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The Polarized Absorption Spectra of Some α-Aminoanthraquinones

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The π–π^* electronic absorption spectra of 1-amino-, 1,4-diamino-, and 1,4,5,8-tetraaminoanthraquinones were investigated by means of the polarized absorption spectra using stretched PVA sheets and theoretical calculations. Each of these compounds has four absorption bands in the near-ultraviolet region (210—340 nm) and one in the visible region. The bands of the aminoanthraquinones which appear in the visible region can be assigned to the intramolecular charge-transfer transitions associated with the charge migration from the amino group to the carbonyl groups.

In a previous paper,[1] the polarized absorption spectra of sodium anthraquinonesulfonates were measured in stretched PVA sheets, and the polarization directions of the bands of anthraquinone and its sulfonates were discussed. It has been found that anthraquinone has four π–π^* absorption bands above 220 nm. The positions and the polarization directions of the bands are as follows; 324 nm (x-polarization), 272 nm (y-), 252 nm (x-), and about 249 nm (y-), where the y- and x-axes are, respectively, parallel and perpendicular to the C=O bond axis of the molecule.

It has been established that the substituted anthraquinones with electron-donating groups, such as hydroxyl or amino groups, have bands in the visible region.[2,3] For instance, Kuboyama and Wada[2] have measured the absorption spectra of several hydroxyanthraquinones; the visible band of each hydroxyanthraquinone corresponded to the 324 nm band of anthraquinone. Labhart[3] has measured the polarized absorption spectra of several aminoanthraquinones under an external electric field and has determined the polarization direction of each band. According to his results, the visible band at 564 nm of 1,4-diaminoanthraquinone is polarized along the x-axis of the molecule.

In the present paper, the electronic absorption spectra of 1-aminoanthraquinone, 1,4-diaminoanthraquinone, and 1,4,5,8-tetraaminoanthraquinone were studied by means of the polarized absorption spectra using stretched PVA sheets and of theoretical calculations.

Method of Calculation

The method of the calculation was the same as that in our previous works,[4–6] that is, the Pariser-Parr-Pople method[7–9] with a variable β approximation. The resonance integrals, β_{rs}'s, were adjusted at every iteration of the SCF calculations by means of the following equations:

$$\beta_{CC} = -1.84 - 0.51p_{CC}$$
$$\beta_{CN} = -2.02 - 0.53p_{CN}$$
$$\beta_{CO} = -2.20 - 0.56p_{CO}$$

where p_{rs} is a bond order between the r and s atoms. The valence-state ionization potentials, $I_p(r)$'s, and the electron affinities, $E_a(r)$'s, for carbon, nitrogen, and oxygen atoms were taken as:

$$I_p(\mathrm{C}) = 11.42\ \mathrm{eV}, \quad E_a(\mathrm{C}) = 0.58\ \mathrm{eV}$$
$$I_p(\mathrm{N}) = 25.00\ \mathrm{eV}, \quad E_a(\mathrm{N}) = 10.0\ \mathrm{eV}$$
$$I_p(\mathrm{O}) = 17.32\ \mathrm{eV}, \quad E_a(\mathrm{O}) = 2.65\ \mathrm{eV}.$$

The geometries of anthraquinone and its derivatives are shown in Fig. 1, in which the interatomic distances in the anthraquinone skeleton are taken from the results of the X-ray analysis by Sen[10]; all the valence angles are assumed to be 120°.

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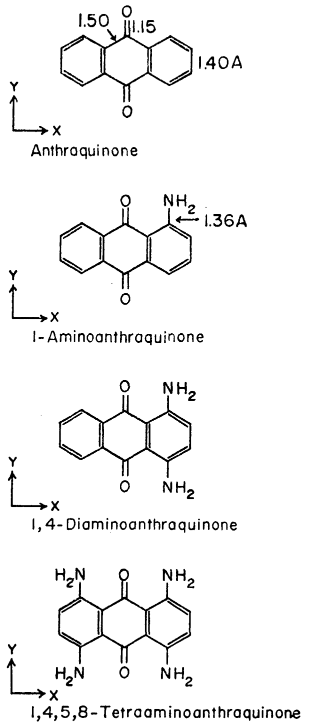

Fig. 1. The geometries of the molecules.

