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The Low-Energy π,π^* S-S Absorption Spectra of 1,4-Dimethyl- and 1,4-Dichloroanthraquinones

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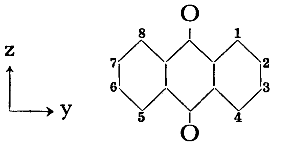
The very broad absorption band of 1,4-dichloroanthraquinone, which corresponds to the allowed ${}^1B_{2u}\pi,\pi^*$ band of anthraquinone (AQ), is shown to consist of two π,π^* bands with comparable intensities. The band which corresponds to the ${}^1A_g$ forbidden band of AQ is at longer wavelengths than the band corresponding to the ${}^1B_{2u}$ band of AQ. MO calculations were made, and MCD spectra and 77 K absorption spectra were measured. The very broad absorption band of 1,4-dimethyl-AQ can probably be similarly interpreted. The strong visible π,π^* bands of 1,4- and 1,5-disubstituted AQ's are shown to arise from the ${}^1A_g$ and ${}^1B_{2u}$ bands of AQ respectively.

In the π,π^* S-S absorption spectrum of anthraquinone (AQ) the ${}^1B_{2u}$ band near 330 nm is the only one so far found in the wavelength region longer than 300 nm.[1-3] According to the P-P-P method[4] calculations,[2,3] a forbidden ${}^1A_g$ level is predicted to be located close to this allowed ${}^1B_{2u}$ level. However, few experimental facts about this ${}^1A_g$ forbidden state have been reported.[5] Recently, we noticed that 1,4-dimethyl-AQ seems to show a rather intense band corresponding to the ${}^1A_g$ band on the longer wavelength side of the band corresponding to the ${}^1B_{2u}$ band, and that the P-P-P method calculations support this interpretation. We have therefore studied the π,π^* S-S absorption spectra of various symmetrically substituted dimethyl-AQ's and dichloro-AQ's in this wavelength region.



(AQ)

Experimental

Measurements. The absorption spectra were measured with a Cary 14 M recording spectrophotometer, using cyclohexane as solvent. A Dewar vessel and 1 mm-path cells[6] were used to obtain the absorption spectra at 77 K, using heptane as solvent. The magnetic circular dichroism (MCD) spectra were obtained by a J-40 circular dichroism spectrometer of the Japan Spectroscopic Co., Ltd.,[7] with a magnetic field of 3500 Gauss, using cyclohexane as solvent.

Materials. Commercially-available AQ was zone-refined (mp 286.6—287.2 °C). Commercially-available 1,4-dimethyl-AQ and 1-chloro-AQ were purified by vacuum sublimation (mp 141.0—142.0 °C and 159.0—160.5 °C). Commercially-available 2,3-dimethyl-AQ and 1,5-dichloro-AQ were twice recrystallized, from a toluene and cyclohexane (1:2) mixture and from acetic acid respectively (mp 207.5—208.8 °C and 243.3—244.0 °C). According to the method described in the literature,[8] 1,4-dichloro-AQ was synthesized, purified by liquid chromatography on alumina using toluene as developer, and obtained as yellow crystals[9] (mp 190.5—191.0 °C). Commercially-available heptane and cyclohexane of spectrograde quality were used.

Results. The absorption and MCD spectra obtained are shown in Figs. 1—4. The wavelengths and molar absorption coefficients of the absorption maxima in these absorption spectra are shown in Table 1. The MCD spectra were obtain-

