

ABSORPTION AND POLARISATION ELECTRONIC SPECTRA OF BENZO- AND DIBENZOANTHRAQUINONES-9,10*

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Spectral characteristics of 1,2-benzoanthraquinone-9,10, 1,2:6,7-, 1,2:5,6-, 1,2:7,8-, and 1,2:3,4-dibenzoanthraquinones-9,10 have been obtained by LCI SCF MO (PPP) method in approximation of ideal geometry. The theoretical data have been compared with the absorption electronic spectra measured at room temperature and at 93 K. For the first three molecules the electronic spectra have been interpreted on the basis of the measured polarisation of phosphorescence (APP); for the remaining two molecules the APP curve could not be measured, although a very slight phosphorescence has been observed with 1,2:7,8-dibenzoanthraquinone-9,10.

In Part IV of this series we dealt with interpretation of absorption electronic spectra of linearly fused polynuclear *p*-quinones; the theoretical data were obtained by LCI SCF MO (PPP) method in the approximation of variable β^{core} and γ integrals or with constant values of these quantities. It was found that except for *p*-benzoquinone the approximation with constant values of β^{core} and γ integrals gives very good results especially with respect to transition energies, whereas the theoretical transitions from the approximation with variable β^{core} and γ using the same parameters are shifted hypsochromically compared to experimental values. These facts were discussed in connection with the extent of alternation of bond lengths of individual linear *p*-quinone molecules.

In the present paper we deal with absorption electronic spectra of angularly fused benzo and dibenzo derivatives of 9,10-anthraquinone. The calculations have been carried out by the LCI SCF MO (PPP) method in approximation with constant values of β^{core} and γ integrals. Identification of the absorption bands has been carried out with the use of polarisation spectra of phosphorescence (APP).

THEORETICAL

With respect to the undesirable shift of the theoretical spectrum (especially that of the first $\pi\pi^*$ transition) obtained by the PPP method in approximation of quasi-real geometry for molecules of linear *p*-quinones¹ and molecules of the phenalenone type², in the present work we have used the classical version of the PPP method³⁻⁵ for

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obtaining spectral characteristics. For all the studied molecules of benzo- and dibenzoanthraquinone-9,10 we presumed regular ideal geometry of all six-membered rings with all angles 120° and all C—C bond lengths 1.40 \AA ; in accord with the experimental data⁶ the C=O bond length was taken 1.20 \AA . For calculation of two-centre core integrals we used the simple relation

$$b_{\mu\nu}^{\text{core}} = b\beta_{\mu\nu}^0, \quad (1)$$

where $\beta_{\mu\nu}^0 = -2.318 \text{ eV}$, and the value b for C—C bond was taken in accord with the given bond length 1.0 . For the b value of C=O bond we used the value 1.1 which proved to be good in the ideal geometry approximation of linear p -quinone molecules¹. Monocentric repulsion integrals $\gamma_{\mu\mu}$ were computed according to the Pariser approximation⁷

$$\gamma_{\mu\mu} = I_\mu - A_\mu, \quad (2)$$

where I_μ and A_μ are the ionisation potential resp. electron affinity of the atom μ in the respective valence state (in eV). Two-centre repulsion integrals $\gamma_{\mu\nu} (\mu \neq \nu)$ were computed in the approximation of Nishimoto and Mataga^{8,9}. The mono-excited configurations involved in the calculation by the method of limited configuration interaction were formed between five highest occupied and five lowest virtual SCF molecular orbitals. The following parameters were used in our calculations: for C^+ core $I = 11.42 \text{ eV}$, $A = 0.58 \text{ eV}$; for O^+ core $I = 17.70 \text{ eV}$, $A = 2.47 \text{ eV}$; for C—C and C=O bonds the constant b values in Eq. (1) were 1.0 and 1.1 , respectively; all the core charges were unity, and $\beta_{\mu\nu}^0 = -2.318 \text{ eV}$.