Experimental

Materials. All the anthraquinone derivatives used here were offered by Dr. Kou Naiki of the Tokyo Institute of Technology. The PVA (polyvinyl alcohol) powder used for the preparation of the sheets was obtained commercially (Nippon Gosei Co., Ltd., NM-14) and was used without further purification.

Measurements of the Polarized Absorption Spectra. The polarized absorption spectra using stretched PVA sheets were measured by the method already described.[1]

Notations. $D_{\parallel}$ and $D_{\perp}$: absorbances measured with the incident light polarized, respectively, parallel and perpendicular to the stretched direction of the PVA sheet. *Rd*: ratio between $D_{\parallel}$ and $D_{\perp}$, $D_{\parallel}/D_{\perp}$. R_s: degree of stretching of the sheet. θ: orientation angle, which indicates the angle between a transition moment and the orientation axis of a molecule.

Results and Discussion

The absorption spectra of 1-amino-, 1,4-diamino-, and 1,4,5,8-tetraaminoanthraquinone are shown in Fig. 2, in which the spectrum of anthraquinone is also shown for the sake of comparison. As has been described in a previous paper,[1] anthraquinone has four absorption bands, at 324 nm, 272 nm, 252 nm, and about 230 nm, which are polarized along the x-, y-, x-, and y-axes respectively, where the x- and y-axes are respectively perpendicular and parallel to the C=O bond axis of the molecule. In the case of the aminoanthraquinones studied here, there are four absorption bands in the near-ultraviolet region and one in the visible region. The former four bands may correspond to those of anthraquinone described above.

Figure 3 shows the polarized absorption spectra of 1-aminoanthraquinone in the stretched PVA sheets.

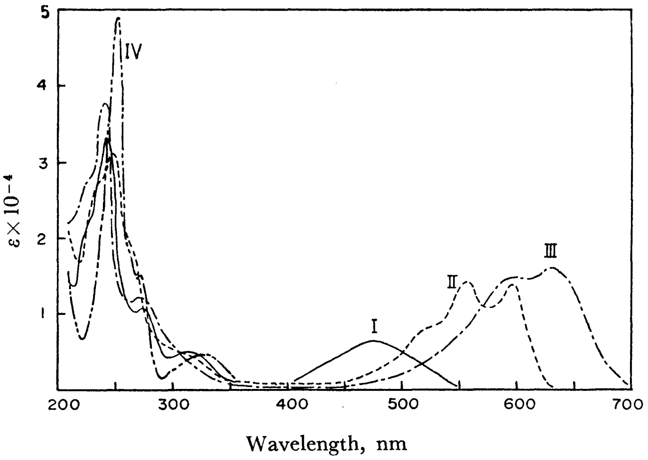

Fig. 2. The absorption spectra of 1-aminoanthraquinone (I), 1,4-diaminoanthraquinone (II), 1,4,5,8-tetraaminoanthraquinone (III), and anthraquinone (IV) in ethanol.

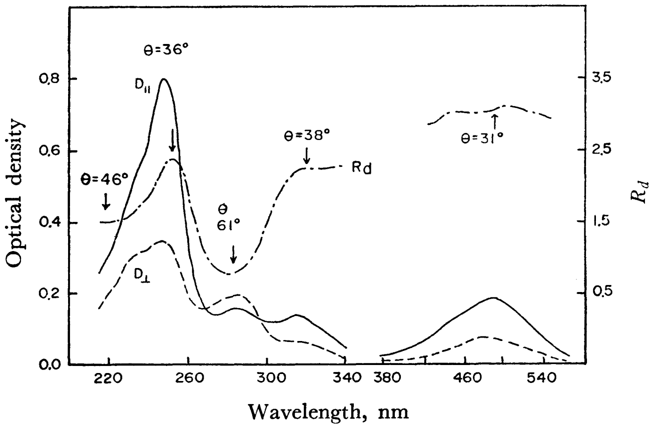

Fig. 3. The polarized absorption spectra of 1-aminoanthraquinone. (R_s=5.8)

From the behavior of the R_d curve, it is clear that the absorption spectrum of this compound consists of five bands in the observed wavelength region. They appear at 490 nm, 315 nm, 282 nm, 248 nm, and 235 nm; the orientation angles of these bands are 31°, 38°, 61°, 36°, and 46° respectively. As has been predicted above, the latter four bands can correspond to those of anthraquinone, because the behavior of the R_d curve in the region of 210—340 nm (Fig. 3) is very similar to that of anthraquinone.[1] A band corresponding to the 490 nm band of 1-aminoanthraquinone is not observed in the case of anthraquinone. The polarization direction of the 490 nm band seems to be almost parallel to those of the 315 nm and 248 nm bands.

