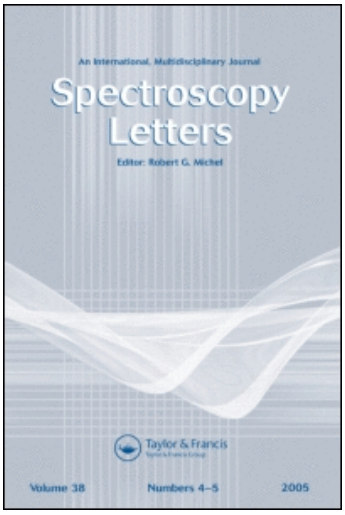

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Singlet (N, π*) Absorption Bands of 1, 4-Anthraquinone, 5, 12-Tetracenequinone and 6, 13-Pentacenequinone

Takao Itoh[a]
[a] Kanto Junior College, Gunma, Japan

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SINGLET (n, π*) ABSORPTION BANDS OF 1,4-ANTHRAQUINONE, 5,12-TETRACENEQUINONE AND 6,13-PENTACENEQUINONE

Key Words: molar extinction coefficient, singlet (n, π*) absorption bands, 1,4-anthraquinone, 5,12-tetracencequinone, 6,13-pentacenequinone

Takao Itoh

Kanto Junior College,
625 Oya-cho, Tatebayashi, Gunma 374, Japan

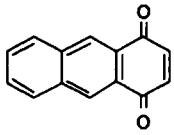
ABSTRACT

The large molar extinction coefficients ε of the first ^{1}(n, π*) absorption band of 1,4-anthraquinone (1,4-AQ), 5,12-tetracencequinone (5,12-TQ) and 6,13-pentacenequinone (6,13-PQ) have been interpreted in terms of the vibronic coupling with the upper allowed ^{1}(π, π*) states. It is indicated that the large ε values of the ^{1}(n, π*) absorption bands of these molecules are mainly due to close proximity to the upper ^{1}(π, π*) states from which the intensity is borrowed.

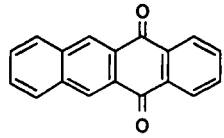
INTRODUCTION

Recently, assignment of the excited states of various types of quinones has received much attention [1, 2]. The first ^{1}(n, π*) absorption bands of 1,4-anthraquinone (1,4-AQ), 5,12-tetracenequinone (5,12-TQ) and 6,13-pentacenequinone (6,13-PQ) are observed as a weak shoulder on the red side of the ^{1}(π, π*) absorption band in non-polar hydrocarbons [3, 4]. The molar extinction coefficients, ε, of these ^{1}(n, π*) absorption bands are comparatively large as compared with other smaller quinones such as *p*-benzoquinone or 1,4-naphthoquinone as well as with other aromatic carbonyl compounds such as benzophenone or benzaldehyde; ε at the apparent origins are 220, 370 and 400 for 1,4-AQ, 5,12-TQ and 6,13-PQ, respectively.

Although these bands have been regarded as due to the n → π* transition [5, 6], no convincing evidence has been given to these assignments. The purpose of present work is to provide an answer to the question "Why are the ε values of these $^1(n, \pi^*)$ bands large?".



1,4-AQ



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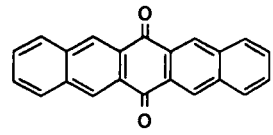

6,13-PQ

EXPERIMENTAL

1,4-AQ and 5,12-TQ synthesized at Alfa Products Chemical Co. (MA, USA), and 6,13-PQ obtained from Aldrich Chemical Co. (USA) were chromatographically purified by passing through a silica gel column using cyclohexane and a mixture of cyclohexane and acetone as the solvents, followed by repeated recrystallization. *n*-Hexane, *n*-pentane, acetic acid and methanol of spectroscopic grade obtained from Wako Pure Chemicals (Tokyo, Japan) were used as the solvents without further purification. Absorption spectra were measured with a Hitachi U-3210 or a Varian DMS 100 spectrophotometer using quartz cells with 10-mm and 100-mm pathlengths. Digital data were analyzed with a Macintosh Quadra 650 microcomputer.

