The Very Weak Visible Absorption Band of p-Benzoquinone

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Recently, in various carbonyl compounds[1-7] and azines[8], very weak absorption bands at the long wavelength sides of the $n\rightarrow\pi^*$ singlet-singlet absorption bands have been found and safely assigned as $n\rightarrow\pi^*$ singlet-triplet absorption bands from the phosphorescence spectra, the temperature-independency, the solvent effect and the substitution effect. Previously, Sidman[9], in his study of the low temperature crystalline spectrum of *p*-benzoquinone, found a very weak absorption band at the long wavelength side of the $n\rightarrow\pi^*$ singlet-singlet absorption band and tentatively assigned it to the $n\rightarrow\pi^*$ singlet-triplet absorption band. Apart from his study, the $n\rightarrow\pi^*$ singlet-triplet absorption bands of quinones have not been studied. Thus, we have studied this very weak visible absorption band of *p*-benzoquinone in solution. Our results are now reported on.

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[1] J. W. Sidman, *Chem. Revs.*, **58**, 689 (1958).

[2] a) J. C. D. Brand, *J. Chem. Soc.*, **1958**, 858; b) A. D. Cohen and C. Reid, *J. Chem. Phys.*, **24**, 85 (1956); c) G. W. Robinson, *Can. J. Phys.*, **34**, 699 (1956).

[3] R. A. Ford, *Spectrochim. Acta*, **13**, 394 (1959).

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[9] J. W. Sidman, *J. Am. Chem. Soc.*, **78**, 2363 (1956).

Experimental

Measurements. — The absorption spectra were measured with a Cary recording spectrophotometer 14 M with 1, 5, 10 cm. path quartz cells. For the measurements of the very weak absorption bands, the slidewire for the scale expansion, the accessory, was used. A thermostated cell jacket was used for measurements at 5 and 42°C.

Materials.—The solvents were purified according to the methods described in our previous work[10]. Ethyl iodide (a commercial product) was washed with a 1N aqueous solution of potassium hyroxide and repeatedly with water, and distilled after being dried over calcium chloride. *p*-Benzoquinone, toluquinone and *p*-xylo-*p*-quinone (commercial products) were purified by cautious sublimation. *o*-[11] and *m*-xylo-*p*-quinones[12] were prepared according to the methods described in the literature and were purified by cautious sublimation. α-Naphthoquinone was prepared according to Fieser's method[13] and purified by charcoal treatment in an ether solution. 2,5- and 2,6-dichlor-*p*-benzoquinones (commercial products) were recrystallized from ethanol and *n*-heptane, successively[*1].

Melting Points (corr.) — *p*-ebnzoquinone 115~116°C, toluquinone 69°C, *o*-xylo-*p*-quinone 56.5~57.5°C, *m*-xylo-*p*-quinone 72.5~73°C, *p*-xylo-*p*-quinone 125°C, α-naphthoquinone 124°C, 2,5-dichloro-*p*-benzoquinone 121.5~122.5°C, 2,6-dichloro-*p*-benzoquinone 162~163°C.

Results

The absorption spectra obtained are given in Figs. 1—6. In these figures ε represents the molecular extinction coefficient.

Discussion

As seen in Figs. 1, 2, 3, 4, 5 and 6, *p*-benzoquinone and its derivatives have very weak adsorption bands ($\varepsilon_{\max}\sim 0.2$) at the long wavelength sides of the $n\rightarrow\pi^*$ singlet-singlet absorption bands. In the following remarks, this band is called the α-band. In many carbonyl compounds (formaldehyde[2], acetaldehyde[3], benzophenone[4], glyoxal[5], diacetyl[6] and camphorquinone[7], very weak absorption bands similar to the α-band, at the long wavelength sides of the $n\rightarrow\pi^*$ singlet-singlet absorption bands, have been found and safely assigned to the $n\rightarrow\pi^*$ singlet-triplet absorption bands by many people on the basis of the phosphorescence spectra, the temperature-independency, the solvent effect and the substitution effect. The maximum molecular extinction coefficient of the α-band (ca. 0.2) is of the same order of magnitude as those of comphorquinone (ca. 0.1) and diacetyl (ca. 0.05), but it is far larger