EXPERIMENTAL

The quinones studied were prepared and purified according to literature. 1,2-Benzoanthraquinone-9,10 (ref.¹⁰) (m.p. 169°C); 1,2 : 5,6-dibenzoanthraquinone-9,10 was prepared by oxidation of commercial 1,2 : 5,6-dibenzoanthracene with chromium trioxide in acetic acid and was purified chromatographically (m.p. 245°C); 1,2 : 6,7-dibenzoanthraquinone-9,10 (ref.¹¹) (m.p. 232°C); 1,2 : 7,8-dibenzoanthraquinone-9,10 (ref.¹²) (m.p. 247°C); 1,2 : 3,4-dibenzoanthraquinone-9,10 (ref.¹³) (m.p. 182°C). The melting points were measured with a Koffler apparatus and are all by 1 to 3°C higher than those given in literature. Purity of all the compounds was checked by thin-layer chromatography (Al_2O_3 and silufol; acetone-cyclohexane of various ratios as eluent) and by excitation phosphorescence spectra. The solvents used were purified by standard methods. 3-Methylpentane (Phillips Petroleum Co., U.S.A.) was used without purification. The absorption spectra were measured with the Unicam SP 700 spectrophotometer; the apparatus used for measurements of the absorption spectra at the temperature 93 K was described in Part IV of this series¹. The APP spectra were measured at 77 K with a Hitachi Perkin-Elmer MPF 2 A spectrophotometer with punched tape data output. Due to low phosphorescence intensity the accuracy of measurements had to be increased by repeated measuring of the starting curves, the polarisation degree being computed from their sum. The emission monochromator was

adjusted at the maximum of the uncorrected phosphorescence curve. The phosphorescence spectra were corrected with respect to spectral dependence of sensitivity of the emission part of the spectrophotometer.

RESULTS AND DISCUSSION

From the measured APP spectra the number of transitions in the molecule can be inferred as well as relative directions of polarisation of the absorption bands (the latter but only approximatively, because the quinones for which it was possible to measure the APP curves have the symmetry C_s or C_{2h} , so that the directions of polarisation of the absorption bands can form whatever angles with one another). 1,2 : 7,8-Dibenzoanthraquinone-9,10 (C_{2v}) exhibits much too slight phosphorescence to obtain APP spectrum, and with 1,2 : 3,4-dibenzoanthraquinone-9,10 (C_{2v}) no luminiscence was observed at all.

From the APP spectrum it follows that 1,2-benzoanthraquinone-9,10 (Fig. 1) has four considerably overlapped bands in the absorption spectral region 2.3 to 3.3 μm^{-1} , which correspond to four electronic transitions in the molecule. The first and the second band have mutually relatively considerably different degree of polarisation. They correspond to the maxima at 2.50 and 2.73 μm^{-1} in the absorption curve (spectrum at 90 K). From the decrease of the APP curve it can be deduced that the maximum at 2.95 μm^{-1} belongs to a further electronic transition. A slight barrier in the APP curve at 3.14 μm^{-1} indicates a further electronic transition which, however,

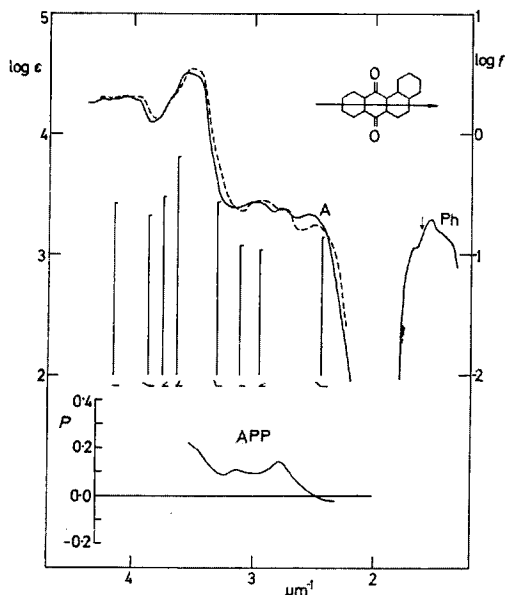


FIG. 1

1,2-Benzoanthraquinone-9,10

A Absorption spectrum at room temperature in cyclohexane; dotted line — absorption spectrum at 93 K in the mixture methanol-ethanol 1 : 4; Ph phosphorescence; full line — PPP calculations; the arrow denotes the wave number at which the APP spectrum was taken.

cannot be seen in the absorption curve — the maximum of the APP curve corresponds to the minimum on the absorption curve. The minimum of the APP curve at $3.25 \mu\text{m}^{-1}$ corresponds obviously to a further electronic transition visible in the absorption spectrum in the form of a deformation of the long-wave descending branch of the intensive absorption band at $3.5 \mu\text{m}^{-1}$. In the region of this band the APP curve has a markedly ascending character; polarisation degree of this band differs considerably from that of the first one. Due to very low intensity of the phosphorescence it was impossible to measure the APP curve towards the region of shorter wavelengths, and, therefore, it is not possible to carry out interpretation of further absorption bands. It can be stated that the theoretical prediction of spectral characteristics of the first five transitions agrees satisfactorily with the above analysis; the first band is predicted very well, the other four discussed transitions show slight hypsochromic shifts with respect to experiment. The band which, on the basis of the APP curve, can be expected at $3.14 \mu\text{m}^{-1}$, *i.e.* at the minimum of the absorption curve, is obviously not expressed in the π electron approximation.