These experimental results are compared with the theoretical ones in Table 1. From the comparison of the observed positions of the bands, the relative intensities, and the orientation angles with the theoretical results, the observed bands at 490 nm, 315 nm, 282 nm, 248 nm, and 235 nm can assigned to the calculated transitions, I, II, IV, VII, and VIII respectively. From the polarized absorption spectra obtained using stretched PVA sheets, we can not determine the precise polarization direction of each band unless the orien-

Table 1. The calculated results for 1-aminoanthraquinone

	Transition energy				Oscillator strength	Polarization direction against x-axis
	Calcd		Obsd		Calcd	Calcd
	eV	(nm)	eV	(nm)		
I	3.06	(405)	2.53	(490)	0.2222	3°
II	3.97	(313)	3.90	(315)	0.0528	2°
III	3.99	(311)			0.0028	−41°
IV	4.40	(282)	4.40	(282)	0.1224	−80°
V	4.59	(270)			0.0923	63°
VI	4.73	(262)			0.4501	80°
VII	5.08	(244)	5.00	(248)	0.5546	−5°
VIII	5.35	(232)	5.28	(235)	0.1882	−89°
IX	5.47	(227)			0.2416	16°
X	5.63	(220)			0.1397	87°
XI	5.74	(216)			0.3919	−20°
XII	6.05	(205)			0.0463	70°

Table 2. The relative polarization directions against the polarization direction of the 490 nm band

	Relative polarization	
	Obsd	Calcd
the 314 nm band	7°	1°
the 282 nm band	92°	97°
the 248 nm band	5°	8°
the 235 nm band	77°	88°

tation axis of the molecule is known. However, the relative polarization directions between two bands may be given by the sum or remainder of the two orientation angles.[11] Thus, the relative polarization directions in relation to the polarization direction of the 490 nm band are found to be as is shown in Table 2. These results are in good agreement with those of the theoretical calculations.

Figure 4 shows the polarized absorption spectrum of 1,4-diaminoanthraquinone. It is clear that this molecule has five absorption bands, at 600 nm, 320 nm, 280 nm, 255 nm, and 235 nm, and that their orientation angles are 34°, 52°, 58°, 41°, and 51° respectively. Since this molecule seems to belong to the C_{2v} point group, each π-π^* electronic transition should be polarized along the x- or y-axis of the molecule. As in the case of the anthraquinonesulfonates described in a previous paper, the x-axis of this molecule is preferentially oriented in the stretched direction of the PVA sheet; this implies that the R_d values of the x-axis polarized bands are larger than those of the y-axis polarized ones. Therefore, it is found that the 600 nm, 320 nm, and 255 nm bands are polarized along the x-axis, and the 280 nm and 235 nm bands, along the y-axis. The 600 nm band may consists of a single electronic band, since this band is isolated from the other bands; the R_d values of this band are almost constant. The sum of the orientation angles of the 600 nm and the 280 nm bands is nearly a right angle (92°), so the 280 nm band may be regarded as being almost pure, whereas the 320 nm and 255 nm bands are overlapped with other ones respectively, because the orientation angles of these bands are smaller than that of the 600 nm band.

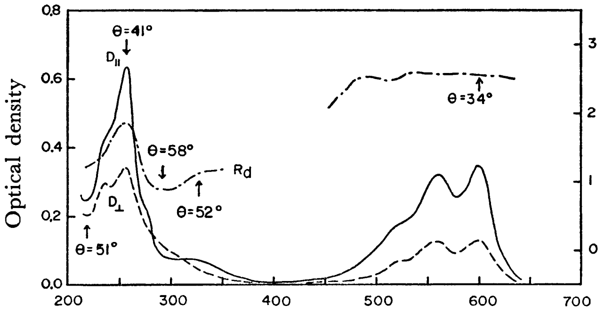

Fig. 4. The polarized absorption spectra of 1,4-diaminoanthraquinone. ($R_s=5.1$)

These experimental results are compared with the calculated results in Table 3. The observed 600 nm, 320 nm, 280 nm, 255 nm, and 235 nm bands can be assigned to, respectively, the calculated transitions I, III, V, IX, and XI.

