The n—π Transition Band of Acenaphthenequinone*

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In a previous paper[1], Nagakura and the present author measured the weak visible bands of *o*- and *p*-quinones in various solvents. From the result on the solvent effect these bands were ascribed to an $n-\pi^*$ transition, namely, the transition from the non-bonding electron orbital of oxygen atom to the excited π-electron orbital. However, the $n-\pi^*$ transition band of acenaphthenequinone has never been studied. Thus, the present author measures the $n-\pi^*$ transition band of acenaphthenequinone in various solvents. Further, for the purpose of comparison, the absorption spectra of various *o*- and *p*-quinones are newly measured. The obtained results are now reported.

Experimental

Measurements. — The absorption spectra were measured with a Cary recording spectrophotometer 14 M. Quartz cylindrical cells with path lengths of 1, 2 and 5 cm. were used. A thermostated cell jacket was used for measurements at 35°C.

Materials. — Acenaphthenequinone[2] (AQ) was prepared through the oxidation of acenaphthene with potassium bichromate and was recrystallized from benzene, m. p. 256°C. *p*-Benzoquinone[3] was prepared through the oxidation of hydroquinone with potassium bichromate and was purified by sublimation, m.p. 114°C. α- And β-naphthoquinones and phenanthrenequinone were prepared according to L. F. Fieser's method[4]. α-Naphthoquinone was purified by charcoal treatment in ether solution, m. p. 124°C. β-Naphthoquinone was used without further purification, according to Fieser's note[4], m. p. with decomp. 145~147°C. Phenanthrenequinone was recrystallized from ethanol, m. p. 208°C. All the solvents used in the present study were of special grade. Benzene and ethyl ether were distilled after being dried over sodium metal. Dioxane was distilled from sodium metal, after being dried with it. Carbon disulfide was distilled after being dried over calcium chloride, and was

1) S. Nagakura and A. Kuboyama, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 74, 499 (1953); S. Nagakura and A. Kuboyama, *J. Am. Chem. Soc.*, 76, 1003 (1954).

2) "Organic Syntheses", Vol. XXIV, p. 1.

3) "Organic Syntheses", Col. Vol. I, p. 469.

4) L. F. Fieser, "Experiments in Organic Chemistry", D. C. Heath and Co., Boston (1941), pp. 230, 232 and 233.

kept in the dark. Chloroform was washed successively with concentrated sulfuric acid and with aqueous sodium hydroxide, and was distilled after being dried over calcium chloride. *n*-Heptane was distilled after being treated as in the case of chloroform and being dried over sodium metal.

Results

The obtained absorption spectra are given in Figs. 1—6. The spectra of AQ in various solvents are given in Figs. 1* and 2 and those of β-naphthoquinone, phenanthrenequinone, *p*-benzoquinone, and α-naphthoquinone are given in Figs. 3**, 4, 5 and 6, respectively.

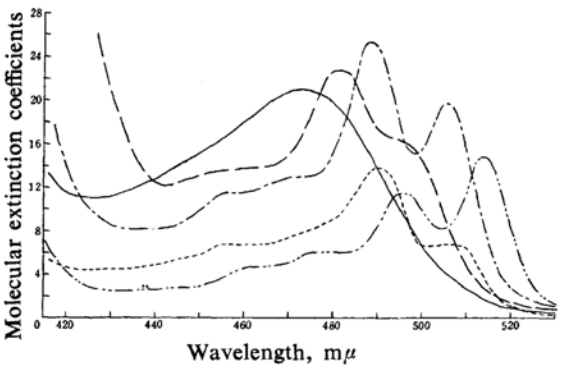

Fig. 1. Absorption spectra of acenaphthenequinone, solvent, —— benzene, —— chloroform, —— dioxane, —— carbon disulfide, ---- ethyl ether (in case of the latter two*, the scale of the ordinate is arbitrary).

