ABSORPTION, LUMINESCENCE, AND POLARISATION SPECTRA OF 1,4-TETRACENEQUINONE*

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Absorption electronic spectrum of 1,4-tetracenequinone has been interpreted on the basis of excitation polarisation spectrum of fluorescence and dichroism on oriented polyvinyl alcohol sheet. The theoretical spectrum has been obtained by the PPP method in the approximation of variable integrals β^c and γ.

In the fourth communication of this series[1] results were given of a study of absorption electronic spectra of six linear *p*-quinones along with the theoretical electronic spectrum obtained by two approximations of the PPP method. A mere visual comparison of electronic spectra of 9,10- and 1,4-anthraquinones can show different electronic structure of these isoelectronic molecules. The study[2] of the protonated states of linear *p*-quinones could differentiate between the *p*-quinone molecules having one or several benzene nuclei adjacent to the quinoid ring (protonation to the first and to the second degree, respectively). The study[3] of phosphorescence of linear *p*-quinone molecules showed a significant difference in distribution of the lowest singlet and triplet excited states of 9,10- and 1,4-anthraquinones. These pieces of knowledge allowed a classification of the linear *p*-quinone molecules (anelation type $Q[m, n]$) by the individual annelation series. Influence of the anelation with benzene ring on electronic absorption spectrum was studied in ref.[4] with the result of distinct differentiation between the anelation series $Q[O, n]$(1,4-quinones) and $Q[m, n]$ (the other quinones). The study[5] of theoretical electronic spectra of linear *p*-quinones (inclusive of 1,4-tetracenequinone) by the method of configuration analysis allowed a more detailed analysis of the electronic spectra with respect to character of the individual excited states, which allowed a deeper understanding of the anelation effect on spectra of 1,4-quinones.

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Since *p*-benzoquinone (being rather a diketone than a quinone) has a special position among *p*-quinones, and the second member of the anelation series of 1,4-quinones, *i.e.* 1,4-naphthoquinone, has no isomeric partner with inner quinoid ring, the first member of this anelation series, in fact, is 1,4-anthraquinone. This fact shows the importance of the molecule of 1,4-tetracenequinone (1,4-naphthacenequinone). Although preparation of this substance has already been described, its absorption and luminescence spectra have not been published yet.

EXPERIMENTAL

1,4-Tetracenequinone was prepared by reduction of 1,4-dihydroxytetracenequinone with sodium borohydride[6]. The starting 1,4-dihydroxytetracene-5,12-quinone was prepared by acylation of 1,4-benzenediol with 2,3-naphthalenedicarboxylic acid anhydride[7]. Experimental conditions are not given in refs[6,7], so the preparation was carried out as follows: 1·58 g sodium borohydride was added to a stirred suspension of 1·9 g 1,4-dihydroxytetracene-5,12-quinone in 190 ml methanol at room temperature during 7 h. After 20 h standing, the red solution was filtered and diluted with a solution of 20 ml acetic acid in 20 ml water. The product was precipitated by pouring of the mixture in 1·7 l water. The orange crystals formed were collected by suction, washed with water, and purified by crystallization from xylene. Yield 1·4 g (84·5%). The obtained product was purified by repeated sublimation in vacuum. After purification it melted at 280—281°C (ref.[6] gives m.p. 281—282°C). The melting point was determined in sealed capillary using a Kofler block.

The used solvents were purified by standard procedures to spectral purity. The measurements of absorption spectra at room temperature and the measurements of dichroism on the oriented sheets were carried out with a Perkin–Elmer 555 spectrophotometer, those of absorption spectra at 88 K were carried out with a Perkin–Elmer 356 spectrophotometer. The measurements of fluorescence and the excitation polarisation spectrum of fluorescence at 77 K were carried out with a Hitachi Perkin–Elmer MPF-2A spectrophotometer. All the spectrophotometers were equipped with a device for data collecting on a punched tape; the experimental data were processed with a computer. The normalized reduced absorption curves[8] A'_z and A'_y were calculated from the experimental dichroitic curves $A_{\parallel}$ and $A_{\perp}$. The A'_y and A'_z spectra are due to transitions with the moments oriented along the y and z axes, respectively.