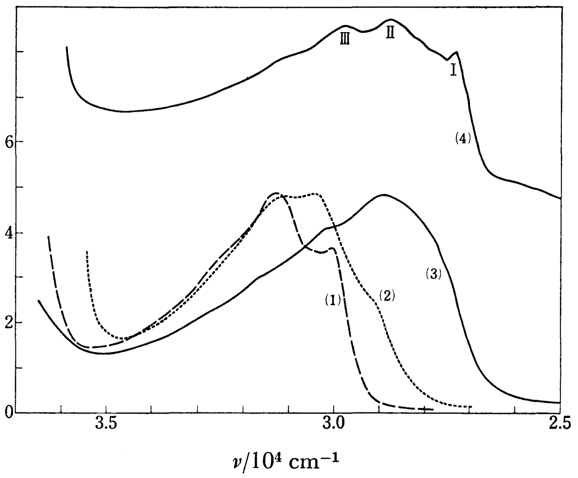


Fig. 1. Absorption spectra of AQ, 2,3-dimethyl-AQ, and 1,4-dimethyl-AQ in solutions.
1) AQ, 2) 2,3-dimethyl-AQ, 3) 1,4-dimethyl-AQ, 4) 1,4-dimethyl-AQ. Solvent: 1)—3) cyclohexane, 4) heptane. Temperature: 1)—3) room temperature, 4) 77K. The ordinates for 2) and 4) are arbitrary.

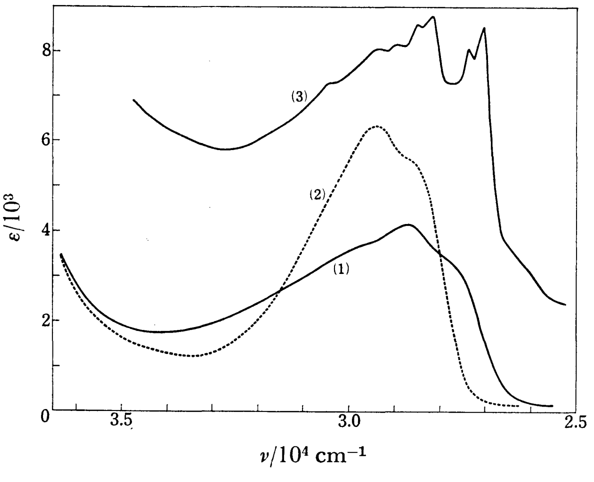


Fig. 2. Absorption spectra of 1,4-dichloro-AQ and 1,5-dichloro-AQ in solutions.
1) 1,4-Dichloro-AQ, 2) 1,5-dichloro-AQ, 3) 1,4-dichloro-AQ. Solvent; 1), 2) cyclohexane, 3) heptane. Temperature: 1), 2) room temperature, 3) 77 K. The ordinate for 3) is arbitrary.

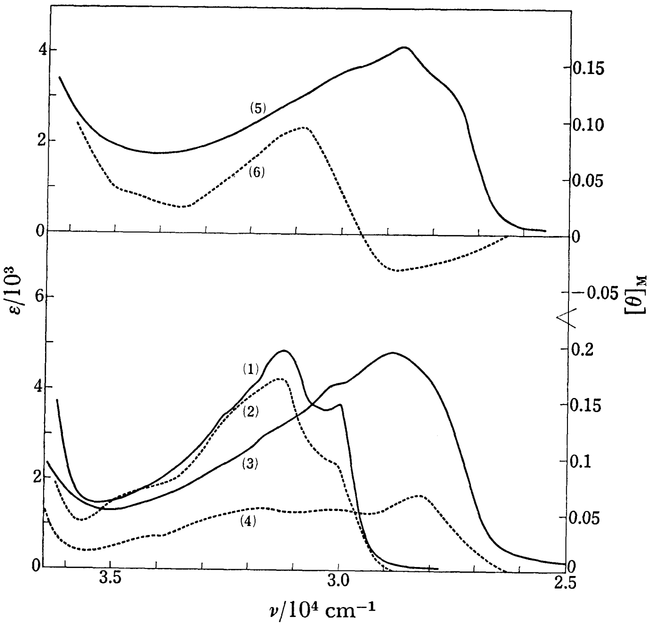


Fig. 3. Absorption and MCD spectra of AQ, 1,4-dimethyl-AQ, and 1,4-dichloro-AQ in the cyclohexane solutions.

1), 2) AQ, 3), 4) 1,4-Dimethyl-AQ, 5), 6) 1,4-Dichloro-AQ. The solid and dotted curves are the absorption and MCD spectra respectively, where the left and right side ordinates are used respectively.

