

BASICITY OF 1,4-TETRACENEQUINONE AND ITS ELECTRONIC SPECTRA IN THE PROTONATED STATES*

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Basicity of 1,4-tetracenequinone to the first and the second protonation degrees has been studied spectrophotometrically. Electronic spectra of mono- and diprotonated 1,4-tetracenequinone have been interpreted on the basis of the PPP method in the approximation of invariable β^c and γ integrals.

In the context of investigation of properties and behaviour of quinoid dyestuffs we studied¹ basicity of 1,4-naphthoquinone, 1,4-antraquinone, 9,10-antraquinone, 5,12-tetracenequinone, and 6,13-pentacenequinone. The cited paper gives results of spectrophotometric determination of the first protonation degree, the pK_a values of the *p*-quinones studied, and correlation of the experimental data with the HMO reactivity indices. Another communication² dealt with theoretical study and interpretation of electronic spectra of these *p*-quinones at the individual protonation degrees in connection with determination of the corresponding protonation positions. Interpretation of electronic spectrum of neutral form of 1,4-tetracenequinone by means of the polarisation spectra is dealt with in the previous communication³.

Basicity of 1,4-tetracenequinone has not yet been published, and, similarly, electronic spectra of its protonated states have not been interpreted. The present paper gives results of spectrophotometric determination of the protonation degree and basicity and interpretation of spectra of mono- and diprotonated 1,4-tetracenequinone.

EXPERIMENTAL

The absorption spectra were measured with a recording spectrophotometer Perkin-Elmer 555. The pK_a determination was carried out in the way described in ref.⁴. Accurate concentration of

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sulphuric acid in solutions of the studied 1,4-tetracenequinone was determined acidimetrically using the Tashiro indicator mixture. The H_0 values of the solutions of sulphuric acid were taken from ref.⁵.

THEORETICAL

The theoretical spectral characteristics (Tables I and II) were obtained by the PPP method (semiempirical version of the LCI SCF MO LCAO method) in the approximation of invariable β^{core} and γ integrals and invariable interatomic distances. The input data of the molecules studied presumed their plane arrangement with ideal geometry of regular hexagons, all the C—C bond lengths being 0.14 nm. The exocyclic C=O bond length was taken equal to 0.12 nm in accordance with experimental data⁶⁻¹⁰; the C—OH bond length was equal to 0.14 nm. Table III gives the used values of ionisation potentials (I.P.) and electron affinities (E.A.) of the conjugated atoms in their valence states and surroundings, the number of electrons (Q) contributed to the conjugation by the individual centres as well as the value of the bond parameter $b_{\mu\nu}$ used in the calculation of the core resonance integral $\beta_{\mu\nu}^{\text{core}}$ according to the relation:

$$\beta_{\mu\nu}^{\text{core}} = b_{\mu\nu} \beta_{\text{CC}}^{\text{core}(0)}.$$

TABLE I

Theoretical spectral characteristics of the singlet transitions $S_0 \rightarrow S_n$ ($\pi\pi^*$) for the monoprotonated 1,4-tetracenequinone molecule

n	$\Delta^1 E_n (S_0 \rightarrow S_n)$		$\log f$	$\varphi (\mathbf{M}, \gamma)$	Main configurations
	eV	μm^{-1}			
1	1.776	1.433	-0.31	168°	1,1'(92.9)
2	2.617	2.111	-0.91	171°	2,1'(60.7); 1,2'(18.0)
3	3.158	2.548	-0.43	25°	1,2'(77.1); 2,1'(10.0)
4	3.256	2.627	-1.12	134°	3,1'(92.5)
5	3.888	3.137	-0.61	61°	4,1'(48.0); 2,1'(18.5); 1,3'(13.1)
6	4.024	3.246	-0.67	162°	2,2'(47.8); 1,4'(27.7); 4,1'(11.2)
7	4.246	3.426	-0.66	94°	5,1'(40.0); 4,1'(19.5); 3,2'(16.6); 1,4'(10.9)
8	4.476	3.611	-0.88	138°	5,1'(32.5); 3,2'(29.9); 1,3'(18.6)
9	4.767	3.846	0.16	11°	1,3'(42.2); 2,2'(25.6); 1,4'(18.3)
10	4.808	3.879	-0.25	146°	3,2'(45.1); 1,4'(29.7)

The monocentric repulsion electronic integrals $\gamma_{\mu\mu}$ were obtained by the Pariser approximation¹¹; the bicentric repulsion electronic integrals $\gamma_{\mu\nu}$ ($\mu \neq \nu$) were calculated by the approximation by Mataga and Nishimoto¹².

The configuration interaction involves the monoexcited configurations corresponding to the electronic transitions between the five highest occupied and the five lowest unoccupied SCF MO's.

