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Abstract

Full Text

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Transmission of the Electronic Effects of Substituents in Aromatic Systems through an Azomethine Group

(Presented by Academician M. I. Kabachnik on 7 IV 1964)

In interpreting the reactivity and physical characteristics of aromatic Schiff bases and related compounds, it is necessary to know how, through the azomethine group, interaction is effected between a substituent and a reaction center located in different rings. The solution of this problem reduces to a quantitative assessment of the electron-conducting action of the groupings —Ph—CH=N—and —Ph —N=CH—and may also be of interest in connection with the general problem of elucidating the ability of various bridging groups to transmit the electronic effects of substituents to a reaction center.

A convenient approach to solving this problem is to compare the effects of substituents R on the constants of acid ionization pK_a in reaction series of the type R—Ph—XH and R—Ph—M—XH, where M is a bridge and XH are acidic groups. In the present work, the pK_a values of Schiff bases of types I—VI were determined, and the dependence of the quantities obtained on the σ-parameters of the substituents was considered. The pK_a values found, as well as the reaction constants ρ, correlation coefficients r, and standard deviations s calculated by the least-squares method, are given in Table 1.

Fig. 1. Correlation of pK_a for compounds of types I—IV, VI with Hammett σ.

As is seen from Fig. 1, the pK_a values of compounds I—VI correlate excellently with the Hammett σ-constants, which indicates (^{1,2}) the presence of conjugation of the arylazomethine bridges with the substituent R and the reaction center and the transmission of polar influences. However, the conducting properties of the arylazomethine bridges are expressed relatively weakly. This is indicated by the small values of ρ, whose absolute magnitudes reflect (for constancy of the type and conditions of the reactions or equilibria being compared) the degree of transmission of the electronic effects of substituents to the reaction center (^{1,3}).

Quantitatively, the electron-conducting action of the bridging group (^{3}) is best characterized by the quantity $\pi' = \rho/\rho_0$, where ρ and ρ_0 are the reaction constants of the investigated and standard (in our case VII) series, determined under identical conditions. In this case, the quantities π', to a first approximation, do not depend on the type of reaction or equilibrium.

Table 1

Reaction series	R	m.p., °C	pK	ρ, r, s	Reaction series	R	m.p., °C	pK	ρ, r, s
I. *p*-R-C_6H_4-CH=N-C_6H_4-OH-*p*	$N(CH_3)_2$	270	10.60	$\rho =$ 0.297r = 0.998s = 0.010	V. *p*-R-C_6H_4-CH=N-$C_6H_2(OH)(NO_2)$	$N(CH_3)_2$	190	8.45	$\rho =$ 0.145r = 0.999s = 0.006
I. *p*-R-C_6H_4-CH=N-C_6H_4-OH-*p*	OCH_3	187	10.49	$\rho =$ 0.297r = 0.998s = 0.010	V. *p*-R-C_6H_4-CH=N-$C_6H_2(OH)(NO_2)$	H	194	8.37	$\rho =$ 0.145r = 0.999s = 0.006
I. *p*-R-C_6H_4-CH=N-C_6H_4-OH-*p*	H	184	10.42	$\rho =$ 0.297r = 0.998s = 0.010	V. *p*-R-C_6H_4-CH=N-$C_6H_2(OH)(NO_2)$	NO_2	235	8.26	$\rho =$ 0.145r = 0.999s = 0.006
I. *p*-R-C_6H_4-CH=N-C_6H_4-OH-*p*	I	210	10.33	$\rho =$ 0.297r = 0.998s = 0.010	VI. *p*-R-C_6H_4-N=CH-naphthyl-OH	$N(CH_3)_2$	170	11.13	$\rho =$ 0.482r = 0.999s = 0.019

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Reaction series	R	m.p., °C	pK	ρ, r, s	Reaction series	R	m.p., °C	pK	ρ, r, s
I. p-R-C_6H_4-CH=N-C_6H_4-OH-p	$N^+(CH_3)_3$	213	10.27	ρ = 0.297r = 0.998s = 0.010	VI. p-R-C_6H_4-N=CH-naphthyl-OH	OCH_3	110	10.96	ρ = 0.482r = 0.999s = 0.019
I. p-R-C_6H_4-CH=N-C_6H_4-OH-p	NO_2	168	10.18	ρ = 0.297r = 0.998s = 0.010	VI. p-R-C_6H_4-N=CH-naphthyl-OH	H	98	10.85	ρ = 0.482r = 0.999s = 0.019
II. p-R-C_6H_4-N=CH-C_6H_4-OH-p	OCH_3	206	9.84	ρ = 0.371r = 0.997s = 0.022	VI. p-R-C_6H_4-N=CH-naphthyl-OH	F	136	10.80	ρ = 0.482r = 0.999s = 0.019
II. p-R-C_6H_4-N=CH-C_6H_4-OH-p	CH_3	214	9.79	ρ = 0.371r = 0.997s = 0.022	VI. p-R-C_6H_4-N=CH-naphthyl-OH	Br	163	10.74	ρ = 0.482r = 0.999s = 0.019
II. p-R-C_6H_4-N=CH-C_6H_4-OH-p	H	191	9.73	ρ = 0.371r = 0.997s = 0.022	VI. p-R-C_6H_4-N=CH-naphthyl-OH	NO_2	224	10.46	ρ = 0.482r = 0.999s = 0.019

