^1H and ^{13}C NMR SPECTRA OF N-AMINOETHYLENEIMINE HYDRAZONES

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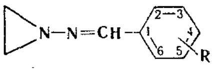
It has been shown [1] that N-aminoethyleneimine hydrazones are characterized by lower pyramidal stability of the nitrogen heteroatom than N-aminoethyleneimine itself. We have synthesized several N-aminoethyleneimine hydrazones with substituted benzaldehydes.

The ^1H and ^{13}C NMR spectra of the products were studied (Tables 1 and 2). In the ^1H NMR spectra the protons of the ethyleneimine ring at –10°C appear as an AA'BB' multiplet. It



I-V

I R = 2-NO_2; II R = 4-NO_2; III R = 4-Br; IV R = H;
V R = 4-OCH_3

TABLE 1. Parameters of the PMR Spectra of N-Aminoethyleneimine Hydrazones

Compound	Chem. shifts, δ, ppm			$\Delta\nu^*_{AB}$, Hz	t_c, °C	$\Delta G_c^{\neq}$, kcal/mole
	$(CH_2)_2N$	–CH=N	remaining protons			
I	2,07	8,27	8,0—7,3	16,1	39	16,0
II	2,07	8,50	8,20 (H^3; H^5) 7,77 (H^2; H^6)	17.2	35	15.8
III	1,97	8,33	7,42	13,8	60	17,2
IV	1,95	8.46	7,8—7.2	13,2	68	17,7
V	1,90	8,32	7,46 (H^2; H^6) 6,74 (H^3; H^5) 3,71 (OCH_3)	13,0	78	18.3

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*At -10°C.

TABLE 2. ^{13}C NMR Chemical Shifts* of N-Aminoethyleneimine Hydrazones

Compound	$(CH_2)_2N$	–C=N	C_1	C_2	C_3	C_4	C_5	C_6	C_R
I	30,8	154,4	127,9	148,9	124.3	130,8	133,1	128,8	—
II	30,9	156,7	128,3	127,9	123,7	148,4	123,7	127,9	—
III	30,6	157,5	128,7	128,8	131,7	124,4	131,7	128,8	—
IV	30,5	157,8	130,1	128,7	128,7	131,0	128,7	128,7	—
V	30,4	158.2	126,9	128,9	114.1	161,4	114,1	128,9	55,1

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*In parts per million relative to tetramethylsilane.

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follows from a calculation of the spectrum of V with a computer that the anisochronicity of these protons arises because of slow inversion of the ethyleneimine nitrogen but not because of retarded rotation about the N—N bond [2]. As the temperature is raised, both portions of the multiplet are broadened and then coalesce. The barriers to inversion of the nitrogen atom ($\Delta G_c \neq$), calculated at the coalescence temperature, are presented in Table 1. A linear correlation between both $\Delta G_c \neq$ and the average chemical shift of the protons of the three-membered ring with the Hammett σ constants is observed:

$$\Delta G_c{\neq} = 17.7 - 2.39\sigma, \ r = 0.99;$$

$$\delta_{(CH_2)_2N} = 1.94 + 0.16\sigma, \ r = 0.99.$$

The shielding of the carbons of the ethyleneimine ring also decreases as the electron-acceptor properties of the substituent increase (Table 2), but the chemical shift of the imine carbon atom increases in this case. These data show that participation of the unshared electron pair in p-π conjugation with the π electrons of the C=N bond is responsible for the decrease in the barrier to inversion of the nitrogen heteroatom. The higher barrier to inversion in I as compared with II should be explained by steric interactions that hinder the indicated conjugation. The chemical shift of the carbons of the three-membered ring also provides evidence for this.

The PMR spectrum of II remains unchanged up to —100°, and this corresponds to the upper limit for the barrier to rotation about the N—N bond (<8 kcal/mole) in these compounds.

The ^{1}H NMR spectra were obtained with a Tesla BS 487C spectrometer (80 MHz), and the ^{13}C NMR spectra were obtained with a Bruker HXF-90 spectrometer (22.63 MHz) under pulse conditions with broad-band quenching of the protons. The spectra of 5% (for ^{1}H) and 20% (for ^{13}C) solutions in $CDCl_3$ were obtained with tetramethylsilane as the internal standard. The PMR spectrum was calculated with an NR 2116S computer with an LAOCN3° program. The barriers to inversion were calculated by the method in [3]. The synthesis of I-V was described in [4-6].

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