for the considerable decrease in the pyramidal stability of the nitrogen of the investigated hydrazones, as compared with I and II. In fact, the lowering of the inversion barrier in hydrazones of I proceeds symbatically with an increase in the degree of p,π-interaction. In addition, judging from the NMR spectra, even the most powerful p,π-interaction among the compounds studied (in p-nitrobenzylidene-N-aminoethylenimine) is insufficient to freeze free rotation about the nitrogen-nitrogen bond (which, because of the indicated conjugation, has partially double-bond character) up to −80°.

EXPERIMENTAL

The NMR spectra were obtained with a YaMR-5535 TsLA spectrometer (40 MHz) equipped with an adapter for thermostating the samples. The compounds were investigated as 25-30% solutions in carbon tetrachloride containing a small amount of tetramethylsilane (TMS) as the internal standard. The chemical shifts were measured by the side-band method with an accuracy of ±0.02 ppm.

1-Hydrazino-2-propanol. Propylene oxide [70 ml (1.0 mole)] was added dropwise with stirring and cooling with an ice bath to 730 ml (15.0 mole) of hydrazine hydrate, the temperature of the mixture was raised to room temperature, and it was then allowed to stand under these conditions for 1 h. The mixture was then heated on a water bath to 70° for 2 h. The excess hydrazine hydrate was removed by distillation at 20 mm, the residue was vacuum-distilled, and the fraction boiling at 108-110 (4 mm) was collected to give 80 g (85%) of a product with n_D^{20} 1.4705.

1-Hydrazino-2-propanol Sulfate (III). A total of 590 g (3.0 mole) of 50% sulfuric acid was added dropwise with stirring and cooling with an ice bath to 360 g of 50% aqueous 1-hydrazino-2-propanol, and the mixture was held at room temperature for 2 h. The water was removed by distillation, initially at 20 mm and then at 3-5 mm and 110-112°. After cooling, the vitreous mass was dissolved in 300 ml of water. The compound was crystallized from aqueous methanol (3:1) to give 250 g (70%) of a product with mp 219-220°.

1-Amino-2-methylethylenimine (II). A) An aqueous alkaline solution of 350 g (2.0 mole) of III was added at the rate of removal of distillate to 500 ml of 30% aqueous sodium hydroxide at the boiling point. II was concentrated by the addition of solid alkali under an inert gas at a temperature no higher than 30°. The organic layer was separated and dried over solid alkali for 10 h and then over calcium hydride. The calcium hydroxide and hydride were filtered to give 98 g (70%) of II. The gas-liquid chromatography of the products formed by Wenker cyclization of III was similar to that described in [3]. The product had bp 114°, n_D^{20} 1.4422, and d_2^{20} 0.8941.

B) A solution of 29 g (0.025 mole) of hydroxylamine-O-sulfonic acid [17] in 100 ml of water was added with stirring and cooling to 0° to 53 g (1 mole) of IV [16] dissolved in 400 ml of 10% aqueous alkali. After the mixture was allowed to stand at room temperature for 1 h, the II was concentrated by addition of solid alkali at 25-30° under argon. The organic layer was separated and dried over calcium hydride. II was isolated according to the method in [3].

N-Aminoethylenimine Hydrazones. These were obtained via the methods in [1, 13, 14].

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