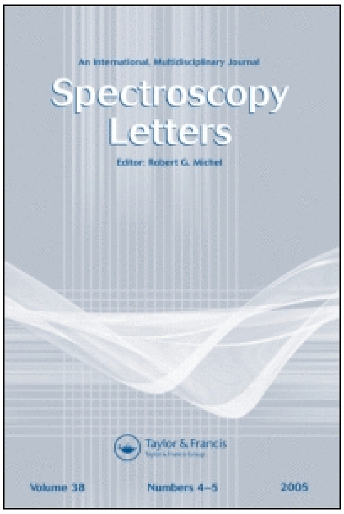

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IDENTIFICATION AND SEPARATION OF THE TWO OVERLAPPING SINGLET 1(π, π^*) ABSORPTION BANDS OF 1, 4-TETRACENEQUINONE

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IDENTIFICATION AND SEPARATION OF THE TWO OVERLAPPING SINGLET $1(\pi, \pi^*)$ ABSORPTION BANDS OF 1,4-TETRACENEQUINONE

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ABSTRACT

Absorption and fluorescence spectra of 1,4-tetracenequinone (1,4-TQ) have been measured in solution and the two overlapping $1(\pi, \pi^*)$ absorption bands with comparable intensities were separated. Based on the spectroscopic data, the energy levels of the low-lying $1(\pi, \pi^*)$ excited states of 6,15-hexacenequinone were discussed in relation to those of 1,4-TQ.

Key Words: Singlet (π, π^*) absorption band; Fluorescence spectrum; Excited-state energy levels; 1,4-Tetracenequinone; 6,15-Hexacenequinone.

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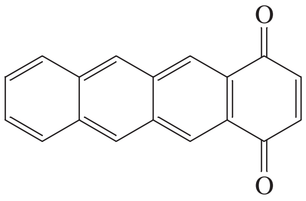
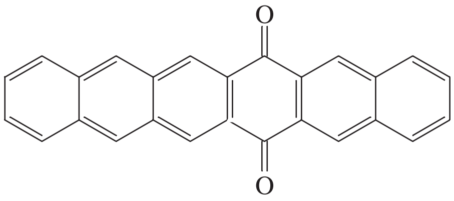
INTRODUCTION

Para-quinones play an important role in biological systems as well as in functional materials (1-3). A detailed understanding of para-quinone electronic states is the foundation on which an understanding at the molecular level of such a role must rest. It is, therefore, of importance to know the information on the excited-state energy levels of para-quinones, especially for the quantum chemists who are engaged in the calculation of the electronic states of various types of quinones. 1,4-Tetracenequinone (1,4-TQ) is known to emit the S1 fluorescence, and the lowest excited singlet state is reported to be (π, π^*) in nature (2-6). However, not only the fluorescence spectrum, but even the UV-VIS absorption spectrum of this molecule has not been fully investigated, presumably because it is not commercially available and because it shows poor solubility in organic solvents. In the present work we have measured absorption and fluorescence spectra of 1,4-TQ in solution and shown the existence of the two overlapping $1(\pi, \pi^*)$ absorption bands with comparable intensities. These two overlapping absorption bands were separated and the energy levels of the low-lying $1(\pi, \pi^*)$ excited states of 1,4-TQ were discussed in relation to those of 6,15-hexacenequinone (6,15-HQ), see Structure Diagram 1.



1,4-TQ



6,15-HQ

Structure Diagram 1.

EXPERIMENTAL

1,4-TQ was synthesized according to the literature (7) and chromatographically purified by passing through an alumina column using ethyl acetate as the solvent. n-Hexane, methylcyclohexane, acetic acid, and methanol, all spectroscopic grade obtained from Wako Pure Chemicals (Tokyo, Japan), were used as the solvents without further purification. Absorption spectra were measured with a Jasco Ubest-50 UV/Vis or a Hitachi model 2000-20 spectrophotometer using 10- and

50-mm pathlength quartz cells. Fluorescence and excitation spectra were measured with a Hitachi F-4010 or a Hitachi 360-10SC fluorescence spectrophotometer. Emission spectra were corrected for the wavelength dependence of the detector response with a hexane solution of N,N-dimethylaminonitrobenzene as the standard. Digital data were analyzed with a Macintosh Quadra 650 microcomputer with a super PC memory (SP32/60).