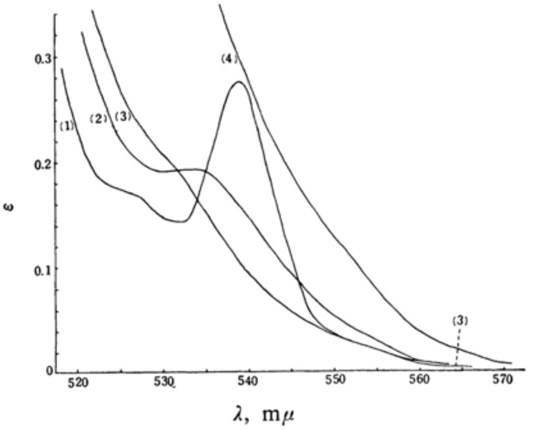

Fig. 1. *p*-Benzoquinone, solvent (1) *n*-heptane; (2) carbon tetrachloride; (3) benzene; (4) ethyl iodide.

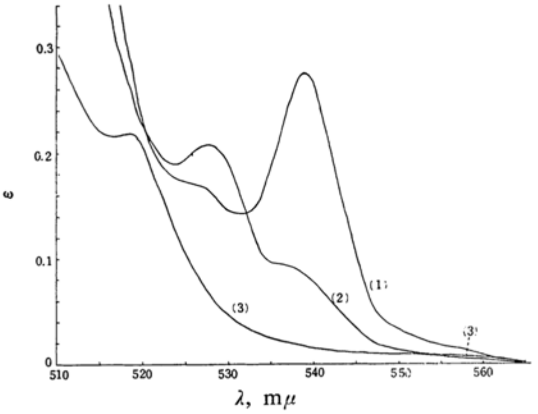

Fig. 2. (1) *p*-Benzoquinone; (2) toluquinone; (3) *p*-xylo-*p*-quinone, solvent *n*-heptane.

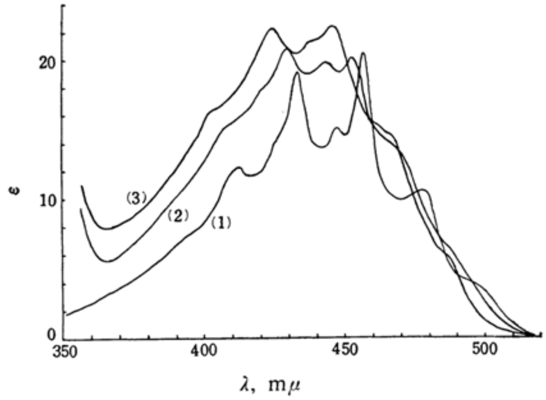

Fig. 3. (1) *p*-Benzoquinone; (2) toluquinone: (3) *p*-xylo-*p*-quinone, solvent *n*-heptane.

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10) A. Kuboyama, This Bulletin, **33**, 1027 (1960); *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 558 (1960).

11) O. H. Emerson and L. I. Smith, *J. Am. Chem. Soc.*, **62**, 141 (1940).

12) L. I. Smith et al., ibid., **63**, 1038 (1941).

13) L. F. Fieser, "Experiments in Organic Chemistry", D. C. Heath and Co., Boston (1941), p. 23.

[*1] In 2,5-dichloro-*p*-benzoquinone, a mixed solvent of *n*-heptane and benzene was used instead of *n*-heptane alone.