The maxima at 2.53 and $2.96 \mu\text{m}^{-1}$ in the absorption spectrum of 1,2:5,6-dibenzoanthraquinone-9,10 (Fig. 2) correspond to two electronic transitions; from the marked difference in the polarisation degree of the both bands it can be deduced that the corresponding electronic transitions will be polarized at about right angle. The increasing tendency of the APP curve in the region $2.4 \mu\text{m}^{-1}$ indicates a little intensive band which can be seen as a shoulder at the long-wave branch of the

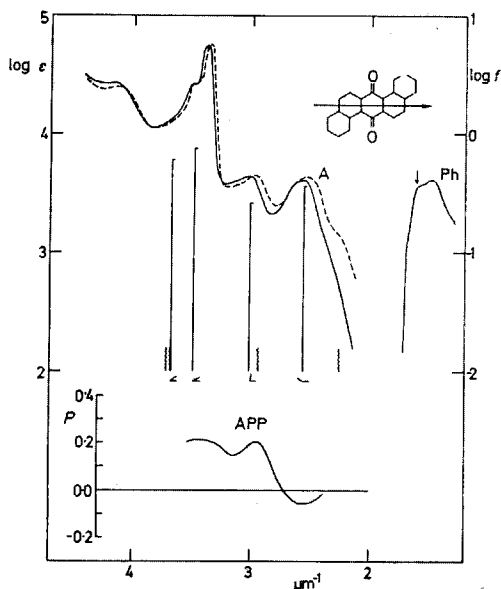


FIG. 2
1,2:5,6-Dibenzoanthraquinone-9,10
See Fig. 1; wavy line — the forbidden transitions.

absorption curve especially in measurements with ethanol at low temperatures. From the bathochromic shift of this band (when passing to a more polar solvent) it can be deduced that the transition is not of $n\pi^*$ type. The minimum of the APP curve at $3.15 \mu\text{m}^{-1}$ indicates a weak band visible as a deformation of the short-wave branch of the second intensive absorption band. In the region 3.30 to $3.60 \mu\text{m}^{-1}$ there are two marked very intensive bands; the polarisation degree has a high positive value in this region. The agreement between theory and experiment is very good with this molecule. Perhaps it is to be noted that from the character of the APP curve and from the shape of the absorption band it can be deduced that the second highly probable transition is the third overall transition, and the second forbidden transition is overall the fourth transition. Theory predicts the opposite sequence of the both transitions (rather close to each other). In the region 3.3 to $3.8 \mu\text{m}^{-1}$ theory predicts two forbidden transitions and two highly probable transitions of practically parallel polarisation. With respect to their identical predicted polarisation no marked changes in the course of the APP curve can be expected; hence it cannot be decided whether there is an intensive band with vibration structure or two overlapped bands belonging to two different electronic transitions with practically the same polarisation.

The APP curve of 1,2 : 6,7-dibenzoanthraquinone-9,10 (Fig. 3) is not so clear-cut as with the above molecules. In spite of that it is possible to deduce four transitions of this molecule from the course of APP curve and from the shape of the absorption curve. In the region 2.2 to $2.8 \mu\text{m}^{-1}$ there are two electronic transitions for which

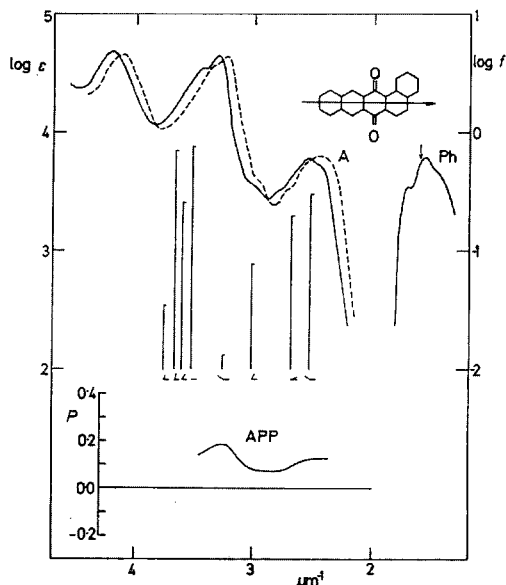


FIG. 3
1,2 : 6,7-Dibenzoanthraquinone-9,10
See Fig. 1.