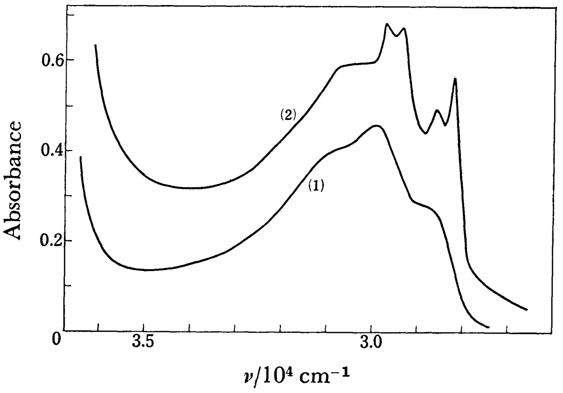


Fig. 4. Absorption spectra of 1-chloro-AQ in the heptane solutions.

1) Room temperature, 2) 77 K. The ordinate is arbitrary.

ed with a relatively high noise-level, because of using the low magnetic field. However, their accuracy is thought to be not so low as to affect the discussion in this work.

Calculations

Method. The electronic integral values for AQ in the P-P-P method[4)] were the same as those[3)] previously used. To account for the effect of methyl-group substitution, the core Coulomb integral of the substituted

Table 1. Wavelengths and molar absorption coefficients of the absorption maxima

	λ (nm)	ε	Solvent	Temperature
AQ	333	3680	Cyclohexane	Room temp
	320	4870		
	≈308			
1,4-Dimethyl-AQ	346	4850	Cyclohexane	Room temp
	≈331.5(sh)			
	366.5		Heptane	77 K
	347.5			
	336.5			
	320			
2,3-Dimethyl-AQ	≈344(sh)		Cyclohexane	Room temp
	328.5			
	321.5			
1,4-Dichloro-AQ	≈361.5(sh)		Cyclohexane	Room temp
	348	4120		
	≈337(sh)			
	369.5		Heptane	77 K
	354.5			
	350.5			
	346			
	340			
1,5-Dichloro-AQ	≈351(sh)		Cyclohexane	Room temp
	339.5	6330		
1-Chloro-AQ	≈349(sh)		Heptane	Room temp
	335			
	≈323(sh)			
	355		Heptane	77 K
	350			
	340.5			
	337			
	≈326(sh)			

Table 2. Calculated results for the dimethyl AQ's

	No.	Symmetry	E(eV)	f_y	f_z
AQ	1	^1A_g	4.17	0	0
	2	$^1B_{2u}$	4.25	0.081	0
	3	$^1B_{3g}$	4.42	0	0
1,4-Dimethyl-AQ	1	$^1A_1$	4.09	0.076	0
	2	$^1A_1$	4.22	0.075	0
	3	$^1B_2$	4.42	0	0.001
1,5-Dimethyl-AQ	1	^1A_g	4.13	0	0
	2	^1B_u	4.19	0.149	0.002
	3	^1A_g	4.43	0	0
1,8-Dimethyl-AQ	1	$^1A_1$	4.13	0	0.001
	2	$^1B_2$	4.19	0.148	0
	3	$^1B_2$	4.43	0.002	0
2,3-Dimethyl-AQ	1	$^1A_1$	4.17	0.000	0
	2	$^1A_1$	4.25	0.065	0
	3	$^1B_2$	4.35	0	0.044
2,6-Dimethyl-AQ	1	^1A_g	4.16	0	0
	2	^1B_u	4.25	0.065	0.011
	3	^1A_g	4.38	0	0
2,7-Dimethyl-AQ	1	$^1A_1$	4.17	0	0.000
	2	$^1B_2$	4.22	0.054	0
	3	$^1B_2$	4.39	0.003	0

carbon atoms was taken as −9.00 eV, considering only the inductive effect of the methyl group, as in the previous work.[3)] The core Coulomb integral and two-center electron repulsion integral of chlorine atoms and the core resonance integral of the C–Cl bonds were taken as −25.00, 14.30, and −0.75 eV respectively.[10)] In the calculations, the lowest thirty singly-excited configurations were included. The dimension of the AQ skeleton in the AQ derivatives was that of AQ.[3)] The bond length of the C–Cl bonds was assumed to be 1.75 Å.

