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Abstract

Full Text

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HAMMETT CONSTANTS OF THE ETHYLENIMINE RING

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In its physicochemical properties ethylenimine (I) differs substantially from aliphatic and higher cyclic amines. The most important features of I are: 1) reduced basicity; 2) shortening of the C—H bonds, increase of the HCH angle, and decrease of the HNC angle; 3) increase in the frequency of valence vibrations for the C—H bonds and decrease for N—H; 4) decrease in the rate of nitrogen inversion (^{1}); 5) transmission of conjugation through the ring via the C—C bond (^{2}); 6) easy opening of the ring (even in comparison with the nearest homolog—trimethylenimine) (^{1}); 7) the distinctive character of N-ethylenimine carbinols (^{3}), which, in particular, occupy a borderline position in the Mannich reaction (easy ethyleniminomethylation of amines and absence of interaction with the labile hydrogen of the HO group of alcohols and of the activated HC group). These features are evidently due to the high strain of the ring, 1-14 kcal/mole (^{1}).

An idea of the quantitative relationship between the chemical structure and reactivity of I and its derivatives can in principle be obtained using the Hammett-Taft apparatus (see, for example, (^{4})). At present, however, the values of the σ constants of the ethylenimine group are unknown. Determination of the latter by the usual method—from the dissociation constants of para- and meta-ethyleniminobenzoic acids—does not appear possible because of the instability of the ring in acidic medium. Therefore, apparently, the only possible method for determining the σ constants is measurement of the chemical shifts of the fluorine nuclear magnetic resonance (NMR) in para- and meta-fluorophenylethylenimines (II and III, respectively).

It is known (^{5}) that the chemical shifts of fluorine signals in para- and meta-substituted fluorobenzenes (δ_{p}^F and δ_{m}^F) reflect with good accuracy the influence of the substituent on the electronic system of the benzene ring by the inductive mechanism (σ_{i}) and through conjugation (σ_{c}^0):

$$\delta_{\mathrm{m}}^F = -6.10\,\sigma_{\mathrm{i}} + 0.5 \qquad (1)$$

$$\delta_{\mathrm{p}}^F - \delta_{\mathrm{m}}^F = -29.7\,\sigma_{\mathrm{c}}^0 \qquad (2)$$

where δ_{p}^{F} and δ_{m}^{F} are measured relative to the fluorobenzene signal.

Compounds II and III were obtained by us according to the following general scheme:

$$\mathrm{H_2N{-}C_6H_4{-}F} \longrightarrow \mathrm{HOCH_2CH_2NH{-}C_6H_4{-}F} \xrightarrow{\mathrm{HBr}} \mathrm{BrCH_2CH_2NH{-}C_6H_4{-}F \cdot HBr} \xrightarrow{\text{NaOH/spirits}} \text{ethylenimi}$$

$$\text{IVa (p), b (m)} \qquad \text{Va (p), b (m)} \qquad \text{II (p), III (m)}$$

Para- and meta-fluoroanilines were obtained from the corresponding nitroanilines (^{6}); the remaining operations were carried out by analogy with the synthesis of N-phenylethylenimine (^{7}). Compound IVa, yield 51.5%, b.p. 145-146°/2.5; IVb, yield 60.2%, b.p. 135-137°/3 mm; Va, yield 73.5%, m.p. 128-129°; Vb, yield

70.5%, m.p. 128.5-129°; II; yield 57.5%, b.p. 73-74°/15; n_D^{20} 1.5228; d_4^{20} 1.1140; MR_D found 37.59; calculated 37.18.

C_8H_8NF. Found: C 70.11; 70.18; H 5.80; 5.84; N 10.32; 10.29; F 14.02; 14.15. Calculated, %: C 70.07; H 5.88; N 10.23; F 13.87.

III, yield 59.5%; b.p. 78.5°/15; n_D^{20} 1.5273; d_4^{20} 1.1141; MR_D found 37.8; calculated 37.18.

Found, %: C 69.85; 69.91; H 5.93; 5.98; N 10.15; 10.08; F 13.70; 13.81.

The structures of II and III were confirmed by NMR spectra on the H^1 and F^{19} nuclei (Fig. 1).

