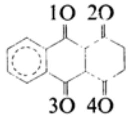
Electronic Spectra of 1, 4, 9, 10-Anthradiquinone and Its Complexes with Aromatics

By Akira Kuboyama and Kōichi Wada*

(Received July 30, 1964)

The electronic spectra of quinones and carbonyl compounds have previously been studied by one of the present authors.1) Moreover, Hartmann and Lorenz2) reported on the electronic spectrum of 1, 4, 9, 10-anthradiquinone3) in dioxane, together with the absorption spectra of many quinones. Except for these reports, however, the electronic spectrum of ADQ has never been studied. Since ADQ has four carbonyl groups in its conjugated system, as is shown below, its electronic spectrum and the charge-transfer absorption bands of ADQ complexes with aromatic compounds are of great interest to us. Accordingly, these spectra were studied. The results obtained will now be reported.



Experimental

Materials.—ADQ was synthesized by the cautious oxidation of quinizarin(1,4-dihydroxy-anthraquinone) with lead tetraacetate in acetic acid, according to the method of Dimroth et al.4) ADQ is so easily reduced to quinizarin that special caution is needed in its purification. Reddish-brown ADQ crystals dissolved in benzene at room temperature were separated from the solution by the addition of a large volume of isooctane. This procedure was repeated several times. The ADQ crystals obtained were straw-yellow needles. The melting point was consistent with that described in the literature.5) Commercially-available, special-grade hydroquinone dimethyl ether, pyrene, and anthracene were purified by recrystallization from ethanol. The solvents were purified according to the methods described in our previous works.1b,1d)

Measurements.—The absorption spectra were measured with a Cary 14M recording spectrophotometer with 1 and 5 cm.-path, fused quartz cells.

Results

After leaving ADQ one day after synthesis, we found in the electronic spectra of ADQ solutions a slight absorption band of quinizarin near 480mμ, an absorption which is characterized by a sharp vibrational structure in *n*-heptane. Therefore, each time ADQ was synthesized in the morning and the electronic spectra of its solutions were measured that afternoon. The electronic spectra of ADQ obtained in various solvents are shown in Figs. 1—4. The wavelengths (λ_{max}) and the molar absorption coefficients (ε_{max}) of the peaks of these spectra are shown in Table I. The wavelengths of the peaks of the charge transfer absorption bands6) of ADQ complexes with aromatic compounds in carbon tetrachloride

---

* On leave of absence from the Yokohama Custom House, Yokohama.

1) A. Kuboyama, a) This Bulletin, **31**, 752 (1958); ibid., **32**, 1226 (1959); ibid., **33**, 917 (1960). b) ibid., **33**, 1027 (1960); *Rep. Gov. Chem. Ind. Res. Inst., Tokyo*, **57**, 541 (1962). c) This Bulletin, **35**, 295 (1962). d) ibid., **37**, 1540 (1964).

2) H. Hartmann and E. Lorenz, *Z. Naturforsh.*, **7b**, 360 (1952).

3) In the following, 1,4,9,10-anthradiquinone is abbreviated as ADQ.

4) O. Dimroth, O. Friedmann and H. Kämmerer, *Ber.*, **53**, 484 (1920).

5) O. Dimroth and E. Schultze, *Ann.*, **A411**, 345 (1916).

6) In the following, the term "charge transfer absorption bands" is abbreviated as CT bands.

are shown in Table II, together with those of the complexes between other quinones and aromatic compounds which were obtained in our previous work.[7] In Table II, the values

TABLE. I. THE PEAKS IN THE ELECTRONIC SPECTRA OF ADQ IN VARIOUS SOLVENTS

Solvent	λ_{max} mμ	ε_{max}
Dioxane	592 344 227.5	22 2650 29800
Chloroform	596 363 232.5	20 2090 28900
Carbon tetrachloride	598 351	20 2080
Carbon disulfide	605	23

TABLE II.[a] THE CT BANDS OF THE QUINONE COMPLEXES IN CARBON TETRACHLORIDE

	Donor		
Acceptor	Hydroquinone dimethyl ether	Pyrene	Anthracene
α-Naphthoquinone		428(mμ) (2550)	435 (3050)
p-Benzoquinone	418 (3200)	448 (2350)	457 (2400)
Chloranil	545 (2700)	599 (2000)	623 (1880)
ADQ	559 (2810)	598 (2040)	620 (2010)

a) The values in parentheses are the distances (in wave number) between the peaks of the CT bands and the positions which situate on the longer wavelength sides of the peaks, and the intensities of which are one-half the intensities of the peaks.