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectrum of 1,4-TQ in n-hexane at room temperature over the entire UV-VIS range. It is clearly seen that the absorption spectrum consists of three electronic bands with the apparent origins observed at 476 nm (e = 5 × 103), 343 nm (e = 2 × 104), and 262 nm (e = 8 × 104 M − 1 cm − 1), with the molar extinction coefficients in parentheses. The weak bands at 402, 380 and 360 nm seem to be the vibrational bands of the first absorption band starting from 476 nm. However, closer inspection revealed that the weak bands seen in the region 350 - 410 nm belong to another electronic transition which is different from that starting from 476 nm. This will be discussed below.

In Figure 2 (a), we show the emission and absorption spectra of 1,4-TQ in methylcyclohexane at room temperature. The emission spectrum exhibits an expected mirror-image relationship with the lowest-energy absorption band and the emission is safely attributed to the S1(π, π^*) fluorescence. The two overlapping

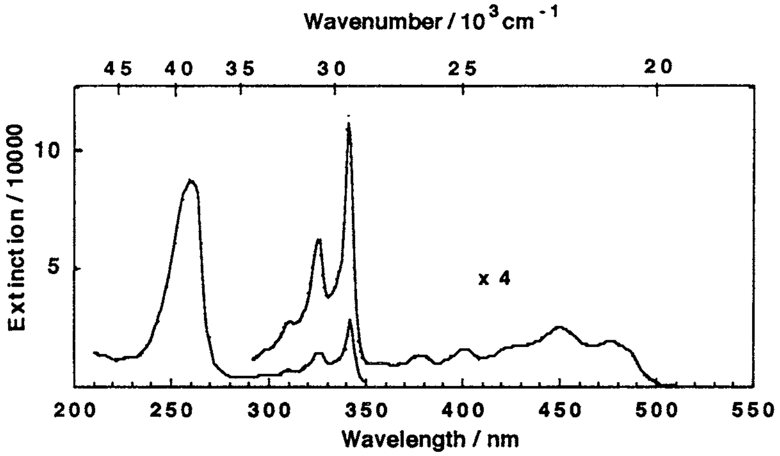


Figure 1. Absorption spectrum of 1,4-tetracenequinone in n-hexane at room temperature.

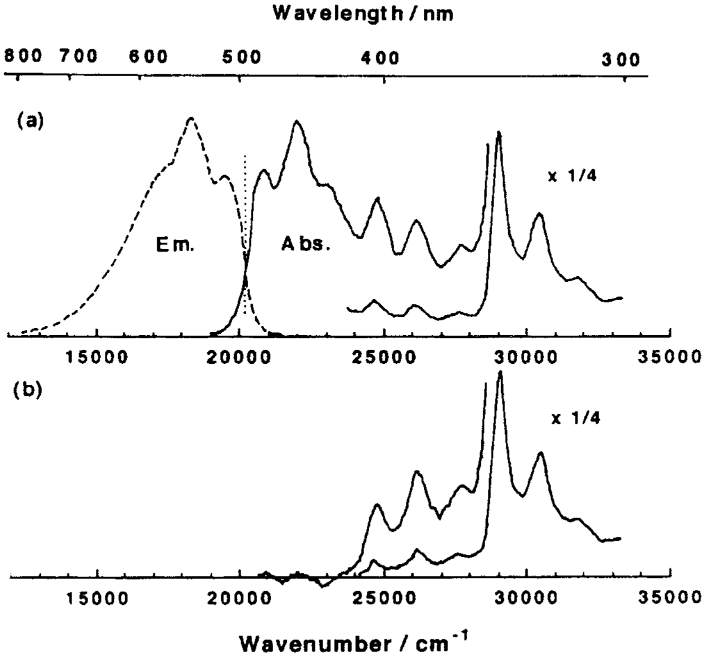


Figure 2. (a) Fluorescence and absorption spectra of 1,4-tetracenequinone in methylcyclohexane at room temperature. (b) The subtracted difference absorption spectrum of 1,4-tetracenequinone in methylcyclohexane at room temperature. (See the text).

