

## ELECTRONIC STRUCTURE AND PROPERTIES OF POLYNUCLEAR AROMATIC KETONES AND QUINONES. II.\*

### ELECTRONIC STRUCTURE AND BASICITY OF POLYNUCLEAR *p*-QUINONES

M. NEPRAŠ, V. KRATOCHVÍL, M. TITZ, A. NOVÁK and V. SLAVÍK

*Research Institute for Organic Syntheses, 532 18 Pardubice - Rybitví*

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Stages of protonation and  $pK_a$  values were determined spectrophotometrically for 1,4-naphthoquinone, 9,10-anthraquinone, 1,4-anthraquinone, 5,12-tetracenequinone, and 6,13-pentacenequinone. Experimental results were correlated with some HMO reactivity indices.

In connection with the study of quinonoid dye properties we examined the basicity of 1,4-naphthoquinone, 9,10-anthraquinone, 1,4-anthraquinone, 5,12-tetracenequinone, and 6,13-pentacenequinone. For 1,4-naphthoquinone and 5,12-tetracenequinone, the  $pK_B$  values  $-7.2$  and  $-8.4$  were reported by Handa<sup>1</sup>. With regard to basicity, 9,10-anthraquinone has been one of the compounds most studied and was a subject of our earlier paper<sup>2</sup>, where a detailed survey of the literature on its behaviour in sulfuric acid is given and the published data on its basicity critically reviewed. The basicity of the other two compounds has not yet been studied.

In this paper we present results of the spectroscopic determination of the stages of protonation,  $pK_a$  values of *p*-quinones studied, and correlations of experimental data with HMO reactivity indices.

#### EXPERIMENTAL

*Compounds used.* Purity of all compounds was tested chromatographically. 1,4-Naphthoquinone was purified by crystallization from cyclohexane; m.p. 125.5–126.5°C (lit.<sup>3</sup> 125.5°C). 1,4-Anthraquinone was prepared by the oxidation of 1,4-diaminoanthracene, which was obtained by reduction of the azo dye resulting from the coupling reaction of benzenediazonium chloride with 1-aminoanthracene. The product obtained was purified by crystallization from ethanol and chromatography on a silica gel column; m.p. 208.5–209.5°C (lit.<sup>4</sup> 208°C). The 9,10-anthraquinone used was the same as in ref.<sup>2</sup> 5,12-Tetracenequinone was prepared by the Friedel-Crafts reaction of benzene with 2,3-naphthalenedicarboxylic anhydride in the presence of aluminum chloride, followed by cyclization in sulfuric acid at 70°C<sup>5</sup>. The product was sublimed and crystallized from tetrahydrofuran, m.p. 294–295°C (lit.<sup>5</sup> 294°C). 6,13-Pentacenequinone was prepared by the condensation of 1,4-cyclohexane-dione (0.005 mol) with *o*-phthalaldehyde (0.01 mol) in ethanol at 50°C in the presence of 5% KOH<sup>6</sup>. The product was sublimed and crystallized from nitrobenzene, m.p. 394°C (lit.<sup>6</sup> 393°C).

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*Reagents.* Concentrated sulfuric acid (Lachema, Brno) was reagent grade. Fuming sulfuric acid (approximately 10%) was prepared from redistilled sulfur trioxide and 99% H<sub>2</sub>SO<sub>4</sub> (Lachema, Brno) in a glass apparatus.

*Apparatus.* A recording spectrophotometer Unicam SP 700 and single-beam spectrophotometer Hilger Uvispek with a photomultiplier housing were used. Quartz cells were of 10 mm optical path length. pK<sub>a</sub> was determined by the procedure described in ref.<sup>2</sup>. Sulfuric acid concentration was determined acidometrically using the composite Tashiro indicator. H<sub>0</sub> values of the sulfuric and fuming sulfuric acid solutions were taken from the paper of Vinnik<sup>7</sup>.

