

ABSORPTION AND POLARIZATION SPECTRA OF POLYNUCLEAR *p*-QUINONES*

A. NOVÁK, M. TITZ and M. NEPRAŠ

Research Institute for Organic Syntheses,
532 18 Pardubice - Rybitví

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This paper presents the results of the study of electronic spectra of six polynuclear *p*-quinones. The calculations undertaken were of the PPP type using the fixed β^{core} and γ or variable β^{core} and γ approximations. Except for 1,4-benzoquinone, the absorption frequency-dependent polarization of the phosphorescence (APP) has also been measured, in order to arrive at a more sound assignment of bands.

In the first paper of this series we reviewed the theoretical papers dealing with polynuclear quinones and reported the results of our own LCI SCF MO (PPP) study. It was shown that one cannot arrive at a satisfactory interpretation of spectra within an inhomogeneous series of *para*-, *ortho*-, and *peri*-condensed quinones by making use of a single parameter set. In the present paper we have attempted to achieve this for a homogeneous series of six polynuclear *p*-quinones. In the calculations we used both the fixed β^{core} and γ and variable β^{core} and γ approximations because of considerable bond-length alternations in some of the systems studied. In the former theoretical approach an idealized geometry is assumed, whereas the latter should account for a "quasi-real" geometry. For the sake of a more sound assignment of bands, we also measured the APP spectra of all compounds studied with the exception of 1,4-benzoquinone.

THEORETICAL

The calculations of spectral characteristics, π -electron bond orders and π -electron densities were based on the standard PPP version of the LCI SCF MO method. We used either the approximation of an idealized geometry by assuming fixed β^{core} and γ or the approximation of a quasi-real geometry by allowing for variations in β^{core} and γ . Idealized geometries were used throughout the calculations of all six polynuclear *p*-quinones derived from polyacenes. All C—C bond distances are 1.40 Å,

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valence angles 120° , and C—O bond distances 1.20 \AA in agreement with the experimental value¹. This geometry was also used as a starting point in calculations that account for the bond length alternation, in particular in the quinonoid ring. In contrast to Part I of this series² we made use of another formula for evaluating the two-center core integrals

$$\beta_{\mu\nu}^c = b\beta_{\mu\nu}^o \exp(-1.862 r_{\mu\nu} + 2.597). \quad (1)$$

The bond length, $r_{\mu\nu}$, between two neighbouring atoms is reevaluated in each iteration by means of the Julg formula³

$$r_{\mu\nu} = (1.517 - 0.18 p_{\mu\nu}) \sqrt{\frac{6.5}{\vartheta_\mu + \vartheta_\nu}}, \quad (2)$$

where $p_{\mu\nu}$ is the π -electron bond order and ϑ_μ and ϑ_ν are the Slater exponents of $2p$ atomic orbitals on atoms μ and ν . The flexibility of the computer program permits to iterate only $\beta_{\mu\nu}$ integrals for those bonds falling into the range close to 1.40 \AA , *i.e.* only for C—C bonds. Hence, it was possible to use a single value of ϑ being equal to 3.25. On starting the calculation with the C—O bond length of 1.20 \AA , the $\beta_{\text{CO}}^{\text{core}}$ is not iterated through Eq. (1) and therefore has the same value in both types of calculations. One-center repulsion integrals, $\gamma_{\mu\mu}$, were calculated by the Pariser approximation⁴

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

where I_μ and A_μ are ionization potential and electron affinity for the atom μ in its valence state. Two-center repulsion integrals, $\gamma_{\mu\nu} (\mu \neq \nu)$, were calculated by the Mataga-Nishimoto approximation⁵.

The following parameters were used: for the C^+ core $I_\mu = 11.42 \text{ eV}$; $A_\mu = 0.58 \text{ eV}$; for the $\text{C}=\text{C}$ bond the b constant in Eq. (1) is 1.0; for the O^+ core $I_\mu = 17.70 \text{ eV}$; $A_\mu = 2.47 \text{ eV}$; for the $\text{C}=\text{O}$ bond the b constant in Eq. (1) is 1.1 (ref.²); all core charges are 1 and $\beta_{\mu\nu}^o = -2.318 \text{ eV}$.