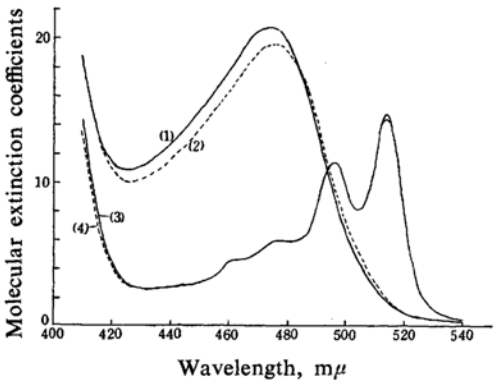

Fig. 2. Absorption spectra of acenaphthenequinone, solvent, (1), (2) dioxane, (3), (4) carbon disulfide; temperature, (1), (3) room temperature (17°C), (2), (4) 37°C (in case of carbon disulfide, the scale of the ordinate is arbitrary).

*1 AQ is sparingly soluble in carbon disulfide and ethyl ether. Thus, the molecular extinction coefficient of the α-band in these solvents could not be determined.

2 The longest wavelength π-π transition band of β-naphthoquinone in chloroform largely shifts towards longer wavelengths as in AQ.

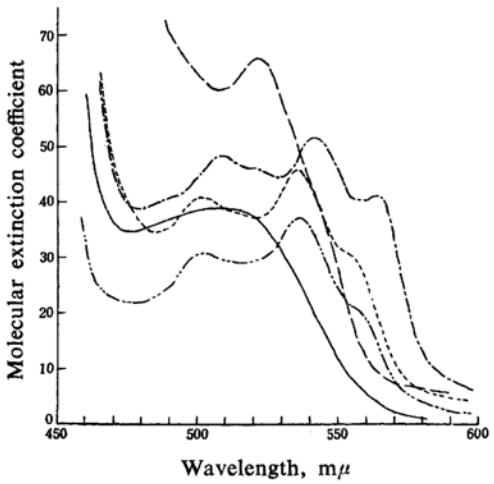

Fig. 3. Absorption spectra of β-naphthoquinone, solvent; —— carbon disulfide, ---- benzene, —— ethyl ether, —— chloroform, —— dioxane.

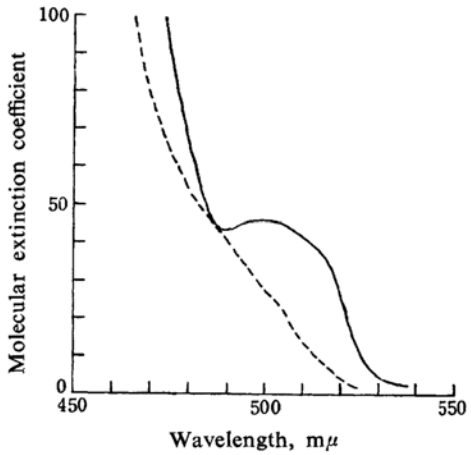

Fig. 4. Absorption spectra of phenanthrenequinone, solvent; —— benzene, ---- dioxane.

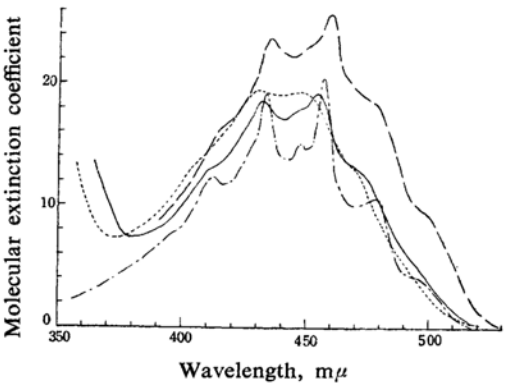

Fig. 5. Absorption spectra of *p*-benzoquinone, solvent; —— carbon disulfide, —— *n*-heptane, —— benzene, ---- dioxane.