Results. The calculated results for the three lowest-energy singlet excited states of AQ and the symmetrically substituted dimethyl-AQ's are shown in Table 2: the first column indicates the numbering of the states in order of increasing excitation energies (calculated). In Fig. 5, the calculated results for 1,4-dichloro-AQ, taking −0.75 and −1.50 eV for the core Coulomb integral values of the C–Cl bonds, are shown together with that for AQ.

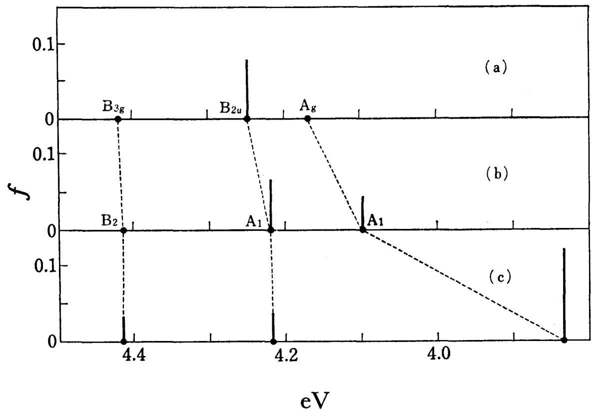


Fig. 5. Comparisons of the calculated excitation energies and oscillator strengths of the low-energy π,π^* states of AQ and 1,4-dichloro-AQ.
a) AQ, b) 1,4-dichloro-AQ (β(C–Cl) = −0.75 eV), c) 1,4-dichloro-AQ (β(C–Cl) = −1.50 eV).

Discussion

The absorption band of AQ in Fig. 1 has been theoretically and experimentally assigned to the $^1B_{2u}$ band by many authors.[1—3)] In the absorption band of 1,4-dimethyl-AQ in Fig. 1, the absorption maximum is at far longer wavelengths than those for AQ and 2,3-dimethyl-AQ, and the half-width (5170 cm^{-1}) is far larger than those for the latter (3850 and 4210 cm^{-1} respectively). In Fig. 2, the absorption spectrum of 1,4-dichloro-AQ, which is far broader than that of 1,5-dichloro-AQ, is similar to that of 1,4-dimethyl-AQ in position and shape. The absorption spectra of 1,8-dichloro-AQ[11)] and 2,6-dichloro-AQ[12)] reported by other authors in this wavelength region are similar to those of 1,5-dichloro-AQ and AQ respectively in position and shape. From these facts, it may be considered that in 1,4-dimethyl-AQ and 1,4-dichloro-AQ, a band corresponding to that ^1A_g band appears with a considerable intensity on the longer wavelength side of the band corresponding to the $^1B_{2u}$ band.

In Table 2, the three lowest-energy π,π^* states, the Nos. 1—3 states, of all the dimethyl-AQ's correspond to the Nos. 1—3 states of AQ: the ^1A_g, $^1B_{2u}$, and $^1B_{3g}$ states respectively. As may be seen in Table 2, only in 1,4-dimethyl-AQ does the No. 1 state have a relatively large oscillator strength; there its energy is considerably lower than that of the ^1A_g state of AQ. Similar calculated results were obtained for 1,4-dichloro-AQ. These calculated results support the above assignment of the π,π^* spectra of 1,4-dimethyl-AQ and 1,4-dichloro-AQ. In these two AQ's, on the basis of the calculated results, it has been proved that the excitations to the Nos. 1 and

2 states have the character of a charge-transfer from the carbon atoms of the 1- and 4-positions and the 5- and 8-positions, respectively, to the carbonyl groups.