Reaction series	R	m.p., °C	pK	ρ, r, s	Reaction series	R	m.p., °C	pK	ρ, r, s
II. p-R-C_6H_4-N=CH-C_6H_4-OH-p	I	208	9.63	ρ = 0.371r = 0.997s = 0.022	Ia. p-R-C_6H_4-CH=$N^+(CH_3)$-C_6H_4-OH-p, TsO^-	OCH_3	260	8.82	ρ = 1.171r = 0.999s = 0.013
II. p-R-C_6H_4-N=CH-C_6H_4-OH-p	$COOCH_3$	197	9.50	ρ = 0.371r = 0.997s = 0.022	Ia. p-R-C_6H_4-CH=$N^+(CH_3)$-C_6H_4-OH-p, TsO^-	H	285	8.52	ρ = 1.171r = 0.999s = 0.013
III. p-R-C_6H_4-CH=N-C_6H_4-OH-o	$N(CH_3)_2$	119	11.02	ρ = 0.225r = 0.999s = 0.016	Ia. p-R-C_6H_4-CH=$N^+(CH_3)$-C_6H_4-OH-p, TsO^-	I	290	8.18	ρ = 1.171r = 0.999s = 0.013
III. p-R-C_6H_4-CH=N-C_6H_4-OH-o	CH_3	108	10.92	ρ = 0.225r = 0.999s = 0.016	Ia. p-R-C_6H_4-CH=$N^+(CH_3)$-C_6H_4-OH-p, TsO^-	NO_2	234	7.60	ρ = 1.171r = 0.999s = 0.013

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Reaction series	R	m.p., °C	pK	ρ, r, s	Reaction series	R	m.p., °C	pK	ρ, r, s
III. p-R-C_6H_4-CH=N-C_6H_4-OH-o	H	91	10.88	$\rho =$ 0.225r = 0.999s = 0.016	IIa. p-R-C_6H_4-$N^+(CH_3)$=CH-C_6H_4-OH-p, TsO^-	OCH_3	230	8.32	$\rho =$ 1.949r = 0.999s = 0.020
III. p-R-C_6H_4-CH=N-C_6H_4-OH-o	Br	126	10.83	$\rho =$ 0.225r = 0.999s = 0.016	IIa. p-R-C_6H_4-$N^+(CH_3)$=CH-C_6H_4-OH-p, TsO^-	H	247	7.82	$\rho =$ 1.949r = 0.999s = 0.020
III. p-R-C_6H_4-CH=N-C_6H_4-OH-o	NO_2	160	10.71	$\rho =$ 0.225r = 0.999s = 0.016	IIa. p-R-C_6H_4-$N^+(CH_3)$=CH-C_6H_4-OH-p, TsO^-	I	222	7.26	$\rho =$ 1.949r = 0.999s = 0.020
IV. p-R-C_6H_4-N=CH-C_6H_4-OH-o	CH_3	93	11.09	$\rho =$ 0.281r = 0.994s = 0.016	VII. p-R-C_6H_4-OH-p	m-CH_3	–	11.40	$\rho =$ 2.010r = 0.998s = 0.014

Reaction series	R	m.p., °C	pK	ρ, r, s	Reaction series	R	m.p., °C	pK	ρ, r, s
IV. *p*-R-C_6H_4-N=CH-C_6H_4-OH-*o*	H	52	11.03	ρ = 0.281r = 0.994s = 0.016	VII. *p*-R-C_6H_4-OH-*p*	H	–	11.25	ρ = 2.010r = 0.998s = 0.014
IV. *p*-R-C_6H_4-N=CH-C_6H_4-OH-*o*	Br	112	10.95	ρ = 0.281r = 0.994s = 0.016	VII. *p*-R-C_6H_4-OH-*p*	CHO	116	9.00	ρ = 2.010r = 0.998s = 0.014
IV. *p*-R-C_6H_4-N=CH-C_6H_4-OH-*o*	NO_2	159	10.82	ρ = 0.281r = 0.994s = 0.016	VII. *p*-R-C_6H_4-OH-*p*	*m*-CHO	108	10.55	ρ = 2.010r = 0.998s = 0.014
					VII. *p*-R-C_6H_4-OH-*p*	NO_2	114	8.70	ρ = 2.010r = 0.998s = 0.014

In Table 2, values of π' are given for various bridging groups that include the azomethine bond, calculated from reaction series I, II, Ia, IIa, and VII, and also calculated using the σ-constants of arylazomethine groups from series VII. For comparison, π' and σ are given for several structurally analogous groups. The small values of π' for arylazomethine bridges agree with the notions (^{4,5}) of the nonplanar structure of molecules of aromatic Schiff bases: as a result of competition between the n- and π-electrons of nitrogen for conjugation with the π-electrons of the aniline ring, the latter is rotated relative to the plane of the aldehyde ring by an angle $\theta \simeq 60^\circ$ (A).