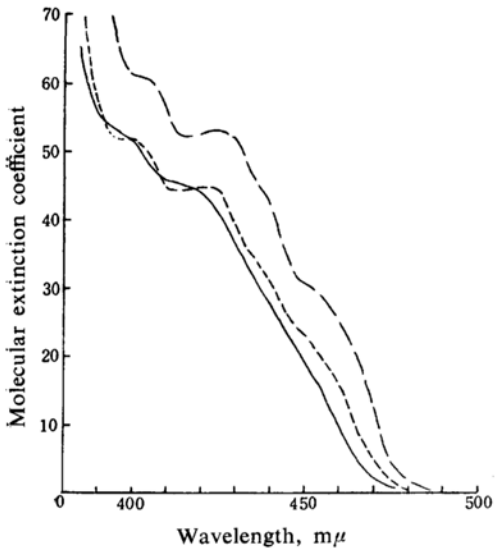

Fig. 6. Absorption spectra of α-naphthoquinone, solvent; —— carbon disulfide, ---- benzene, —— dioxane.

Discussion

In the visible and near UV regions, AQ has three main peaks at 225 mμ, 300 mμ, and 500 mμ. It is thought that strong peaks at 225 mμ and 300 mμ correspond to the β and the p bands of naphthalene[5], respectively, while a weak peak at 500 mμ which is given in Fig. 1 is assumed to be an $n-\pi^*$ transition band from the consideration of its intensity and position. Hereafter, this band will be called the α-band. As for the solvent effect on the α-band, which is shown in Fig. 1, two points are noticeable. First, the α-band in dioxane and chloroform largely shifts towards shorter wavelengths and almost completely loses vibrational structures. Secondly, the relative height of the two main peaks of the α-band markedly depends upon solvents such as carbon disulfide, benzene, ethyl ether etc. As for the first point, the blue-shift of the α-band in chloroform is attributed to hydrogen bond formation[6]. This fact verifies the assignment of the α-band to the $n-\pi^*$ transition band. The large blue-shift of the α-band in dioxane may be attributable to molecular complex formation. Here, dioxane is an n-type donor[7]. The blue-shift of an $n-\pi^*$ transition band due to molecular complex formation has never been pointed out. The mechanism of this blue-shift is thought to be similar to the one[8] due to the substitutions of electron-donating groups to a π-electronic system containing carbonyl groups. The fact that such a large blue-shift of the α-band as in dioxane is not seen in ethyl ether, may be attributable to the large steric hindrance caused by the side chains of ethyl ether in the molecular complex formation. As is seen from Figs. 1, 3, 4, 5 and 6, the blue-shift of the α-band in dioxane is much larger in the ortho-type quinones than in the para-type quinones***. This fact may be explained as follows. The oxygen atoms of dioxane are expected to coordinate themselves to carbon atoms of carbonyl groups of the quinones by the electrostatic interaction as well as by the charge transfer interaction. The electrostatic interaction is thought to be caused by the interaction between the atomic dipoles of the oxygen atoms of dioxane and the positive charges of the carbon atoms of the carbonyl groups. Hence, the magnitude of the electrostatic interaction is determined by the amount of the positive charges of the carbon atoms. The charge transfer interaction can be approximately represented by the interaction between the lowest unfilled orbitals of the quinones and the lone pair orbitals of the oxygen atoms of dioxane. Therefore, the magnitude of the charge transfer interaction is roughly determined by the coefficients of the atomic orbitals of the carbonyl carbon atoms in the lowest unfilled orbitals of the quinones. The greater those coefficients are, the greater is the charge transfer interaction. From our previous calculations[9] for o- and p-quinones, it is seen that the above two requirements are best fulfilled by the carbon atoms of the carbonyl groups of the quinones. The above requirements are also expected to be satisfied for AQ, which may be regarded as one of the o-quinones. Since in o-quinones the two carbon atoms of the two carbonyl groups are jointed with each other, the interaction between the oxygen atoms of dioxane and the carbonyl carbon atoms of o-quinones**** is expected to be larger than that of p-quinones. It is naturally expected that the above fact is ascribed to this point.