## RESULTS AND DISCUSSION

With 1,4-naphthoquinone and 9,10-anthraquinone, protonation of the first oxygen atom so reduces the basicity of the second one that it does not protonate<sup>8</sup> even in fuming sulfuric acid. By examination of electronic absorption spectra in cyclohexane, ethanol, and sulfuric acid of various concentrations, we found that with 1,4-anthraquinone, 5,12-tetracenequinone, and 6,13-pentacenequinone twofold protonation occurs. The solutions in inert solvents turn from yellow to red in the first stage of protonation and blue to blue-green in concentrated sulfuric acid in the second stage. Theoretical study, interpretation of electronic spectra, and determination of sites of protonation in the two successive stages are discussed in the next paper

TABLE I  
pK<sub>a</sub> Values of Polynuclear *p*-Quinones

Compound	Stage of protonation	H <sub>0</sub> <sup>a</sup>	λ, nm	m <sup>b</sup>	pK <sub>a</sub>
1,4-Naphthoquinone	1	— 8.92	281	0.72	
		— 8.90	422	0.90	—8.01
9,10-Anthraquinone	1	— 8.67	313	0.98	—8.50
		— 8.69	413	0.96	—8.34
1,4-Anthraquinone	1	— 7.63	571	1.01	—7.71
	2	—10.31	680	0.89	—9.18
5,12-Tetracenequinone	1	— 7.52	516	1.09	—8.20
	2	— 9.94	326	0.69	
		—10.19	606	0.85	—8.66
6,13-Pentacenequinone	1 <sup>c</sup>	— 7.03	535	1.69	
	2 <sup>c</sup>	— 8.90	630	1.04	—9.26
	2	— 8.75	352	0.99	—8.66
		— 8.77	629	1.01	—8.86

<sup>a</sup> Half protonation; <sup>b</sup> Calculated by the least squares fit; <sup>c</sup> Values obtained by the analysis of the three-component mixture.

of this series. Table I presents the results; the  $m$  factor, which is a slope in the linear dependence  $\log(C_{\text{BH}^+}/C_{\text{B}})$  vs  $H_0$ , serves as a criterion of  $H_0$  function validity for the base studied and reflects the medium effect of the solvent used. This is particularly significant with very weak bases in sulfuric acid of high concentration.

Accurate thermodynamic  $pK_a$  values can be determined provided, first, that values calculated from the equation

$$pK_{\text{BH}^+} = H_0 + \log(E - E_{\text{B}})/(E_{\text{BH}^+} - E),$$

where  $E$  is extinction of the solution measured,  $E_{\text{B}}$  and  $E_{\text{BH}^+}$  are extinctions of the base and its protonated form, are independent of medium acidity and, second, that the dependence  $\log(C_{\text{BH}^+}/C_{\text{B}})$  vs  $H_0$  is linear with unit slope. The first condition was fulfilled in all cases except for the first stage protonation of 6,13-pentacenequinone and second stage protonations of 5,12-tetracenequinone at 326 nm and 1,4-naphthoquinone at 281 nm. A linear dependence of  $\log(C_{\text{BH}^+}/C_{\text{B}})$  vs  $H_0$  was found in all cases. The  $pK_a$  value for 9,10-anthraquinone is taken from our earlier paper<sup>2</sup>. The  $pK_a$  value determined by us for 1,4-naphthoquinone is lower than that published by Handa<sup>1</sup> ( $pK_a - 7.2$ ). For 5,12-tetracenequinone Handa reports only one value ( $pK_a - 8.4$ ) but without any wavelength specification. Therefore it is difficult to judge the stage of protonation to which this value should be assigned.