absorption bands were separated based on the following procedures: First, the maximum intensities of the absorption spectrum in the 350 - 500 nm region and the corrected fluorescence spectrum were normalized to a common magnitude. Then, the fluorescence spectrum reflected with respect to the line on the crossing point of the normalized fluorescence and absorption spectra, was subtracted from the normalized absorption spectrum to get the difference spectrum in wavenumber scale. The resulting difference absorption spectrum is shown in Figure 2 (b), in which we can see clearly the weak band starting from 400 nm. This weak band is attributed to the $1(\pi, \pi^*)$ band, since the molar extinction coefficient is about 1.5 × 103 M-1 cm-1 in the subtracted absorption spectrum, and since it does not show any blue shift upon the addition of alcohol or acetic acid, as is clearly seen in Figure 3. Thus, there are at least four singlet (π, π^*) excited states for 1,4-TQ in a range 220 $\sim$ 500 nm with the apparent origins at 476 (S1), 400 (S2), 343 (S3), and 262 nm (S4).

It should be noted that the reported absorption spectrum of 6,15-hexacenequinone (6,15-HQ) exhibits the spectral feature quite similar to that of 1,4-TQ and

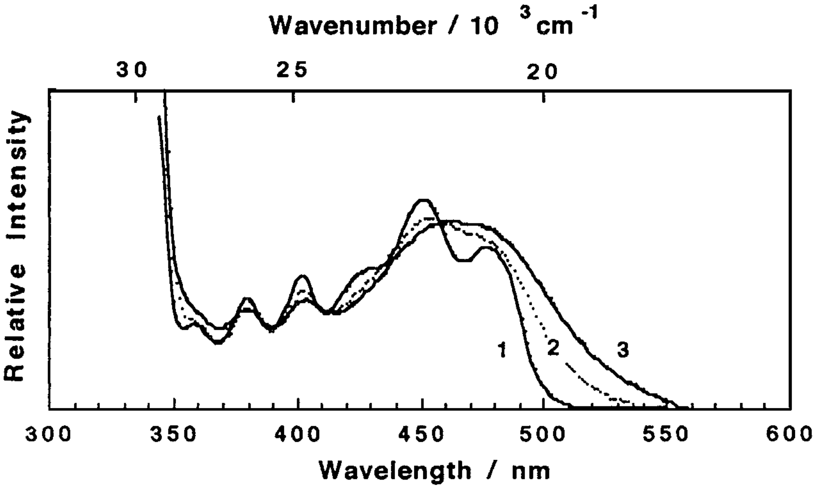


Figure 3. Absorption spectra of 1,4-tetracenequinone in n-hexane–acetic acid mixtures with different acetic acid contents at room temperature.

that the absorption spectrum in the 350 - 500 nm region of 6,15-HQ is very likely to consist of the two overlapping absorption bands belonging to the different 1(π, π^*) electronic excited states. In light of the reported spectroscopic data for 6,15-HQ, the apparent origins of the two overlapping 1(π, π^*) absorption bands of 6,15-HQ are seen at 455 and 390 nm. The similarity in the excited-state ordering as well as the energy levels of 1,4-TQ and 6,15-HQ indicates that not only the lowest singlet (π, π^*) level, but also the higher singlet (π, π^*) levels are primarily determined by the size of the larger acene group attached to the central quinoid structure.

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