As for the second point previously described, there occurs a question whether the two main peaks of the α-band are ascribed to the vibrational structure of the one $n-\pi^*$ transition

5) E. Clar, "Aromatische Kohlenwasserstoffe" 1st Edn., Springer, Berlin (1941).
6) G. J. Brealey and M. Kasha, *J. Am. Chem. Soc.*, 77, 4462 (1955).
7) R. S. Mulliken, *J. Chem. Phys.*, 56, 801 (1952).
8) H. Baba, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 72, 341 (1951); S. Nagakura, This Bulletin, 25, 164 (1952).
*3 Previously, L. S. Forster found that the weak visible absorption band of biacetyl in dioxane shows relatively large shift towards shorter wavelengths (*J. Am. Chem. Soc.*, 77, 1417 (1955)). But this blue-shift is not so large as the ones of ortho-type quinones, here found.
9) a) A. Kuboyama, This Bulletin, 31, 752 (1958); b) A. Kuboyama, ibid., 32, 1226 (1959).

band, to the two different $n-\pi^*$ transition bands of the one form of AQ or to the two different $n-\pi^*$ transition bands belonging to the two different forms of AQ. As is seen in Fig. 2, the α-band in dioxane and in carbon disulfide are almost independent of temperature. Thus, the third possibility is probably denied. As is seen in Fig. 3, the behaviors of the two peaks in the longer wavelength side of β-naphthoquinone are, though less marked, similar to the ones of the two main peaks of the α-band of AQ and the distance (ca. 700 cm^{-1}) between the two peaks of β-naphthoquinone is almost equal to that of the α-band*****. Previously, J. W. Sidman[10] experimentally concluded that *p*-benzoquinone in crystalline state has two distinct singlet-singlet $n-\pi^*$ transition bands in the wave number region of 20000 cm^{-1} to 25000 cm^{-1}. In that case, the wave number difference between the two 0—0 bands corresponding to these two transitions was determined to be 797 cm^{-1}. In connection with Sidman's conclusion mentioned above, it[11] may safely be assumed that the two main peaks of the α-band may be due to the two $n-\pi^*$ transitions whose energy difference is ca. 700 cm^{-1}.

As is seen in Figs. 3, 5 and 6, in carbon disulfide the intensities of the $n-\pi^*$ transition bands of the quinones, especially of *p*-benzoquinone, are considerably larger than the ones in the other solvents. This fact is probably attributed to the large refractive index of carbon disulfide[12].

*4 The signs of the two atomic orbitals of the two carbonyl carbon atoms in the lowest unfilled orbitals of *o*-quinones[9b] are equal.

5 Forster[3] found the fact, similar to the one of β-naphthoquinone, for the n-π^* transition band of biacetyl, where the distance between the two peaks is ca. 1300 cm^{-1}. He thought that these two peaks respectively result from two electronic transitions.

10) J. W. Sidman *J. Am. Chem. Soc.* **78**, 2363 (1956).
11) H. L. McMurry, *J. Chem. Phys.*, **9**, 245 (1941).
12) N. Q. Chako, *J. Chem. Phys.*, **2**, 644 (1934).

Summary

The weak absorption band (α-band) ($\varepsilon_{max}\sim$ 20) near 500 mμ of acenaphthenequinone was measured in various solvents. This band was determined as the $n-\pi^*$ transition band on the basis of the observed results on intensity and solvent effect. In dioxane, the $n-\pi^*$ transition bands of the *o*-quinones, including the α-band, largely shift towards shorter wavelengths. This fact, which is thought to be due to molecular complex formation, was discussed from the qualitative point of view. The relative height of the two main peaks of the α-band markedly depends upon solvents. The similar, though less marked, fact is seen in β-naphthoquinone. The two main peaks of the α-band were assumed to be due to the two $n-\pi^*$ transitions, whose transition energy difference is ca. 700 cm^{-1}. It was found that the $n-\pi^*$ transition bands of the quinones, especially of *p*-benzoquinone, are markedly intensified in carbon disulfide. This fact is probably attributed to the large refractive index of this solvent.

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