ELECTRONIC EFFECTS IN CATIONS OF AZA-AROMATIC COMPOUNDS

I. HYDROXY DERIVATIVES OF QUINOLINIUM AND BENZO[h]QUINOLINIUM CATIONS

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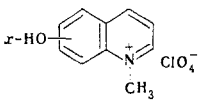
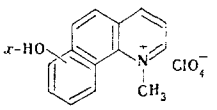
The ionization constants of quaternary salts of hydroxy derivatives of quinolinium and benzo[h]quinolinium ions correlate satisfactorily (r = 0.99, s = 0.07) with the σ_j constants calculated by a modified F,M method. Correlation analysis makes it possible to assume that the electron distribution in the benzene fragments of the investigated cations is determined by the electrostatic effect of the quaternized nitrogen atom and direct polar conjugation of the hydroxyl group with it.

Until now, systematic investigations of the electronic interactions in molecules of aza-aromatic compounds [1] have not touched upon two-ring and three-ring cations. The present research was undertaken to evaluate the electronic effects in the benzene fragments of hydroxy derivatives of quinolinium and benzo[h]quinolinium cations. The subjects of the investigation were quaternary salts I-IX, of which V-IX were synthesized for the first time. As possible azo components, V-IX are of interest for the preparation of water-soluble azo dyes.



I-IV



V-IX

The ionization constants in aqueous solutions and the IR spectra of KBr pellets were measured in order to obtain the experimental characteristics of the relative electron distribution in the cations of salts I-IX. In analyzing the results (Table 1), one should take into account the fact that the pK_a values and the frequencies of the stretching vibrations of the hydroxyl group of salts I, IV-VI and IX are determined not only by electronic factors but also by steric factors. The IR spectral data in this case also depend on the intermolecular interactions in the solid phase.

The ionization constants of salts I-VIII were subjected to correlation treatment. It initially seemed possible to use the F,M method for the correlation analysis [2, 3]. However, it was found that the σ_{ij} constants of the ring nitrogen atom calculated by the Dewar–Grisdale scheme did not follow the trend of the ionization constants. Satisfactory correlation was obtained by modification of the F, M method: by evaluation of the field effect, as recommended by Wells and Adcock for substituted naphthalenecarboxylic acids [4], with allowance for the orientation of the substituent relative to the bond of the reaction center – the adjacent carbon atom.

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TABLE 1. Ionization Constants, ν_{OH}, and Electronic Effects in I-IX

Compound	x	ν_{OH}, cm^{-1}	$pK_a^{25°}\pm0,06$	σ_{1j}	σ_{j1}	σ_j	$\left[\frac{\sigma_{j1}}{\sigma_j}\right]$, %
I	5	3310	6,40	0,89	−0,21	1,10	19,4
II	6	3263	7,40	0,79	0,0	0,79	0,0
III	7	3300	5,95	0,89	−0,30	1,19	25,2
IV	8	3060– sh	7,14	0,83	0,0	0,83	0,0
V	6	3310	7,03	0,79	0,0	0,79	0,0
VI	7	3330, 3290	7,97	0,59	0,0	0,59	0,0
VII	8	3315	7,54	0,59	−0,13	0,72	18,1
VIII	9	3395	8,05	0,59	0,0	0,59	0,0
IX*	10	3180– sh 3160					

*We were unable to obtain the pK_a value of salt IX with the necessary accuracy in view of the inconstancy of the optical density of solutions of IX at pH > 7.5 in the region of the analytical wavelength (460 nm).

TABLE 2. Synthesized Compounds

Compound	Quaternization time, min	Yield during quaternization, %	mp, °C	Empirical formula*
I	—	—	175—177	$C_{10}H_{10}ClNO_5$
II	—	—	176—178	$C_{10}H_{10}ClNO_5$
III	—	—	206—207	$C_{10}H_{10}ClNO_5$
IV	—	—	155—156	$C_{10}H_{10}ClNO_5$
V	180	75	204—205 (dec.)	$C_{14}H_{12}ClNO_5$
VI	60	90	228—230 (dec.)	$C_{14}H_{12}ClNO_5$
VII	10	85	247—250 (dec.)	$C_{14}H_{12}ClNO_5$
VIII	30	96	201—202 (dec.)	$C_{14}H_{12}ClNO_5$
IX	120	50	235 (dec.)	$C_{14}H_{12}ClNO_5$
X	—	60†	205	$C_{13}H_9NO$
XI	—	65†	270	$C_{13}H_9NO$

*The compositions of I-IX were confirmed by determination of the Cl content, whereas the compositions of X and XI were confirmed by the determination of the C, H and N content.
†The yields of hydroxy derivatives during alkaline fusions are indicated.