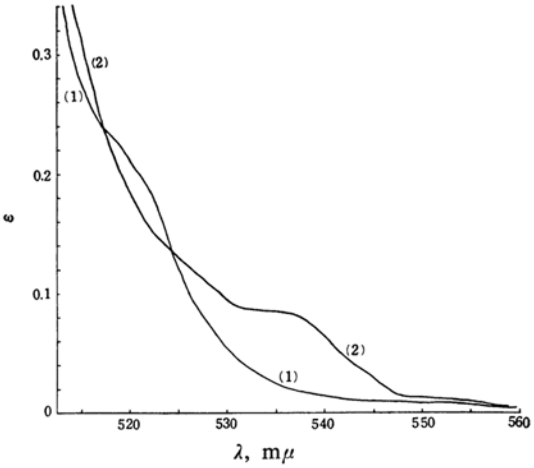

Fig. 4. (1) *o*-Xylo-*p*-quinone; (2) *m*-xylo-*p*-quinone, solvent *n*-heptane.

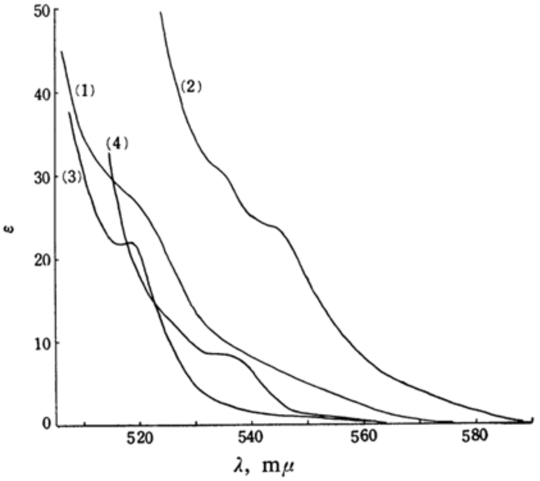

Fig. 5. (1) 2, 5-Dichloro-*p*-benzoquinone; (2) 2, 6-dichloro-*p*-benzoquinone; (3) *p*-xylo-*p*-quinone; (4) *m*-xylo-*p*-quinone, solvent *n*-heptane.

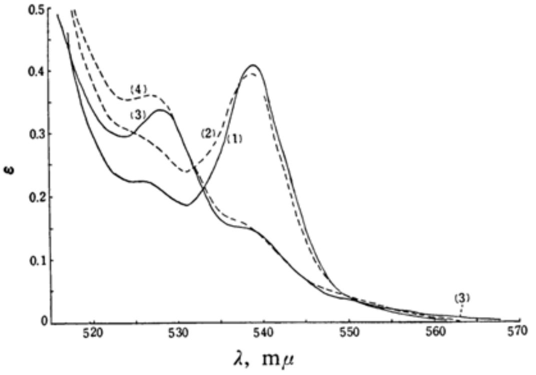

Fig. 6. (1), (2) *p*-Benzoquinone; (3), (4) toluquinone; (1), (3) 4 °C; (2), (4) 42°C, solvent *n*-heptane.