EXPERIMENTAL

Preparation and purification of 1,4-naphthoquinone, 1,4-anthraquinone, 9,10-anthraquinone, 5,12-tetracenequinone, and 6,10-pentacenequinone were described in Part II of this series⁶. Cyclohexane, methanol, and ethanol were purified as usual⁷. 3-Methylpentane (pure grade, Phillips Petroleum Co., USA) was used without purification.

The absorption spectrum of 1,4-benzoquinone was taken from literature⁸. The absorption spectra of 1,4-naphthoquinone, 1,4-anthraquinone, 9,10-anthraquinone, 5,12-tetracenequinone, and 6,13-pentacenequinone were measured on a Unicam SP 700 spectrophotometer. Spectral measurements at 93 K were performed in a special device instead of a standard cell compartment. In this device the cells with a sample and solvent were placed in a copper holder with thick walls. The holder was placed in a Dewar vessel with quartz windows and its lower finger-like part was

immersed into liquid nitrogen. Changing cells in the optical path was carried out by turning the holder round a vertical axis by 90° . The absorption spectrum results from the difference in spectra of a sample and solvent, measured against the air. The temperature of samples was measured by a resistance thermometer. The APP spectra¹⁰⁻¹² were measured on a fluorescence spectrophotometer Hitachi Perkin-Elmer MPF 2A at 77 K; a digital output of measured phosphorescence intensities, punched on a tape with the step of 1 nm, was worked up on a computer. In the measurements of the APP spectra the emission monochromator of the apparatus was set as follows (band center, nm/half-width of the band of the transmitted light, nm): 1,4-naphthoquinone 543/20; 9,10-anthraquinone 494/40; 1,4-anthraquinone 580/30; 5,12-tetracenequinone 512/40; 6,13-pentacenequinone 520/40.

RESULTS

The directions of polarization of bands determined from the APP spectra are not comparable within the series of compounds studied because the phosphorescence was not scanned at the 0—0 band in all cases. A relative comparison is still possible because of the molecular symmetry; the latter implies that mutual polarizations of absorption bands can only be parallel or perpendicular.

A weak band of a distinct vibration structure, located in the region at $23\,000\text{ cm}^{-1}$ of the electronic spectrum of *p*-benzoquinone (Fig. 1), corresponds to a $n-\pi^*$ transition. A medium strong band at $35\,000\text{ cm}^{-1}$ is due to a symmetry forbidden $\pi - \pi^*$ transition. The strongest absorption band, located at $42\,000\text{ cm}^{-1}$, is due to the allowed $\pi - \pi^*$ transition. From the polarization spectra of a *p*-benzoquinone single crystal^{13,14}, the strong band at $42\,000\text{ cm}^{-1}$ was found to be polarized in the direction along the C=O bonds. The theoretical prediction given by the PPP calculation in the variable β^{core} and γ approximation is in very good agreement with the experimental spectrum, in both location and polarization of the band.

A weak band of a distinct vibration structure, located in the electronic spectrum of 1,4-naphthoquinone (Fig. 2) at $25\,000\text{ cm}^{-1}$, is due to a $n - \pi^*$ transition. From the absorption and APP spectra it is evident that the absorption observed at $27\,000$ to $45\,000\text{ cm}^{-1}$ is due to four bands corresponding to four $\pi - \pi^*$ transitions. The region $27\,000 - 35\,000\text{ cm}^{-1}$ is due to two strongly overlapping bands that are mutually perpendicularly polarized. The result given by APP supports what was found by Singh and coworkers¹⁵ on the basis of the substituent effect. In the region $36\,000$ to $45\,000\text{ cm}^{-1}$, once again, two strongly overlapping bands are present. The longer-wavelength band is polarized in accordance with the second absorption band in the spectrum, the shorter-wavelength band with the first absorption band. Considerable overlap and differing intensities of bands make the degrees of polarization of the first and fourth bands opposite in sign, though the two bands are consistently polarized. For the same reason the degree of polarization of the second absorption band is 0.12 whereas that of the third absorption band is 0.3, though the two bands are consistently polarized. There is evidence that a next band of polarization opposite to the first band

is present in the region at 45000 cm^{-1} — the APP curve there tends to increase. Theoretical transitions given by the variable β^{core} and γ approximation conform to experiment in accounting properly for directions of polarization and close spacings of the first and second bands as well as of the third and fourth bands. The energies, however, are also overestimated. The fixed β^{core} and γ approximation gives good transition energies for the first, second and fourth bands; the third transition energy is underestimated and the directions of polarization for the first two transitions are interchanged.