The polarized absorption spectrum of 1,4,5,8-tetra-

Table 3. The calculated results for 1,4-diaminoanthraquinone

	Transition energy				Oscillator strength	Polarization direction against x-axis
	Calcd		Obsd		Calcd	Calcd
	eV	(nm)	eV	(nm)		
I	2.59	(479)	2.07	(600)	0.3062	0° (x)
II	3.77	(329)			0.0041	90° (y)
III	4.00	(310)	3.88	(320)	0.0330	0° (x)
IV	4.18	(297)			0.0062	0° (x)
V	4.20	(295)	4.43	(280)	0.0198	90° (y)
VI	4.48	(277)			0.2614	90° (y)
VII	4.67	(266)			0.0120	90° (y)
VIII	4.94	(251)			0.6774	90° (y)
IX	5.11	(243)	4.86	(255)	0.6270	0° (x)
X	5.39	(230)			0.2231	0° (x)
XI	5.66	(219)	5.28	(235)	0.1534	90° (y)
XII	5.94	(209)			0.1895	0° (x)
XIII	5.99	(207)			0.0947	90° (y)

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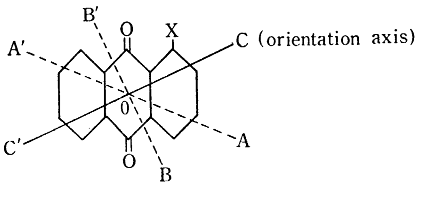
[11] If the directions of the transition moments of two bands of a molecule are represented by $\overrightarrow{AA'}$ and $\overrightarrow{BB'}$, the relative polarization direction between the two bands is expressed by ∠AOB′ or ∠AOB. The former angle (∠AOB′) is given by the sum of two orientation angles (∠AOC+∠COB′), whereas the latter angle (∠AOB) is given by the difference between the two orientation angles (∠BOC−∠AOC), where $\overrightarrow{CC'}$ represents the orientation axis of the molecule.



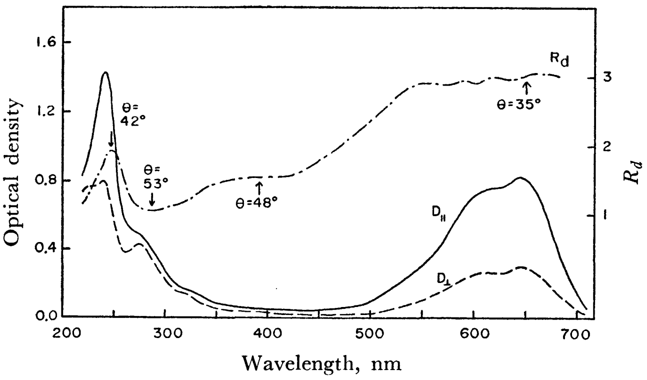


Fig. 5. The polarized absorption spectra of 1,4,5,8-tetraaminoanthraquinone. (R_S=9.6)

Table 4. The calculated results for 1,4,5,8-aminoanthraquinone

	Transition energy				Oscillator strength Calcd	Polarization direction against x-axis Calcd
	Calcd		Obsd			
	eV	(nm)	eV	(nm)		
I	2.48	(501)	1.92	(645)	0.5058	0° (x)
II	2.88	(430)			0.0000	
III	3.71	(334)			0.0000	
IV	4.12	(301)			0.0000	
V	4.14	(300)			0.0155	90° (y)
VI	4.31	(288)			0.0000	
VII	4.36	(285)	3.82	(325)	0.0005	0° (x)
VIII	4.72	(263)	4.51	(275)	0.7761	90° (y)
IX	4.85	(256)			0.0000	
X	5.18	(239)	5.39	(230)	0.6934	90° (y)
XI	5.27	(235)			0.0000	
XII	5.38	(230)	5.06	(245)	0.9103	0° (x)
XIII	5.64	(220)			0.0000	

aminoanthraquinone is shown in Fig. 5. From the features of the absorption and R_d curves, in this case also, the absorption bands corresponding with those of the above compounds are found at 645 nm (x-axis polarized), 325 nm (x), 275 nm (y), 245 nm (x), and 230 nm (y).