In the absorption spectra of 1,4-dimethyl-AQ and 1,5-dichloro-AQ, the two $^1A_1$ bands corresponding to the excitations to the Nos. 1 and 2 states can not be discriminated by the usual dichroism measurements. In this work, therefore, their MCD spectra and that of AQ[13] in this wavelength region have been measured. Since these compounds have no electronic degenerate states, all the MCD spectra obtained are B-type.[13,14] In Fig. 3, the MCD spectrum of 1,4-dichloro-AQ consists of a negative and a positive band in the longer and shorter wavelength regions, respectively, while those of AQ and 1,4-dimethyl-AQ show only a positive spectrum. On the basis of these results, the absorption spectrum of 1,4-dichloro-AQ may be concluded to consist of two absorption bands, one of which is at longer wavelengths than the other. This result proves the previous assignment of the spectrum of 1,4-dichloro-AQ to be correct. On the other hand, the sign of the MCD in the longer wavelength region of the absorption spectrum of 1,4-dimethyl-AQ is opposite to that for 1,4-dichloro-AQ. In general, the MCD for originally forbidden bands may be expected to depend strongly on the substituents, as in the case of the L_b bands of benzene derivatives.[15] In 1,4-dimethyl-AQ, the calculated results show that the electron-donative inductive effect of the two methyl groups plays an important role in the intensity enhancement of the longer wavelength $^1A_1$ band. On the other hand, in 1,4-dichloro-AQ, the calculated results show that the electron-attractive resonance effect of the two chlorine atoms does so. Therefore, this difference of the electronic property between these two substituents may be expected to bring about the above mentioned difference of the MCD sign.

In the absorption spectra of 1,4-dichloro-AQ (Fig. 2) and 1-chloro-AQ (Fig. 4) in the heptane solutions at 77 K, four sharp peaks[16] are observed in the longer wavelength region; they may be assigned to the $^1A_1$ band corresponding to the ^1A_g band of AQ. In the absorption spectrum of 1-chloro-AQ in the heptane solution at room temperature (Fig. 4), therefore, the shoulder on the longer wavelength side may also be assigned in the same way. In the absorption spectrum of 1,4-dimethyl-AQ at room temperature (Fig. 1), a small but relatively sharp shoulder is observed near 330 nm on the broad absorption curve; this may be considered to belong to the $^1A_1$ band corresponding to the $^1B_{2u}$ band of AQ. This peak may correspond to Peak III in the 77 K spectrum (Fig. 1), and the sharp Peak I in the latter spectrum may be considered to belong to the $^1A_1$ band corresponding to the ^1A_g band of AQ, as in the case of 1,4-dichloro-AQ. On the basis of the theoretically and experimentally obtained results for the absorption spectrum of 1,4-dimethyl-AQ, it may be considered that the assignment of that spectrum is also likely to be correct.

In Fig. 5, an increase of the absolute value of the core Coulomb integral of the C–Cl bonds means an increase of the electron-donative power of the chlorine atoms. In 1,4-dichloro-AQ (Fig. 5), the lower $^1A_1$ level (the No. 1 level) drops significantly and its oscillator strength becomes strikingly larger, with an increase in the absolute value of that integral, while the higher $^1A_1$ level (the No. 2 level) shows almost no change and its oscillator strength becomes considerably smaller. On the other hand, in 1,5-dichloro-AQ, the ^1A_g levels are the forbidden levels, and the ^1B_u level drops considerably and its oscillator strength becomes markedly larger with an increase in the absolute value of that integral. On the basis of these calculated results, the strong π,π^* bands of 1,4-dihydroxy-AQ[17] and 1,4-diamino-AQ[18,19] and 1,5-dihydroxy-AQ[17] and 1,5-diamino-AQ[18] in the visible range may be concluded to arise from the $^1A_g \leftarrow {}^1A_g$ and $^1B_{2u} \leftarrow {}^1A_g$ transitions of AQ respectively, and the relatively weak π,π^* bands of 1,4-dihydroxy-AQ and 1,4-diamino-AQ near 330 nm to arise from the $^1B_{2u} \leftarrow {}^1A_g$ transition of AQ. This conclusion about the spectra of these 1,4-disubstituted AQ's is consistent with the polarized absorption spectra of 1,4-diamino-AQ reported by Inoue *et al.*[19] and Labhart.[20]

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