The spectrum of 9,10-anthraquinone (Fig. 3) again exhibits a weak $n - \pi^*$ band of a distinct vibration structure at 25000 cm^{-1} . The first strong band is located in the region $30000 - 34000\text{ cm}^{-1}$ and corresponds to the $\pi - \pi^*$ transition. The APP curve

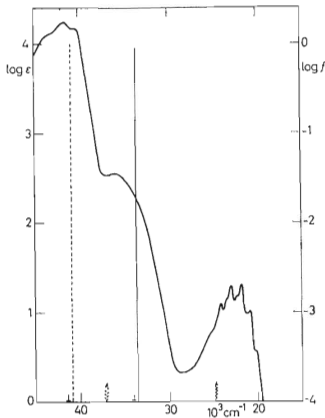


FIG. 1

1,4-Benzoquinone (absorption spectrum in *n*-hexane at 300 K; — PPP calculation, fixed β^{core} and γ ; --- PPP calculation, variable β^{core} and γ ; ~~~~~, ~~~~~ forbidden transitions)

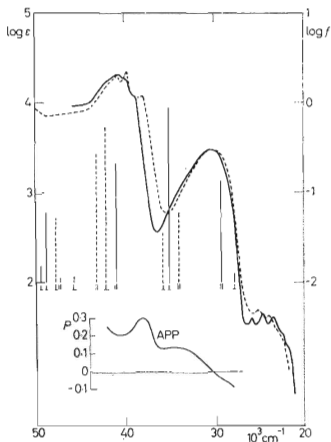


FIG. 2

1,4-Naphthoquinone (absorption spectrum at the room temperature in cyclohexane; dashed curve absorption spectrum at -180° in the mixture methanol-ethanol 1 : 4; — PPP calculation, fixed β^{core} and γ , --- PPP calculation, variable β^{core} and γ ; the first line from right: transition with $\log f < -2$; ~~~~~, ~~~~~ forbidden transitions)

suggests a next $\pi - \pi^*$ band at 37000 cm^{-1} polarized perpendicularly to the first strong band. A very strong band with the maximum at 40000 cm^{-1} is due to the third $\pi - \pi^*$ transition, its polarization being parallel to that of the first $\pi - \pi^*$ band. The polarization measurements are in agreement with the results reported previously^{16,17}. Compared to other quinones, 9,10-anthraquinone has a remarkably clean-cut shape of its APP curve and high absolute values of degrees of polarization. This is likely due to a less significant overlapping of bands and experimental conditions; a rather high intensity of phosphorescence of 9,10-anthraquinone permitted us to carry out measurements with narrow slits. The fixed β^{core} and γ approximation is superior to the variable β^{core} and γ approximation. The former provides a very good account of both the locations and directions of polarization of the observed bands, whereas the latter drastically overestimates the transition energies.

In contrast to the isoelectronic 9,10-anthraquinone, the first strong band of 1,4-anthraquinone (Fig. 4), which is due to a $\pi - \pi^*$ transition, is located at much longer wavelengths. Its maximum being at 25000 cm^{-1} , the $n - \pi^*$ transition is only observed as a shoulder on the long-wavelength tail of the first band. It is evident from the

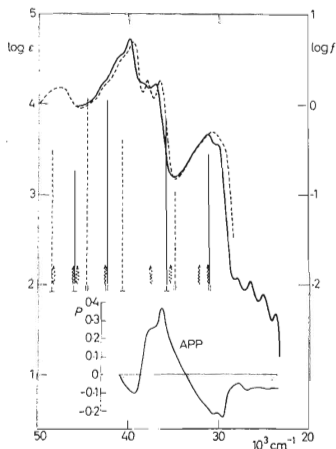


FIG. 3

9,10-Anthraquinone (for caption see Fig. 2)