Fig. 1. NMR spectra at 20.529 MHz. *a*—II; *b*—III

The spectra were obtained on a spectrometer with a resolution of $5 \cdot 10^{-8}$ (8). The chemical shifts for protons and fluorine nuclei were measured relative to the signal of an internal standard (hexamethyldisiloxane and benzotrifluoride, respectively) and expressed in units

$$\delta = \frac{\Delta f}{20{,}529},$$

where Δf is the distance between the investigated and standard signals (in Hz). To eliminate the influence of the medium, the F^{19} spectra were measured at different concentrations of II and III in n-heptane, with extrapolation to infinite dilution. In Fig. 2 the reduced molar fraction is plotted along the abscissa:

$$M\% = \frac{W_{xM}y}{W_{xM}y + W'M_x}, \quad \text{where } W' =$$

$$= \frac{W_{xM}\mathrm{e}}{W_{xM}\mathrm{e} + W_{\mathrm{e}} M_x};$$

W_x, W_{e} are the weighed portions of the sample and the standard; M_x, M_{e}, and M_y are the molecular weights of the investigated substance, the standard, and the solvent (see also Table 1).

The σ-constants of compounds II and III were calculated from equations (1) and (2) (Table 2).

Thus, in the series of inductive effects the group $\triangleright$N— occupies a position characteristic of amino groups, while in its ability for conjugation it is weaker than the latter (which agrees with the dependence of $\varepsilon_{\max}$ of the UV spectra (7)) and is close to halogens (4).

Table 1

Chemical shifts of F^{19} of fluorophenylethylenimines (ppm), extrapolated to infinite dilution in n-heptane

Compound	δ_K^F $C_6H_5CF_3$	δ_K^F C_6H_5F
Fluorobenzene	45.62	(0.00)
II	54.14	8.52
III	45.72	0.10

In terms of the quantum-mechanical model of three-membered rings (9), the weakening of conjugation can be explained as follows. According to (9), with optimal hybridization the endo orbitals have an increased p-character ($sp^{4,12}$), owing to which the angle between them is somewhat reduced, leading to greater overlap of the endo orbitals as compared with sp^3-hybridization. Thus, if in the case of $(CH_3)_2N$— and H_2N— substituents the nitrogen practically does not hinder conjugation and the weight of the form

$$\substack{R\\R}{>}\overset{\oplus}{\mathrm{N}} = \langle\rangle \ominus \ (A),$$

in which nitrogen is in sp^2-hybridization, is sufficiently high (as evidenced by the σ_c^0-constants and $\varepsilon_{\max}$ in the UV spectra—Table 2), then in the case of $\triangleright$N —the weight of the analogous form

Table 2

σ-Constants of the ethylenimine, dimethylamino, and amino groups, and the UV spectra of the corresponding benzene derivatives

Group	σ_u by pK_a (4)	σ_u by NMR (5)	σ_c^0 by pK_a (4)	σ_c^0 by NMR (5)	UV spectra in isooctane (s), $\lambda_{\max}$, mμ	UV spectra in isooctane (s), $\varepsilon_{\max}$
$\triangleright N-$	–	+0.066	–	0.290	235277.5	119001160
$(CH_3)_2N-$	+0.10	+0.098	−0.54	−0.530	250297.5	155002250
H_2N-	+0.10	+0.115	−.486	−0.486	288	1900

$\triangleright\overset{+}{N} = \between\ominus$ (B) must be smaller, since with increasing *s*-character of the endo-orbitals their overlap decreases. At the same time the strain of the ring increases and, consequently, the energy of form B is higher than A. Indeed, in the UV spectra the $\lambda_{\max}$ of N-phenylethylenimine are shifted into the short-wavelength region (the principal band by 15 mμ) in comparison with NN-dimethylaniline (Table 2) and

$$\begin{matrix} CH_2 \\ (CH_2)_{n-2} \end{matrix} > N - \between$$

$$n = 4 - 6 \tag{7}$$

which corresponds to an increase in the energy of the electronic transition by approximately 7 kcal/mole.

Thus, a decrease in σ_c^0 corresponds to a smaller weight of B in comparison with A. From the standpoint of the model of three-membered rings, which assumes the presence of three-center orbitals and sp^2 hybridization of the atoms in the ring (10), an increase in σ_c^0 would be expected. Moreover, this model is unable to explain the inversion of nitrogen in I (1).

Fig. 2. Dependence of the chemical shift of F^{19} in II, III, and fluorobenzene on concentration in *n*-heptane.

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Note: Figure translations are in progress. See original paper for figures.