RESULTS AND DISCUSSION

Figure 1(a) shows the absorption spectra of 1, 4-AQ, 5, 12-TQ and 6, 13-PQ in n-hexane at room temperature. Each of these absorption spectra exhibits a weak band with the apparent origin at 453 nm for 1,4-AQ, 426 nm for 5,12-TQ, and 414 nm for 6,13-PQ, all on the blue side of the first $^1(\pi, \pi^*)$ band. All of these weak bands disappear and the first $^1(\pi, \pi^*)$ bands show a slight shift to the red upon addition of a small amount of methanol or acetic acid to the solutions, as exemplified in Figure 1(b) for 1, 4-AQ. These observations indicate that the weak bands are based on the n → π* transition. However, the molar extinction coefficients, ε, at the apparent origins of these $^1(n, \pi^*)$ absorption bands are comparatively large as compared with those of other smaller quinones as well as other aromatic carbonyl compounds such as benzaldehyde: The ε values at the $^1(n, \pi^*)$ origins of 1,4-AQ, 5,12-TQ and 6,13-PQ are 220, 370 and 400, respectively, while those of *p*-benzoquinone, 1,4-naphthoquinone and 9,10-anthraquinone are 4, 20 and 65, respectively. Since the large ε values of these $^1(n, \pi^*)$ absorption bands seem to originate partly from a significant overlapping between the $^1(n, \pi^*)$ absorption and the tail of the first $^1(\pi, \pi^*)$ absorption bands, each of the $^1(\pi, \pi^*)$ absorption spectra is approximated by a sum of gaussians, $A(\nu) = \Sigma_i A(\nu_i)\exp[-(\nu - \nu_i)^2/\sigma^2]$ ($A(\nu_i)$, ν_i and σ varied), to fit only the region near the origin of the $^1(\pi, \pi^*)$ absorption and it was subtracted from the observed absorption spectrum to get only the $^1(n, \pi^*)$ absorption spectrum. The ε values at the apparent origin of the subtracted $^1(n, \pi^*)$ absorption bands are found to be 190,

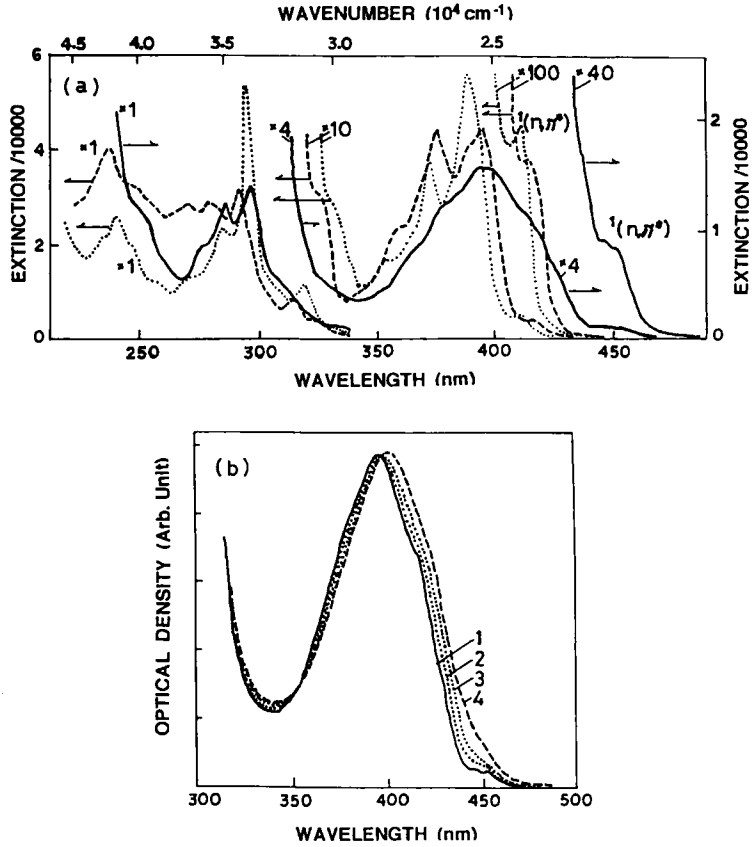

FIG. 1 (a) Absorption spectra of 1,4-anthraquinone (———), 5,12-tetracenequinone (---------) and 6,13-pentacenequinone (·····) in *n*-hexane at room temperature.
(b) Absorption spectra of 1, 4-anthraquinone (1, 4-AQ) in *n*-pentane containing different amounts of methanol at room temperature: (1) in pentane; (2) in pentane + 1 volume % of MeOH; (3) + 3 volume % of MeOH; and (4) + 10 volume % of MeOH.