theory predicts practically perpendicular polarisation. Obviously, the third transition is manifested by a shoulder at $3.0 \mu\text{m}^{-1}$ of the absorption curve. Maximum of the APP curve agrees accurately with the maximum of the intensive band at $3.25 \mu\text{m}^{-1}$ in the absorption spectrum. According to the theory the very probable transition at $3.52 \mu\text{m}^{-1}$ corresponds to this band. Little probable theoretical transition at $3.25 \mu\text{m}^{-1}$ cannot be ascribed to any band in the absorption spectrum. From the descending character of the APP curve in its short-wave part it can be deduced that there is a further transition in the region 3.6 to $3.8 \mu\text{m}^{-1}$; the corresponding band is strongly overlapped by an intensive one with the maximum at $3.25 \mu\text{m}^{-1}$. In the region 3.6 to $3.8 \mu\text{m}^{-1}$ theory predicts one less probable and two very probable transitions, all of them with mutual practically parallel polarisation. It is impossible to give any more detailed statement about this region of the absorption spectrum.

In the case of 1,2 : 7,8-dibenzoanthraquinone-9,10 (Fig. 4) and 1,2 : 3,4-dibenzoanthraquinone-9,10 (Fig. 5), where the APP curves are lacking, it is only possible to state a satisfactory agreement between theory and experiment on the basis of position and height of abscissas expressing the energy and probability of the theoretical transitions.

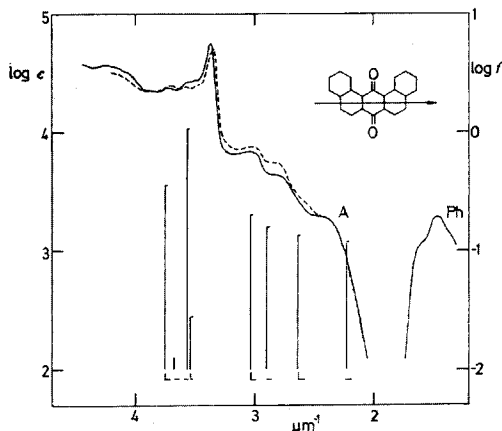


FIG. 4

1,2 : 7,8-Dibenzoanthraquinone-9,10

See Fig. 1; the little intensive theoretical transition at $3.7 \mu\text{m}^{-1}$ cannot be pictured with the used drawing scale.

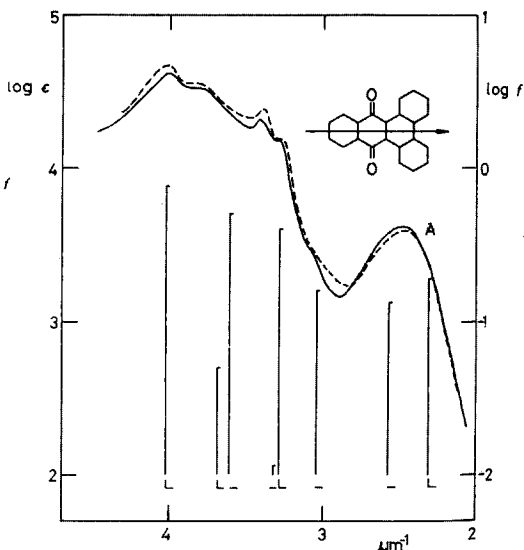


FIG. 5

1,2 : 3,4-Dibenzoanthraquinone-9,10

See Fig. 1.

Four of the five studied quinones show a slight luminiscence with the lifetime of the order 10^{-1} s (*i.e.* phosphorescence). All the phosphorescence spectra show little marked vibrational structure and are similar in shape and position. From the experimental results yet obtained it cannot be decided with certainty whether the matter is phosphorescence from the triplet state of the type $n\pi^*$ or $\pi\pi^*$.

It can be concluded that the used theoretical method with the given set of parameters can express the experimental spectra of the studied systems quite well. It is worth mentioning the comparison of spectra of 1,2 : 5,6- and 1,2-7,8-dibenzoanthraquinones-9,10. The change of symmetry from C_{2h} to C_{2v} results in that the first two theoretical symmetrically forbidden transitions become allowed, their energy being practically unchanged. This theoretical prediction was experimentally confirmed.

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