TABLE II

Theoretical spectral characteristics of the singlet transitions $S_0 \rightarrow S_n$ ($\pi\pi^*$) for the diprotonated 1,4-tetracenequinone molecule

n	sym.	$\Delta^1 E_n (S_0 \rightarrow S_n)$		$\log f$	$\chi (\mathbf{M}, \mathbf{y})$	Main conformations
		(eV)	(μm^{-1})			
1	A_1	1.845	1.489	0.08		1,1'(93.3)
2	B_1	2.021	1.631	-2.24	⊥	2,1'(77.6)
3	B_1	2.660	2.146	-1.98	⊥	1,2'(89.2)
4	A_1	3.052	2.463	-1.46		3,1'(95.5)
5	B_1	3.386	2.732	-0.74	⊥	4,1'(77.6); 2,1'(11.5)
6	A_1	4.018	3.241	0.24		2,2'(75.0); 1,4'(11.9)
7	B_1	4.140	3.340	-1.17	⊥	3,2'(48.7); 1,3'(30.0); 5,1'(17.4)
8	B_1	4.181	3.373	-0.89	⊥	5,1'(68.3); 3,2'(12.3)
9	A_1	4.560	3.679	-0.05		1,4'(67.8); 2,2'(10.1)
10	B_1	4.902	3.955	-0.28	⊥	1,3'(55.4); 3,2'(36.0)

TABLE III

The parameters used for the calculations by the PPP method

Atomic core	I.P., eV	E.A., eV	Q	$b_{\mu\nu}$
C^+	11.42	0.58	1	1.0 (C—C)
O^+ (C=O)	17.70	2.47	1	1.1 (C=O)
O^{2+} (C—OH)	32.90	10.0	2	1.0 (C—OH)

Fig. 1 gives electronic absorption spectra of 1,4-tetracenequinone (*a*), its mono-protonated (*b*) and diprotonated forms (*c*); the theoretical electronic spectra given in the same figure were obtained by the PPP method in the approximation of invariable β^{core} and γ , which makes them consistent with the spectra of other protonated linear *p*-quinones studied by us².

RESULTS AND DISCUSSION

Absorption electronic spectra of 1,4-tetracenequinone in cyclohexane, methanol and sulphuric acid of various concentrations revealed that the substance is protonated to the second degree. Table IV gives results of spectrophotometric measurements of the protonation. The dependence of $\log ((A - A_B)/(A_{BH^+} - A))$ or $\log ((A - A_{BH^+})/(A_{BH_2^{2+}} - A))$ vs the H_0 acidity function was investigated at the given wavelengths (A means absorbance of the solution investigated, A_B is absorbance of the non-protonated form, A_{BH^+} is absorbance of the monoprotinated form, and $A_{BH_2^{2+}}$ is absorbance of the diprotonated form). The found dependence was treated by the linear regression method of the least squares, *i.e.* the parameters m and a_0 were

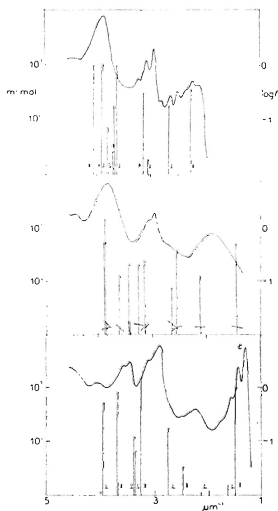


FIG. 1

Electronic absorption spectrum of 1,4-tetracenequinone: (*a*) neutral form in cyclohexane; (*b*) mono-protonated form in 67.5% H_2SO_4 ; (*c*) diprotonated form in 90.0% H_2SO_4 ; the vertical line segments denote the theoretical transitions (those without flat serif denote the transition with $\log f < -2$); direction of polarisation of the transitions relates to the long axis of the molecule.

found of the dependence:

$$\log((A - A_B)/(A_{BH^+} - A)) = -m \cdot H_0 + a_0.$$

Similar procedure was carried out for the diprotonated form. If solvent has negligible effect on shape of spectra of the individual forms of the compounds, then the slope of the dependence is $m \approx 1$, and

$$(A - A_B)/(A_{BH^+} - A) = C_{BH^+}/C_B, \quad (A - A_{BH^+})/(A_{BH_2^{2+}} - A) = C_{BH_2^{2+}}/C_{BH^+}$$

hence also $a_0 = pK_a$. In our case the said condition is fulfilled for protonation to the second degree measured at 723 nm. Table IV gives, for all the measurements, the H'_0 values, i.e. the acidity function value at which it is

$$(A - A_B)/(A_{BH^+} - A) = 1, \quad (A - A_{BH^+})/(A_{BH_2^{2+}} - A) = 1.$$

Fig. 1 gives absorption spectrum of 1,4-tetracenequinone in its non-, mono-, and diprotonated forms. Calculation of theoretical spectrum of mono- and diprotonated 1,4-tetracenequinone started from the findings obtained from interpretation of spectra of other linear *p*-quinones in their protonated states². It was shown² that the optimum agreement of theoretical spectrum and experimental curve can be obtained, if the monoprotinated linear *p*-quinone is modelled by the corresponding system with one hydroxyl group and one delocalized positive charge (*b*), the diprotonated linear *p*-quinone having two hydroxyl groups and two delocalized positive charges (*c*). As hydroxyl group contributes two electrons to the conjugation (Table III), the mono- and diprotonated linear quinones are obviously π -isoelectronic with respect to the nonprotonated quinone. From Fig. 1 there again follows a good