THEORETICAL

The theoretical spectral characteristics were obtained by the PPP method (a semiempirical version of LCI SCF MO LCAO method) in the approximation of quasi-real geometry, *i.e.* in the approximation of variable integrals β^c and γ as well as interatomic distances of the conjugated atoms. The input data on molecular geometry were derived from ideal geometry with regular hexagons and 0·14 nm bond lengths between all atoms in conjugation. The $r_{\mu\nu}$ bond lengths between two adjacent atoms in conjugation were calculated in each iteration by means of π-electron bond orders ($p_{\mu\nu}$) using the Julg's formula[9]

$$r_{\mu\nu} = (1{\cdot}517 - 0{\cdot}18p_{\mu\nu})\,(6{\cdot}5/(\vartheta_\mu + \vartheta_\nu))^{1/2}\,, \qquad (1)$$

where ϑ_μ and ϑ_ν mean the Slater exponents of $2p_z$ AO's at the atoms μ and ν, respectively. From the $r_{\mu\nu}$ values thus obtained we calculated, in each iteration, new values of bicentric core integrals $\beta^c_{\mu\nu}$ according to the formula:

$$\beta^c_{\mu\nu} = b\beta^c_{\mu\nu} \exp\left(-1\cdot862 r_{\mu\nu} + 2\cdot597\right). \qquad (2)$$

The parameter b is considered to be adjustable and was obtained, for the C=O bonds of 1,4-tetracenequinone molecule, from a parameter study (Table I). The monocentric repulsion integrals $\gamma_{\mu\mu}$ were obtained by the Pariser approximation[10]:

$$\gamma_{\mu\mu} = I_\mu - A_\mu\,, \qquad (3)$$

where I_μ and A_μ mean the ionisation potential and electron affinity, respectively, of the atom μ in its given valence state and surroundings. The bicentric repulsion electronic integrals $\gamma_{\mu\nu}$ $(\mu \neq \nu)$ were calculated by the Mataga and Nishimoto approximation[11]. The used parameters are given in Table I.

Simultaneously, we also obtained the spectral characteristics by the PPP method in the approximation of invariable β^c and γ integrals, *i.e.* invariable interatomic distances (this method is consistent with that used for calculation of theoretical electronic spectrum of the protonated *p*-quinones[2]). For this method, the molecular skeleton again was given in its ideal geometry with regular hexagons and all C—C bonds of 0·14 nm length except for the C=O bond length for which the experimental value 0·12 nm was used. The parameters of atoms were the same as those in the approximation of quasi-real geometry (Table I), the value $b = 1\cdot1$ being used for the parameter of C=O bond.

TABLE I

The parameters used for calculation of 1,4-tetracenequinone by the PPP method in the approximation of quasi-real geometry

Atomic core	Z_π	I_μ, eV	A_μ, eV	ϑ_μ	b
C^+	1	11·42	0·58	3·25	1·0 (C—C)
O^+	1	17·70	2·47	3·95	0·65 (C=O)[a]

[a] The value obtained from a parameter study for 1,4-tetracenequinone; the value of this parameter is adjusted for the optimum agreement with position of the first three bands in the absorption spectrum: $\beta^0_{\mu\nu} = -2\cdot318$ eV.

The configuration interaction involved the mono-excited configurations corresponding to electronic transitions between the five highest occupied and the five lowest unoccupied SCF MO's.

RESULTS AND DISCUSSION

If electronic absorption spectrum of 1,4-tetracenequinone is compared with that of the isoelectronic 5,12-tetracenequinone[1], then the fine structure of the former is surprising, as it resembles that of 1,4-anthraquinone[1] in its containing three distinct absorption bands (at 2·0, 3·0, and 3·8 μm^{-1}) due to $\pi\pi^*$ transitions. In contrast to spectrum of 1,4-anthraquinone, the $n-\pi^*$ transition does not make itself felt (not even by a shoulder in the long-wave section of the first absorption band). The first absorption band in the region 2·0 μm^{-1} shows no vibration structure in alcoholic mixtures even at temperatures of liquid nitrogen. The vibration structure of the first band appears, together with hypsochromic shift of the whole spectrum, in the measurements in cyclohexane. From the courses of the curves APF, D and especially A'_y and A'_z (Fig. 1) it follows that the vibration structure in the region 2·3–2·7 μm^{-1} belongs to a further absorption band which has opposite polarisation and smaller intensity than the first band. From the polarisation measurements on PVA sheet

TABLE II

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

n	sym.	$\Delta^1 E_n$ ($S_0 \rightarrow S_n$) (eV)	$\Delta^1 E_n$ ($S_0 \rightarrow S_n$) (μm^{-1})	log f	$\sphericalangle(\mathbf{M}, \mathbf{y})$	Main configurations[a]
1	A_1	2·816	2·272	−0·46	‖	1,1′ (93·8)
2	B_1	3·360	2·711	−1·56	⊥	1,2′ (48·3); 3,1′ (21,6); 2,1′(20·6)
3	B_1	3·654	2·948	−0·88	⊥	1,2′ (48·6); 3,1′ (22·6); 2,1′ (14·2); 5,1′ (13·6)
4	A_1	3·910	3·155	−0·28	‖	2,2′ (53·1); 1,4′ (23·0); 3,2′ (14·9)
5	B_1	4·167	3·362	0·00	⊥	2,1′ (60·1); 3,1′ (35·2)
6	A_1	4·333	3·496	−1·46	‖	4,1′ (99·6)
7	A_1	4·618	3·725	−0·33	‖	2,2′ (37·6); 1,4′ (29·9); 3,2′ (22·1)
8	B_1	4·675	3·772	−0·75	⊥	1,3′ (92·9)
9	B_1	4·725	3·812	−2·95	⊥	4,2′ (98·2)
10	A_1	4·976	4·015	0·14	‖	3,2′ (54·6); 1,4′ (36·6)
11	B_1	5·254	4·239	−1·42	⊥	5,1′ (73·0); 3,1′ (16·7)
12	A_1	5·623	4·536	−0·83	‖	2,3′ (45·6); 5,2′ (28·0); 3,3′ (15·2)