Fig. 2. Correlation of pK_a of compounds of types Ia, IIa with Hammett σ.

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Obviously, the molecule can be made coplanar if the nitrogen n-orbital is removed from conjugation with the aromatic ring. This can be achieved by quaternization of the azomethine nitrogen in compounds of types Ia and IIa, whose π-skeleton is analogous to I, II. For these compounds, pK_a values correlate excellently with σ-values (Fig. 2), and realization of the planar configuration B leads to a sharp increase in the factor π' (Table 2). Thus, the principal reason for the inhibition of substituent-effect transmission by arylazomethine groups is the noncoplanarity of the system.

However, for planar systems with trans-arylazo and arylethylene bridges, the values of π' are also small. It may therefore be assumed that the trans isomers of azobenzenes and stilbenes participate in reactions in the form of their nonplanar conformations.

[Structural schemes A, B, and C are shown.]

The values of ρ and π' presented in Tables 1 and 2 show that the M-grouping —N=CH—-phenylene-in the molecule R-phenylene-M—OH connects the reaction center with the substituent better than —CH=N—-phenylene-, just as —$\overset{+}{\mathrm{N}}$=CH—-phenylene-is better than —CH=$\overset{+}{\mathrm{N}}$—-phenylene-. This is readily understood if one takes into account that the influence of the M-group on pK_a is determined by the effective charge of atom t, by which it is connected with OH (^{3}). It is clear that the direction of polarization of the azomethine bond provides a larger positive charge on the t-M atom precisely in the first cases C.

Reaction series III-VI characterize the influence of intramolecular H-bonding on pK_a. In compounds of this type, the location of the reaction center in the o-position is not associated with additional steric hindrance, since there are no substituents at nitrogen other than the trans-aryl group. If it is assumed that conjugation of the reaction center in the o-position is equivalent to n-conjugation —this follows from the approximate equality of the σ_n and σ^0-constants (^{2,11})— then the decrease in the acidic properties of III in comparison with I, and of IV in comparison with II, may be attributed to the effect of the H-bond. In this case the difference in pK_a values corresponds to the contribution of the H-bond to the free energies of ionization:

$$\Delta G^{\mathrm{H}} - \Delta G = 2.3\,RT\,(pK_a^{\mathrm{H}} - pK_a)\,,$$

where the superscript H refers to compounds with an intramolecular H-bond.

As follows from the data in Table 1, the order of the ΔpK_a values is consistent with the concept of greater stabilization of H-bonds in six-membered rings IV as compared with five-membered rings III.

For compounds of types IV and VI, papers $^{(12,13)}$ assume the existence of a prototropic benzenoid-quinoid equilibrium, shifted in ethanol toward the neutral quinoid form. However, the pK_a values measured by us for compounds of this type depend strictly linearly on σ (Table 1, Fig. 1), which, in agreement with the data (14), indicates (15) the absence of the quinoid form in detectable amounts.

Experimental Part

Compounds of types I-VI were obtained by condensation of the corresponding aldehydes and amines in ethanol or by direct fusion and were purified by repeated recrystallization from ethanol or benzene. Salts Ia and IIa were synthesized according to the procedure (5).

pH measurements were carried out in 0.005 M solutions using an LP-58 pH meter with a glass electrode at a temperature of $25 \pm 0.2°$, with standardization against phosphate (pH 8) and borate (pH 9, 10, 11) buffers. The titration procedure is described in the handbook (16). The pK_a values (concentration values) were calculated by the Henderson equation from pH data at 4-5 neutralizations within the range 25-70%. The maximum deviations from the mean value in each series did not exceed 0.03-0.04 pK_a.

Table 2

M-group in R—⟨Ph⟩—M—XH (Y)	π'	σ_n of the MH group
$-CH=CH-$	0,508^6; 0,5^7	–
–⟨Ph⟩–	0,303^6; 0,25^7; 0,36*	0,009^1
$-N=N-$⟨Ph⟩–	0,16^9; 0,26*	0,64^1
$-CH=CH-$⟨Ph⟩–	0,24*	–0,050^{10}
$-N=CH-$⟨Ph⟩–	0,184	0,75**
$-CH=N-$⟨Ph⟩–	0,148	0,41
$-\overset{+}{N}(CH_3)=CH-$ ⟨Ph⟩–	0,968	1,71
$-CH=\overset{+}{N}(CH_3)-$ ⟨Ph⟩–	0,583	1,36

* Calculated from the values of ρ and $f^{25°}$ found in the acylation reactions of amines in benzene in the work of L. M. Litvinenko (8).
** The constants for this and the following substituents are, in meaning, σ^--constants.

The requirement of constant ionic strength was met by using, as solvent, a 0.2 M solution of $LiNO_3$ in 98% methanol. Thin-layer chromatography on alumina showed that in no case did decomposition of the compounds under study occur upon dissolution or in the course of titration.

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