TABLE IV
Basicity of 1,4-tetracenequinone

Protonation degree	H'_0 ^a	λ , nm	<i>m</i>	pK_a
1st	-4.61	347	2.65	
	-4.45	530	1.98	
2nd	-7.12	723	1.01	-7.12
	-7.40	804	1.15	

^a Half protonation.

agreement between the theoretical and the experimental spectra. For the mono-protonated system (b) theory of the said model predicts two transitions of mutually parallel polarization in the region of the broad long-wave absorption band, the first transition being distinctly shifted bathochromically. Their assignment cannot be carried out without the polarisation spectrum. The absorption spectrum of the diprotonated system (c) is represented by the theoretical spectrum quite well.

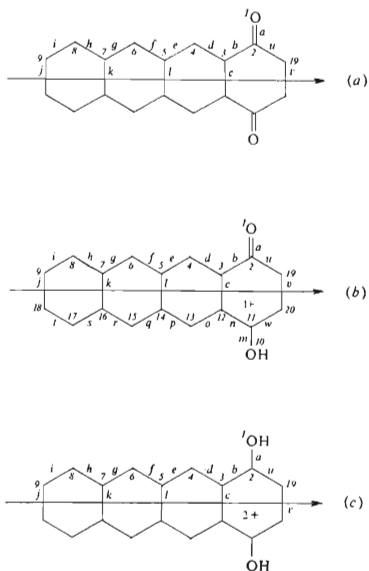


Fig. 2 represents graphically the π -electronic charges q_{μ}^{LCl} for the non-, mono- and diprotonated 1,4-tetracenequinones in their ground electronic states. The exocyclic C=O bond introduces into the neutral system in the ground electronic state an alternation of π -electronic charge which rapidly decreases with increasing distance, so that charge density at the most distant centres from this bond is practically equal to one, *i.e.* to the charge density of an alternating aromatic hydrocarbon. A much more distinct charge alternation in the whole skeleton can be observed in the mono- and diprotonated systems due obviously to one and two delocalized positive charges, respectively.

In ref.¹³ we applied configuration analysis to investigation of character of electronic excited states of linear *p*-quinones; the 1,4-quinones were fragmented to enedione and aromatic hydrocarbon. Fig. 3 shows that alternation of bond orders in the anthracene fragment of 1,4-tetracenequinone (neutral form) has, according to expectation, the same character as that of the anthracene itself. Monoprotonation (connected, according to our model, with transformation of one carbonyl group into C—OH bond) does not fundamentally change nature of alternation of the bond orders in the anthracene fragment except for the bonds *o* to *t* (i.e. the bonds of the perimeter part adjacent to OH group) where the bond alternation is less distinct than in the perimeter part adjacent to the C=O group. In the diprotonated system the bond

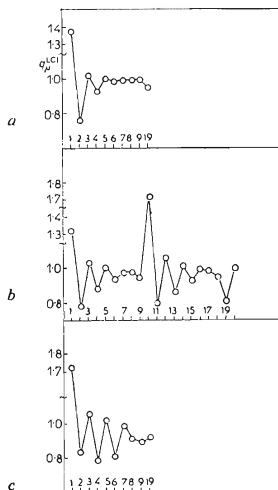


FIG. 2

π -Electronic densities q_{μ}^{LCI} for the non-protonated (a), monoprotonated (b) and diprotonated (c) 1,4-tetracenequinones

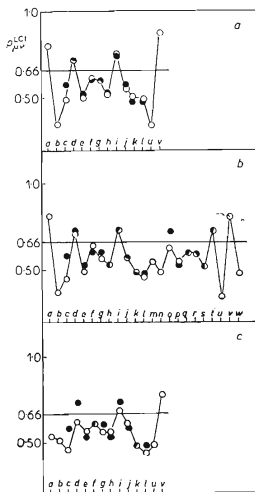


FIG. 3

π -Electronic bond orders $p_{\mu\nu}^{LCI}$ for the non-protonated (a), monoprotonated (b), and diprotonated (c) 1,4-tetracenequinones; the daggers denote the corresponding bond orders in anthracene

alternation in the whole perimeter of the hydrocarbon fragment has the same character as that in anthracene, being less distinct only. The *k* and *l* bonds retain a distinct single bond character regardless of the protonation degree, the *c* bond has a greater single bond character as compared with anthracene. The carbonyl group has, of course, double bond character, the same being true of the C=C bond *v*, regardless of the protonation degree. The decreased alternation of bond orders in anthracene fragment of the protonated systems is probably a consequence of delocalization of positive charge.

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