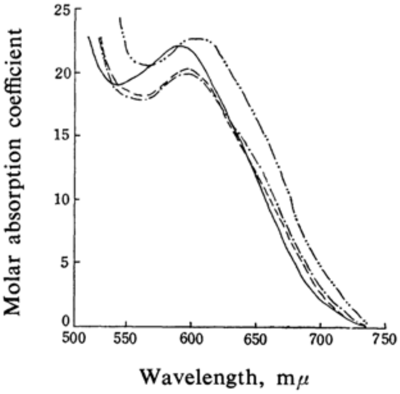


Fig. 1. ADQ, Solvent, —— Dioxane, - - - Chloroform, — - — Carbon tetrachloride, — - - - — Carbon disulfide.

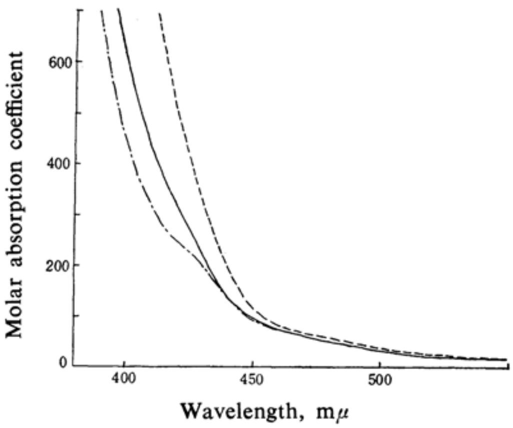


Fig. 2. ADQ, Solvent, —— Dioxane, - - - Chloroform, — - — Carbon tetrachloride.

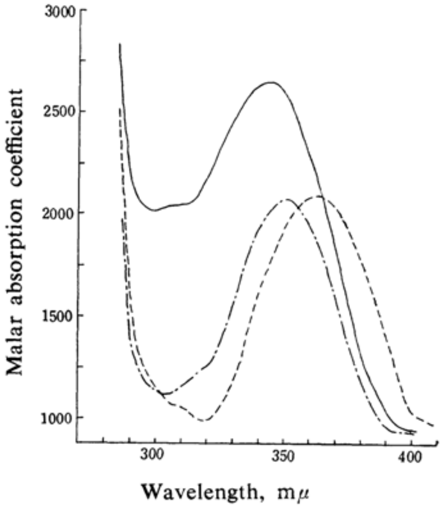


Fig. 3. ADQ, Solvent, —— Dioxane, - - - Chloroform, — - — Carbon tetrachloride.

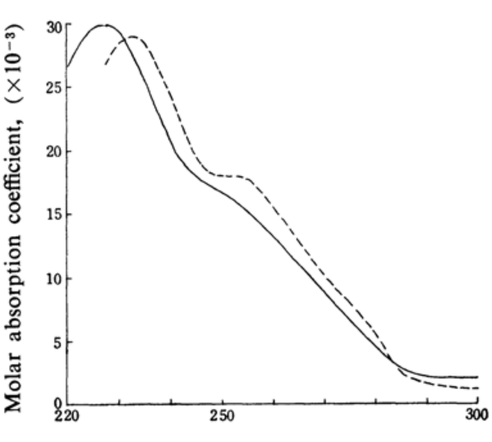


Fig. 4. ADQ, Solvent, —— Dioxane, - - - Chloroform, — - — Carbon tetrachloride.

---

[7] A. Kuboyama, a) *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 558 (1960); *Rep. Gov. Chem. Ind. Res. Inst., Tokyo*, **57**, 546 (1962). b) *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **83**, 375 (1962); *Rep. Gov. Chem. Ind. Res. Inst., Tokyo*, **85**, 1 (1964).

in parentheses are thought to be nearly parallel to the half-widths of the CT bands and to be representative of the broadness of the CT bands.

Discussion

Comparing Figs. 1—4 with the absorption spectrum reported by Hartmann and Lorenz,[2] two distinct differences between these two absorption spectra can be found. One is that, in the absorption spectrum reported by Hartmann and Lorenz, the weak absorption band near 600 mμ shown in Fig. 1 is not found. The other is that, in the absorption spectrum reported by them, an absorption band near 480 mμ ($\varepsilon_{max}\sim150$) is found, while in Fig. 2 no such absorption band is found. As has been described before, this absorption band near 480 mμ is thought to be that of quinizarin contained in ADQ.