[a] The y axis is perpendicular to the connecting line of C═O bonds, *i.e.* it is a two-fold symmetry axis of the molecule studied.

it follows that the first absorption band has parallel polarisation with the $C_2(y)$ axis of the molecule (which is also identical with effective axis of orientation). Another distinct absorption band with fairly regular vibration structure appears at 3·0 μm^{-1} and represents a superposition of two absorption bands with opposite polarisation, which follows from the course of the reduced A'_y and A'_z curves. In the minimum of the absorption curve in the region of 3·4 μm^{-1}, the reduced A'_y curve shows a local maximum indicating a little intensive absorption band having parallel polarisation to y axis. In the region 3·8 – 4·2 μm^{-1} there appears the most intensive absorption band; absence of symmetry of the reduced A'_y curve (as well as of D curve) in this region indicates that this band is formed by overlap of two bands of the same polarisation, but the increase of the A'_z curve in this region suggests that the superposition of the absorption bands also involves one or several bands polarized perpendicularly to y axis. From Fig. 1 it follows that the theoretical electronic spectrum represents the experimental absorption spectrum with sufficient accuracy; assignment of the individual $^1(\pi\pi^*)$ transitions to the absorption bands at the reduced A'_y and A'_z curves is shown by arrows (Fig. 1).

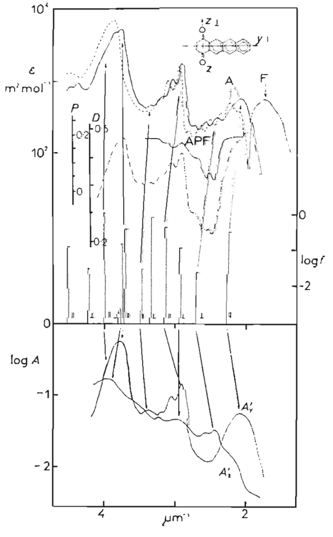
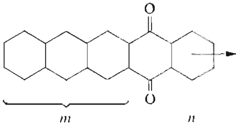


FIG. 1

Electronic spectrum of 1,4-tetracenequinone: (——— A) absorption spectrum in ethanol at 88 K; (– – – – – A) absorption spectrum in cyclohexane at room temperature; (——— F) fluorescence spectrum (the arrow denotes the wave number of fluorescence at which the APF spectrum was measured) and (——— APF) excitation polarisation spectrum of fluorescence in ethanol at 77 K: (–·–·–·) curve of dichroism D (λ) on oriented polyvinyl alcohol sheet; P degree of polarisation of fluorescence, D degree of dichroism: A'_y and A'_z are normalized reduced absorption curves

The theoretical electronic spectrum obtained by the approximation of non-variable geometry differs only little from that obtained by the approximation of quasi-real geometry which is given in Fig. 1 and corresponds better to the absorption spectrum interpreted by means of APF and D spectra and by means of the reduced curves.

1,4-Tetracenequinone exhibits only a weak fluorescence, which means that the $S_{n\pi^*}$ and $T_{n\pi^*}$ states lie above the first $S_{\pi\pi^*}$ state and do not affect luminescence properties of the molecule which is analogous to aromatic polynuclear hydrocarbons as far as the order of the first two excited states is concerned. The same is also true of 6,15-hexacenequinone and 7,16-heptacenequinone, which exhibit fluorescence, too[12]. From the point of view of the anelation type, these three quinones belong to the $Q[m, n]$ type, where $m = 3$, $n = 0, 1, 2, 3$ (spectrum of $Q[3, 1]$ has not been described yet) (Scheme A).



SCHEME A

Thus is can be stated that, if there are at least three benzene nuclei anelled at one side of quinone ring, then the $T_{n\pi^*}$ state has higher energy than the first $S_{\pi\pi^*}$ state, and such quinones can be expected to exhibit fluorescence from the $S_{\pi\pi^*}$ state and possibly also phosphorescence from the $T_{\pi\pi^*}$ state (in the *p*-quinones of the type $Q[m, n]$ for $m = 2$, $n = 0, 1, 2$, the two $n\pi^*$ states are between the $T_{\pi\pi^*}$ and $S_{\pi\pi^*}$ states, and these compounds exhibit phosphorescence form the $T_{\pi\pi^*}$ state[3]).

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