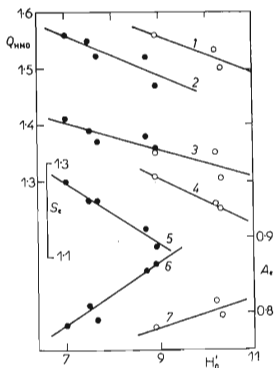


FIG. 1

Dependence of the  $H'_0$  Values for the First ( $\circ$ ) and Second ( $\bullet$ ) Stages of Protonation on  $Q_{\text{HMO}}$  (curves 1 and 2) and  $Q_{\text{SCF}}$  (curve 3) Electron Densities, Electron Superdelocalizabilities  $S_e$  (curves 4 and 5), and Electron Localization Energies  $A_e$  (curves 6 and 7)

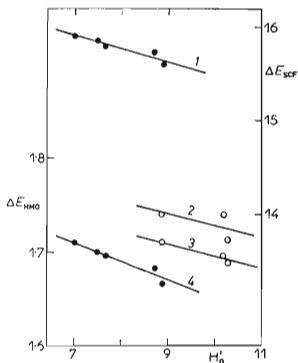


FIG. 2

Dependence of the  $H'_0$  Values for the First ( $\circ$ ) and Second ( $\bullet$ ) Stages of Protonation on  $\Delta E_{\text{SCF}}$  (curves 1 and 2) and  $\Delta E_{\text{HMO}}$  (curves 3 and 4)

In determining molar extinction coefficients of individual quinone forms it was found possible to measure at least 95% of the respective form at a given wavelength in solutions of a given  $H_0$ . 6,13-Pentacenequinone was the sole exception because of the very slight difference in basicity between its first and the second stages of protonation. Therefore its  $H'_0$  values were calculated by analyzing the three-component mixture composed of the unprotonated, singly and doubly protonated forms. A special problem which we met was the determination of the extinction coefficient for the singly protonated form. An accurate value was obtained by extrapolating the dependence of the extinction at 535 nm of the mixture containing the unprotonated and singly protonated forms to the concentration of the doubly protonated form. The latter was determined from the extinction at 630 nm where neither the unprotonated form nor the singly protonated form absorb. Table I also presents  $H'_0$  values for the second stage of protonation obtained in the usual way at two different wavelengths.

In HMO calculations we used the parameters  $h_O = 1$ ,  $k_{CO} = 1$  for unprotonated quinones, and  $h_{OH^+} = 2$ ,  $k_{C-OH^+} = 1$  for singly and doubly protonated quinones,  $h_X$  and  $k_X$  being characteristic constants in expressions for Coulomb and resonance integrals:

$$\alpha_X = \alpha_C + h_X \beta_{C-C}; \quad \beta_{C-X} = k_{C-X} \beta_{C-C}.$$

It may be noticed that for the protonated oxygen, we use parameters typical of the hydroxy group, assuming the same number of  $\pi$  electrons for singly and doubly protonated molecules as in the respective unprotonated quinones (*i.e.* quinone and its protonated forms are assumed to be isoelectronic). In a theoretical approach to the proton affinity of oxygen in the first stage protonation, we used the HMO reactivity indices for oxygen in the neutral quinone and the differences in the total  $\pi$  electron energy ( $\Delta E_{HMO}$  or  $\Delta E_{SCF}$ ) for the neutral and singly protonated quinones. With the second stage protonation we used analogous HMO indices for the unprotonated oxygen in the singly protonated quinone and differences between total  $\pi$  electron energies for singly and doubly protonated quinones.

Since differing  $m$  factors make it difficult to compare  $pK_a$  values, for the correlations with the HMO reactivity indices we selected the half-protonation  $H'_0$  values. The plots in Figs 1 and 2 show that the observed  $H'_0$  values are well correlated with quantum chemical data in all cases, although only three experimental points were available with doubly protonated quinones. The plot for the HMO data shows a split into two dependencies, one for singly protonated quinones and the other for doubly protonated quinones. On introducing the effective electronic repulsion (the usual Pople version<sup>9</sup> of the SCF-MO-LCAO approximation) this split disappears in the case with electron densities (Fig. 1, curve 3) but becomes very clean-cut in the case with  $\Delta E$  values (Fig. 2). The closest linear dependence was obtained for the electron superdelocalizabilities (Fig. 2, curves 4 and 5). A good correlation with  $\pi$  electron

localization energies is understandable because in our model localization of the  $\pi$  electron pair on oxygen occurs with protonation. The proton is bonded to the negatively charged centre and  $\pi$  electronic structure with the hydroxy group, with the positive charge delocalized along the quinone skeleton is formed.

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