The weak absorption band near 600 mμ in Fig. 1 may reasonably be assigned to an $n\rightarrow\pi^*$ band judging from its position and intensity. The fact that this band in carbon disulfide is found at longer wavelengths than in other solvents is characteristic of the $n\rightarrow\pi^*$ bands of the quinones, as has been studied in our previous work.[1b] From this fact, the band near 600 mμ may safely be assigned to an $n\rightarrow\pi^*$ band. The fact that this band in dioxane is found at shorter wavelengths than in other solvents may be attributed to the relatively strong charge transfer interaction between ADQ and dioxane.[1b] Indeed, as is shown in Table II, the CT bands of the ADQ complexes and of the chloranil complexes are at nearly the same position in a fixed electron-donor. Accordingly, the electron affinity of ADQ is thought to be nearly the same as that of chloranil, which is a strong electron-acceptor. The CT band of the ADQ complex with pyrene or anthracene is at almost the same position as that of the corresponding chloranil complex, while the CT band of the ADQ complex with hydroquinone dimethyl ether is at considerably longer wavelengths than that of the corresponding chloranil complex. This fact is thought to be due to the fact that the charge transfer interaction between ADQ and pyrene or anthracene is stronger than that between ADQ and hydroquinone dimethyl ether.[8] In Table II the values in parentheses which are representative of the broadness of the CT bands, in general become larger with an increase in the energies of the CT bands in a fixed electron-donor. The large values of this quantity in hydroquinone dimethyl ether in comparison with those ones in other electron-donors are thought to be related to the fact that the molecular structure of hydroquinone dimethyl ether is not so rigid because of the methoxyl groups not being fixed in this compound.

It is thought that ADQ has the four filled molecular orbitals, consisted of the lone pair orbitals of the four oxygen atoms, $((n_1+n_2)\pm(n_3+n_4)$ and $(n_1-n_2)\pm(n_3-n_4))$,[9] where n_i denotes the lone pair orbital of the i-th oxygen atom in ADQ. Therefore, it may be expected that ADQ will show some $n\rightarrow\pi^*$ bands except for the band near 600 mμ. In Fig. 2, the non-selective absorption band in the range from 550 mμ to 450 mμ is thought to contain some of these $n\rightarrow\pi^*$ bands. In Fig. 2, the spectrum of ADQ in carbon tetrachloride shows a shoulder near 425 mμ. In other solvents the corresponding shoulders are masked by the absorption bands at the shorter wavelengths. Therefore, the solvent effect for this shoulder cannot be examined, and it is difficult to determine whether this shoulder should be interpreted as an $n\rightarrow\pi^*$ band or not.

In Fig. 3 a distinct peak near 350 mμ and a slight shoulder near 310 mμ are found, while in Fig. 4 a shoulder near 255 mμ and a strong peak near 230 mμ are found. In Figs. 3 and 4, all the absorption bands except for the slight shoulder near 310 mμ are assigned to $\pi\rightarrow\pi^*$ bands on the basis of their large intensities. The shoulder near 310 mμ may be assigned to an $n\rightarrow\sigma^*$ band on the basis of its weak intensity. Regarding Fig. 3, two points should be noticed about the distinct absorption band near 350 mμ. First, this band in chloroform is found at far longer wavelengths than in other solvents. It is thought that this fact should be attributed mainly to the hydrogen bond formation between ADQ and chloroform. Second, the intensity of this band in dioxane is far larger than in other solvents. Since, as has been described before, ADQ is nearly as strong as chloranil as an electron-acceptor and since the CT band of the chloranil complex with dioxane is found near 330 mμ,[7a] the CT band of the ADQ complex with dioxane is also expected to appear near 330 mμ. Therefore, this CT band is thought to contribute much to the large intensity of the band near 350 mμ of ADQ in dioxane.

Summary

The electronic spectrum of 1, 4, 9, 10-anthradiquinone, and the charge transfer absorption bands of molecular complexes between

---

[8] A. Kuboyama, *J. Am. Chem. Soc.*, **86**, 164 (1964).

[9] The normalizing factor is omitted.

1, 4, 9, 10-anthradiquinone and aromatic compounds in solutions, have been studied. The weak absorption band near 600 mμ (ε_{max}~20) of 1, 4, 9, 10-anthradiquinone has been assigned to an $n \rightarrow \pi^*$ band. The charge transfer absorption bands of the molecular complexes are found at nearly the same positions as those of the corresponding chloranil complexes. From this fact it has been concluded that the electron affinity of 1, 4, 9, 10-anthradiquinone is nearly the same as that of chloranil.

Government Chemical Industrial
Research Institute, Tokyo
Shibuya-ku, Tokyo