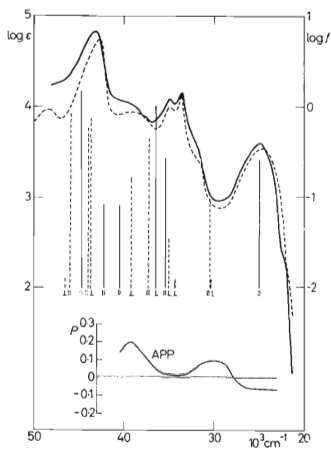


FIG. 4

1,4-Anthraquinone (for caption see Fig. 2)
the second and fourth line from right: transitions with $\log f < -2$

APP curve that two bands fall into the region $28000-37000\text{ cm}^{-1}$, their directions of polarization being mutually perpendicular. That one lying at longer wavelengths is polarized perpendicularly to the first band; owing to low intensity this band is seen on the absorption curve only as a shoulder at 32000 cm^{-1} . The band of shorter wavelength with maximum at 33600 cm^{-1} is stronger and its polarization is parallel to that of the first band. On both sides of this band there are bands of opposite polarization, which is probably a reason why the degree of polarization does not become negative. A next band at 40000 cm^{-1} is polarized perpendicularly to the first band. The decreasing nature of the APP curve in the region over 40000 cm^{-1} suggests that a very strong absorption band with the maximum at 43000 cm^{-1} is of a polarization parallel to the first band. As regards the number of bands and their polarizations, the variable β^{core} and γ approximation gives good results, but the first transitions are overestimated by about 4000 cm^{-1} . The method assuming fixed β^{core} and γ gives a good account of the first and third bands. In the region between these two bands it predicts two weak bands that are polarized perpendicularly to the first transition (the variable β^{core} and γ approximation predicts here only one band). The transition energy for the band at 40000 cm^{-1} is predicted at too long wavelengths. In the region

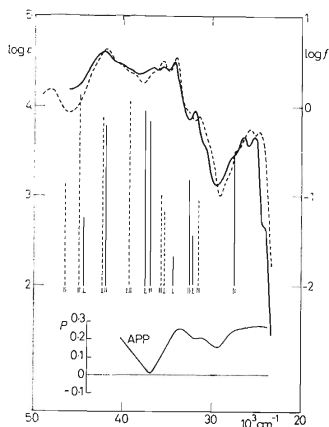


FIG. 5

5,12-Tetracenequinone (for caption see Fig. 2)

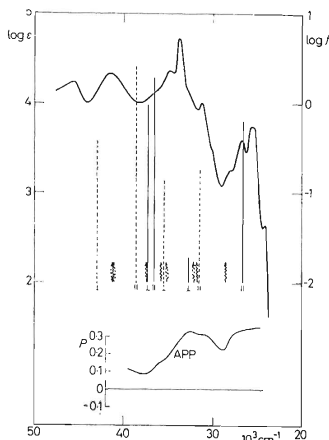


FIG. 6

6,13-Pentacenequinone (for caption see Fig. 2)

over 40000 cm^{-1} the theory gives a large number of transitions, which makes an assignment prohibitive.

In the absorption spectrum of 5,12-tetracenequinone (Fig. 5) the $n - \pi^*$ band is only observable as a shoulder on the long-wavelength tail of the first absorption band. The band extending over the range $24000 - 28000\text{ cm}^{-1}$ is due to the first $\pi - \pi^*$ transition; for the degree of polarization the APP curve gives here the positive value of 0.27. The region $29000 - 32000\text{ cm}^{-1}$ is covered by a weak absorption band, which is polarized perpendicularly to the first band. The degree of polarization of this band is not negative because of the overlap with a strong band, of opposite polarization, with a maximum at 34000 cm^{-1} . The APP curve exhibits a distinct minimum at 37000 cm^{-1} , which indicates the presence of a band perpendicularly polarized to the first band. It is however difficult to find a corresponding band in the absorption spectrum. The increasing tendency of the APP curve in the region at 40000 cm^{-1} suggests that the strong band at 42000 cm^{-1} is of parallel polarization to the first absorption band. The calculation based on the fixed β^{core} and γ approximation predicts well the positions of the first three bands; the assignment of the next bands is uncertain. The variable β^{core} and γ approximation again gives values that are greatly shifted to lower wavelengths.