than that of acetaldehyde (ca. 0.0001). For *p*-benzoquinone, the distance[*2] (wave number) between the peak (at 539 mμ) of the α-band and the longest wavelength peak (at 479 mμ) of the $n \rightarrow \pi^*$ singlet-singlet band in *n*-heptane is 2330 cm^{-1}. If this value is regarded as the separation between the $n \rightarrow \pi^*$ singlet and triplet excited states, it is of the same order of magnitude as the reported values (2000~3000 cm^{-1}) for the above carbonyl compounds. As seen in Fig. 1, the α-band of *p*-benzoquinone is partly masked by the tail of the $n \rightarrow \pi^*$ singlet-singlet absorption band, and, especially in ethyl iodide, the α-band is so almost entirely masked that the spin-orbit interaction effect of iodine atom on the α-band cannot be examined. In *n*-heptane one peak and one shoulder are observed at 539 mμ and ca. 527.5 mμ respectively. The distance between the peak and the shoulder is ca. 410 cm^{-1}; this vibrational sequence probably corresponds to that in the crystalline spectrum assigned to the totally symmetric ring deformation vibration of the *p*-benzoquinone molecule by Sidman[9]. The α-band shifts toward shorter wavelengths in the order of *n*-heptane, carbon tetrachloride, and benzene, like the $n \rightarrow \pi^*$ singlet-singlet absorption band of *p*-benzoquinone. On the other hand, the $\pi \rightarrow \pi^*$ adsorption bands of the quinones are at shorter wavelengths in *n*-heptane than in carbon tetrachloride and in benzene. As for the methyl group substitution effect, in Fig. 2 the peak of the α-band shifts towards shorter wavelengths as the number of methyl groups increases, in the same manner as in the $n \rightarrow \pi^*$ singlet-singlet bands in Fig. 3. This fact is characteristic of the $n \rightarrow \pi^*$ absorption band[14]. The peaks of the α-band of toluquinone and *p*-xylo-*p*-quinone in *n*-heptane are at 528 and 519 mμ respectively[*3]. From the solvent effect and the methyl group substitution effect, the α-band is safely assigned to the $n \rightarrow \pi^*$ absorption band. As seen in Fig. 2, toluquinone alone has a shoulder at the long wavelength side of the peak. In the $n \rightarrow \pi^*$ singlet-singlet bands in Fig. 3, such an abnormality of toluquinone as the above cannot be observed. Therefore, this abnormality of toluquinone seems to be intrinsic to the α-band. In Fig. 4, the α-band of *o*-xylo-*p*-quinone is similar to that of *p*-xylo-*p*-quinone, while the band of *m*-xylo-*p*-quinone has a shoulder similar to that of toluquinone. Therefore, it is concluded that

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[*2] The corresponding one in the crystalline state, studied by Sidman[9], was 2060 cm^{-1}.

14) H. Baba, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **72**, 341 (1951); S. Nagakura, This Bulletin, **25**, 164 (1952); A. Kuboyama, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 1062 (1956).

[*3] α-Naphthoquinone has a peak at 491 mμ in *n*-heptane, similar to that of *p*-xylo-*p*-quinone.

these shoulders are characteristic of the structure where two carbonyl groups of *p*-benzoquinone are not equivalent. As seen in Fig. 2, *p*-benzoquinone has a tail which extends over the long wavelength side of the peak. This tail may be enhanced to become the shoulders in toluquinone and *m*-xylo-*p*-quinone mentioned above. It is uncertain whether this tail and the α-band are due to the same electronic transition or not. As seen in Fig. 5, in dichloro-*p*-benzoquinones the intensities of the α-band are considerably enhanced in comparison with those of dimethyl-*p*-benzoquinones. This enhancement of the intensity of the α-band is surely to be attributed to the spin-orbit interaction effect of chlorine atoms. Therefore, this fact is indicative of the α-band being the singlet-triplet absorption band. Further, we have examined the temperature-dependency of the α-band of *p*-benzoquinone and toluquinone. Though, as seen in Fig. 6, owing to the tails of the $n\rightarrow\pi^*$ singlet-singlet bands the temperature-dependency cannot be fully examined, it seems that no noticeable temperature-dependency can be observed in the temperature range 4∼42°C. In conclusion, from the results obtained in this work, the α-band is reasonably assigned to the $n\rightarrow\pi^*$ singlet-triplet absorption band.

Summary

The very weak absorption bands at the long wavelength sides of the $n\rightarrow\pi^*$ singlet-singlet absorption bands of *p*-benzoquinone and its derivatives were examined with regard to the solvent effect, the substitution effect and the temperature-dependency. From the obtained results, this absorption band is reasonably assigned to the $n\rightarrow\pi^*$ singlet-triplet absorption band. As for its absorption curve, a distinct difference between the structure where the two carbonyl groups of *p*-benzoquinone are equivalent and that where the two carbonyl groups are not equivalent is observed.

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