The calculated results are tabulated in Table 4. The observed 645 nm (x), 325 nm (x), 275 nm (y), 245 nm (x), and 230 nm (y) bands are assigned to, resectively, the calculated transitions I, VII, VIII, XII, and X.

As has been described above, the electronic spectra of aminoanthraquinones consist of four bands in the near-ultraviolet region and one in the visible region; the former four bands correspond well to those of anthraquinone.

Table 5. The first excited state wave functions of 1-amino-, 1,4-diamino-, and 1,4,5,8-tetraaminoanthraquinone

1-Aminoanthraquinone

$$\Psi_\mathrm{I}=0.0054\phi_{5,10}+0.0407\phi_{5,11}-0.0100\phi_{5,12}-0.0226\phi_{5,13}$$
$$-0.0149\phi_{5,14}+0.0435\phi_{6,10}-0.0043\phi_{6,11}+0.0344\phi_{6,12}$$
$$+0.0069\phi_{6,13}-0.0054\phi_{6,14}+0.0189\phi_{7,10}+0.0497\phi_{7,11}$$
$$+0.0108\phi_{7,12}-0.0762\phi_{7,13}+0.0116\phi_{7,14}-0.0684\phi_{8,10}$$
$$-0.0795\phi_{8,11}+0.0042\phi_{8,12}+0.1389\phi_{8,13}-0.0074\phi_{8,14}$$
$$-0.9535\phi_{9,10}+0.0844\phi_{9,11}+0.1667\phi_{9,12}-0.0412\phi_{9,13}$$
$$-0.0054\phi_{9,14}$$

1,4-Diaminoanthraquinone

$$\Psi_\mathrm{I}=0.0643\phi_{6,12}-0.0617\phi_{6,14}-0.0361\phi_{7,11}-0.0334\phi_{7,13}$$
$$+0.0076\phi_{7,15}+0.0106\phi_{8,12}-0.0446\phi_{8,14}-0.0395\phi_{9,12}$$
$$+0.1134\phi_{9,14}-0.9777\phi_{10,11}+0.1302\phi_{10,13}$$
$$-0.0136\phi_{10,15}$$

1,4,5,8-tetraaminoanthraquinone

$$\Psi_\mathrm{I}=0.0773\phi_{8,14}-0.0735\phi_{9,14}-0.0907\phi_{10,16}-0.1580\phi_{11,15}$$
$$+0.9774\phi_{12,13}-0.0111\phi_{12,17}$$

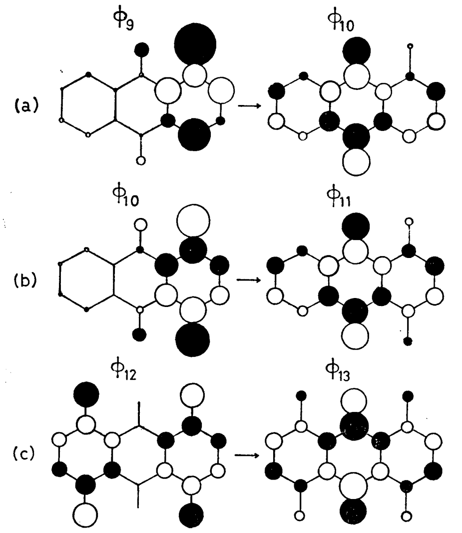


Fig. 6. The coefficients for the MO's.
(a): 1-aminoanthraquinone, (b): 1,4-diaminoanthraquinone, (c): 1,4,5,8-tetraaminoanthraquinone

Table 5 shows the first excited state wave functions, Ψ's, of 1-amino-, 1,4-diamino-, and 1,4,5,8-tetraaminoanthraquinone. The Ψ_I of 1-aminoanthraquinone can be approximately represented by $\phi_{9,10}$; that of 1,4-diaminoanthraquinone, by $\phi_{10,11}$, and that of 1,4,5,8-tetraaminoanthraquinone, by $\phi_{12,13}$. The coefficients of the wave functions associated with these configurations are shown pictorially in Fig. 6. From this figure, it may be concluded that the transitions, I, of these compounds are to be assigned to the intramolecular charge-transfer transitions from the amino groups to the carbonyl groups.