With 6,13-pentacenequinone (Fig. 6), the analysis of the spectrum is difficult. The bands are considerably overlapped and the APP is rather flat owing to very low intensity of the phosphorescence (it was necessary to carry out measurements with extremely large slits). A band in the region $25000 - 28000\text{ cm}^{-1}$ is due to the first transition. The APP curve gives here almost a constant degree of polarization of 0.33. As with tetracenequinone, the APP curve suggests that there is a weak and considerably overlapped absorption band in the region $28000 - 31000\text{ cm}^{-1}$ which is perpendicularly polarized with respect to the first band. The theory gives a good interpretation of the first band if the fixed β^{core} and γ approximation is used. The assignments of other bands are questionable.

DISCUSSION

The literature dealing with the theoretical study of electronic spectra of polynuclear quinones is reviewed in the introduction in Part I (ref.²). Part I also presents results of our calculations on the electronic spectra of some linear polynuclear quinones (1,4-benzoquinone, 1,4-naphthoquinone, 9,10-anthraquinone); the computational method used was the PPP method adopting the variable β^{core} approximation but keeping the γ integrals fixed for the idealized geometry with the C=O bond length of 1.15 \AA . In spite of accounting for a quasireal geometry through the β^{core} variation, the calculations did not reproduce the observed spectrum of 1,4-benzoquinone and predicted the polarization directions of the first two $\pi - \pi^*$ transitions in 1,4-naphthoquinone in disagreement with the polarization spectra. For this reason we considered

it expedient to study the electronic spectra and π -electronic structure of six polynuclear *p*-quinones in more detail in this paper. The presented theoretical results again were obtained by the PPP method. We performed all calculations with and without the variable β^{core} and γ approximation in parallel, in order to ascertain the effect of accounting for the quasireal geometry for *p*-quinones of various types — the series of linear polynuclear *p*-quinones studied comprises systems with both the outer and inner quinonoid rings. We attempted to arrive at a better agreement with experiment for 1,4-benzoquinone and 1,4-naphthoquinone by making two modifications in the computational scheme. Firstly, we used another formula for the evaluation of β^{core} integrals (the results suggest its superiority). Secondly, the effect of the quasireal geometry was also accounted for in evaluation of γ integrals. Compared to Part I, the method appears now to be more consistent. It reproduces very well the experiment for 1,4-benzoquinone, in contrast to the method of Part I or to the method using the fixed β^{core} and γ approximation. With 1,4-naphthoquinone, the results based on the variable β^{core} and γ approximation do not conform to experiment, the transition energies being predicted at too short wavelengths. For the first two bands, however, the directions of polarization are predicted correctly (the fixed β^{core} and γ approximation leads here to a reversed order of the two bands). The overall overestimation of transition energies, brought about by the variable β^{core} and γ approximation, was found with 1,4-anthraquinone, 9,10-anthraquinone, 5,12-tetracenequinone, and 6,13-pentacenequinone, too. For these molecules, the fixed β^{core} and γ approximation provides a very good account of the first $\pi - \pi^*$ bands. The next $\pi - \pi^*$ transition energies match, however, the absorption curves and the APP data less closely. In general, it is possible to state that, except for 1,4-benzoquinone, the calculations within the variable β^{core} and γ approximation overestimate transition energies by about 4000 cm^{-1} . But as regards intensities and polarizations of bands, the variable β^{core} and γ approximation is superior in giving an overall true picture of the spectrum. The overestimation of transition energies could possibly be avoided by fitting the parameter set within the variable β^{core} and γ approximation (in this study we limited ourselves to a single parameter set for both theoretical approaches).

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