The proposed method reduces to the following.

1) In the general case, the σ_{ij} constants are calculated from Eq. (1)

$$\sigma_{ij}=F\frac{\cos\theta}{R^2}-M\pi_{ij}. \quad (1)$$

where F and M are parameters that characterize the field and conjugation effects, respectively [2]; π_{ij} is the atom–atom polarizability in the hydrocarbon analog of the unsubstituted heterocyclic cation [5]; R is the length of the segment connecting the $\overset{\oplus}{N}_1$ or C_i atoms with the middle of the C_{ij}–O bond; and θ is the acute angle between the line connecting the $\overset{\oplus}{N}_1(C_i)$ atoms with the middle of the C_j–O bond and this bond.*

2) The relative electron density in the j-th position is characterized by the magnitude of the σ_j constant, which is found from the difference between the σ_{1j} constant of the quaternized nitrogen atom and the σ_{j1} constant of the hydroxyl group: $\sigma_j=\sigma_{1j}-\sigma_{j1}$.

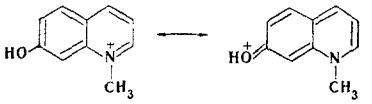
3) The σ_{ij} constant is calculated without allowance for the conjugation effect from the equation

$$\sigma_{1j}=9.85\frac{\cos\theta}{R^2},$$

where 9.85 is the value of the F parameter of the quaternized nitrogen atom. It is found from Eq. (1) with the aid of the σ_β and σ_γ constants of the nitrogen atom in the pyridinium cation [6].

*The lengths of the C–C, N–C, and C–O bonds are denoted by l and were assumed to be 1.40 Å [3]. All of the distances were measured in units of $3l$.

4) The electronic interaction of the hydroxyl group with the nitrogen atom is characterized by the σ_{j1} constant calculated from Eq. (1). The F_{OH} (– 0.45) and M_{OH} (8.49) parameters necessary for this were found from Eq. (1) by means of the electrophilic σ_m and σ_p constants of the hydroxyl group [7, 8]. The constant is determined principally by the $M_{OH}\pi_{j1}$ value in Eq. (1) and therefore characterizes the direct polar conjugation of the hydroxyl group with the quaternized nitrogen atom. Considering that direct polar conjugation is manifested practically only in those cations whose molecules can be depicted in the form of the corresponding resonance structures (for example, for the cation of salt III), the σ_{j1} constants were calculated only for the cations of salts I, III, and VII.



The results of the calculation are presented in Table 1. The pK_a value of salts I-VII correlate satisfactorily ($r = 0.99$, $s = 0.07$) with the corresponding σ_j constants.

The results obtained in this study make it possible to assume that the electron distribution in the benzene fragments of the cations under consideration is determined principally by the electrostatic effect of the quaternized nitrogen atom. In the cations of salts I, III, and VII, one should also take into account the considerable direct polar conjugation of the hydroxyl group with the ring nitrogen atom.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The pK_a values were determined spectrophotometrically in water with an SF-4 spectrophotometer and a pH-340 pH-meter at J 0.03 and 25 ± 0.1°.

Salts I-IV (Table 2) were obtained from aqueous solutions of the corresponding methiodides [9] by means of perchloric acid. Salts I-III were crystallized from alcohol, whereas salt IV was purified by reprecipitation from alcohol solution by the addition of ether. The synthesis of V-IX consisted in the preparation of benzo[h]quinolinesulfonic acids from α-aminonaphthalenesulfonic acids via the Skraup reaction [10] and subsequent alkaline fusion of the sulfonic acids and quaternization of the hydroxybenzo[h]quinolines isolated as a result of alkaline fusion [10]. The 6- and 7-hydroxybenzo[h]quinolines wree purified by chromatography of alcohol solutions of them with a column filled with Al_2O_3 and subsequent crystallization from alcohol. 8-Hydroxybenzo[h]quinoline (X) was crystallized from benzene. 9-Hydroxybenzo[h]quinoline (XI) was purified by chromatography, as in the case of the 6- and 7-hydroxyisomers, and was crystallized from chlorobenzene (Table 2). The 10-hydroxy isomer was extracted from the alkaline melt with hexane.

Quaternary Salts V-IX (Table 2). These compounds were obtained by heating a mixture of 9.75 g (0.05 mole) of the hydroxybenzo[h]quinoline and 55.8 g (0.3 mole) of methyl p-toluenesulfonate at 120-130°, after which the reaction mixture was treated with 15 ml of alcohol and 100 ml of ether, the liberated N-methylhydroxy[h]quinolinium toluenesulfonate was dissolved in water, and the perchlorate salts were precipitated by the addition of perchloric acid.

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