260 and 350, respectively, for 1,4-AQ, 5,12-TQ and 6,13-PQ. These values seem to be still large as the molar extinction coefficients of the $^1(n, \pi^*)$ bands, and can be regarded numerically as those between the ε values of the $^1(n, \pi^*)$ and $^1(\pi, \pi^*)$ absorption.

The intensity of the origin band, as well as most of the over-all intensity of the forbidden singlet $n \rightarrow \pi^*$ transition, may be due to a perturbation which mixes the two excited electronic states. In such a case, the oscillator strength of the singlet $n \rightarrow \pi^*$ transition, f, should obey an expression of the form, $f = \Sigma_n f_n V_n^2/\Delta E_n^2$, where f_n is the oscillator strength of

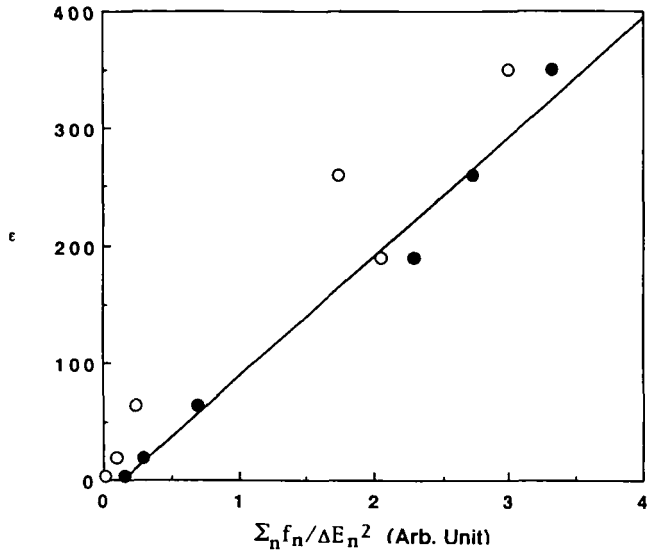

FIG. 2 The ε values at the apparent $^1(n, \pi^*)$ origins plotted versus the values $\Sigma_n f_n/\Delta E_n^2$ for six para quinones (*p*-benzoquinone, 1, 4-naphthoquinone, 9, 10-anthraquinone, 1, 4-anthraquinone (1, 4-AQ), 5,12-tetracenequinone (5,12-TQ) and 6,13-pentacenequinone (6,13-PQ): n = 1 for open circles, and n = 2 for closed circles.

the n-th allowed singlet $\pi \rightarrow \pi^*$ transition, ΔE_n is the energy separation between the lowest $^1(n, \pi^*)$ and n-th $^1(\pi, \pi^*)$ states, and V_n is the matrix element connecting the two excited states. This matrix element may be of vibronic nature or due to the environmental perturbation so far as the over-all intensity is concerned. The ε values at the apparent $^1(n, \pi^*)$ origins are plotted versus the values $\Sigma_n \int \varepsilon_n(\nu)\, d\nu/\Delta E_n^2$ ($f_n \sim \int \varepsilon_n(\nu)\, d\nu$) in Figure 2 for six para quinones (*p*-benzoquinone, 1,4-naphthoquinone, 9,10-anthraquinone, 1,4-AQ, 5,12-TQ and 6,13-PQ). When only the first $^1(\pi, \pi^*)$ absorption bands are considered (n = 1), the linearity of the plots is not satisfactory. However, when the second $^1(\pi, \pi^*)$ absorption bands are included (n = 2), the linearity is significantly improved as is seen in Figure 2. (The correlation coefficient between $\Sigma_{n=2} f_n V_n^2/\Delta E_n^2$ and ε is 0.98.) Although the electronic states exist in the VUV (vacuum ultra violet) region, these are not expected to play an important role for the intensity borrowing for the $^1(n, \pi^*)$ absorption bands, because of the large energy gaps between the $^1(n, \pi^*)$ and the VUV states. The good linearity of the plots may indicate that the coupling matrix element V_n does not depend strongly on the compounds as well as on the electronic states to which the $^1(n, \pi^*)$ state couples, as far as the systems used in the present study are concerned. It is suggested that the large ε values of the $^1(n, \pi^*)$ absorption bands of

1,4-AQ, 5,12-TQ and 6,13-PQ are mainly due to close proximity to the upper $^1(\pi, \pi^*)$ states from which the intensity is borrowed. As is seen in Figure 1, the energy separations between the two lowest $^1(n, \pi^*)$ and $^1(\pi, \pi^*)$ states are comparatively small for 1,4-AQ, 5,12-TQ and 6,13-PQ, as compared with those of smaller quinones.

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