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The Polarized Absorption Spectra of Some β-Substituted Anthraquinones

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The polarized absorption spectra of 2-hydroxy-, 2-amino-, and 2,3-diaminoanthraquinones were measured in stretched PVA sheets below 47 kK, and semiempirical ASMO-SCF-CI calculations, including the variable β method, were carried out for these compounds. By a comparison of the observed and the calculated results, the π–π^* bands of these compounds were assigned. Each of these compounds has six bands in the observed wave number region, four of which correspond to those of anthraquinone; the other two bands can be assigned to the intramolecular charge-transfer transitions.

In a previous paper,[1] we measured the polarized absorption spectra of the α-aminoanthraquinones and discussed the assignment of the electronic bands of these compounds. For instance, it has been found that 1-aminoanthraquinone has five absorption bands, at 20.4, 31.8, 35.5, 40.3, and 42.6 kK, in a PVA sheet. From the comparison of the observed and calculated results, the latter four bands have been found to correspond to those of anthraquinone,[2] and the band at 20.4 kK has been assigned to the intramolecular charge-transfer transition associated with a charge migration from the amino group to the carbonyl groups. The polarization direction of the charge-transfer transition was found to be along the C=O bond axis.

Also, in the case of β-substituted anthraquinone with a hydroxyl or amino group, the intramolecular charge-transfer transition is expected to occur. However, its polarization direction may be different from that of the corresponding α-substituted anthraquinone.

In the present paper, the electronic absorption spectra of 2-hydroxy-, 2-amino-, and 2,3-diaminoanthraquinones are studied by means of the polarized absorption spectra and theoretical calculations.

Experimental

Materials. The anthraquinone derivatives used here were kindly presented to us by Dr. Mitsuhiko Hida of The University of Tokyo. The PVA sheets were prepared from the commercially-available powder (mean degree of polymerization, 1500).

Measurements of the Polarized Absorption Spectra and Notations. The methods of the determination and analysis of the polarized absorption spectra were the same as have been described elsewhere.[3] The notations used in the figures are as follows:

$D_{\parallel}$ and $D_{\perp}$: Absorbances measured for incident light polarized parallel to and perpendicular to the stretched direction of the PVA sheet respectively.

R_d: Ratio between $D_{\parallel}$ and $D_{\perp}$, $D_{\parallel}/D_{\perp}$.

R_s: Degree of stretching of the PVA sheet.

θ: Orientation angle for a transition moment of a band, which can be calculated from the values of R_d and R_s; it indicates an angle between the transition moment and the orientation axis of a molecule.

Method of MO Calculation

We have used the semiempirical ASMO–SCF–CI method[4,5] with the variable β approximation.[6] The

1) H. Inoue, T. Hoshi, J. Yoshino, and Y. Tanizaki, This Bulletin, **45**, 1018 (1972).

2) H. Inoue, T. Hoshi, and Y. Tanizaki, *Nippon Kagaku Zasshi*, **92**, 501, (1971).

3) Y. Tanizaki and S. Kobudera, *J. Mol. Spectry.*, **24**, 1 (1967); Y. Tanizaki, This Bulletin, **38**, 1798 (1965); H. Inoue, T. Hoshi, T. Masamoto, J. Shiraishi, and Y. Tanizaki, *Ber. Bunsenges. Phys. Chem.*, **75**, 441 (1971); T. Hoshi, H. Inoue, J. Shiraishi, and Y. Tanizaki, This Bulletin, **44**, 1743 (1971).

4) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

5) J. A. Pople, *Proc. Phys. Soc.* (London), **A68**, 81 (1955).

6) K. Nishimoto and L. S. Forster, *Theoret. Chem. Acta*, **3** 407 (1965).

resonance integrals, β_{rs}'s, were adjusted at every iteraction of the SCF calculations by using the following equations:

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

where P_{rs} is a π bond order between the r and s atoms. The one-center repulsion integrals were evaluated by use of the following valence-state ionization potentials (I_p(r)) and the electron affinities (E_a(r)):

I_p(C) = 11.42 eV, E_a(C) = 0.58 eV
I_p(N) = 25.00 eV, E_a(N) = 10.00 eV
I_p(O) = 17.32 eV, E_a(O) = 2.65 eV.

The two-center repulsion integrals were obtained from the Nishimoto-Mataga equation.[7] All singly-excited configurations associated with the transitions between each of the five highest occupied levels and each of the five lowest vacant levels were taken into account in the CI calculations.

Results and Discussion

Figure 1 shows the absorption spectra of 2-hydroxy-, 2-amino-, and 2,3-diaminoanthraquinones in ethanol solutions. The spectrum of anthraquinone is also shown for comparison. By comparing each spectrum of the β-substituted anthraquinones with that of anthraquinone, we can find an additional band in the visible region for the β-substituted anthraquinone. Moreover, an additional band may exist also in the near-ultraviolet region, because the absorption curve in this region is intricate in shape compared with the absorption curve of anthraquinone. In contrast with the present cases, α-aminoanthraquinones have one additional band in the visible region.[1]

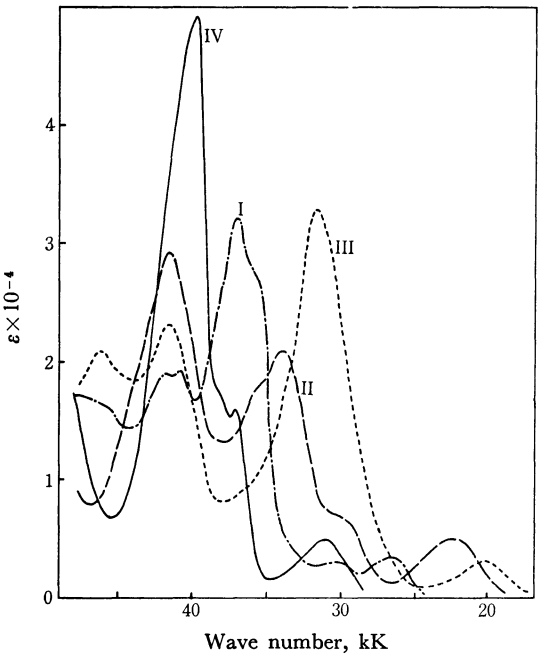

Fig. 1. Absorption spectra in ethanol solutions.
I: 2-Hydroxyanthraquinone, II: 2-Aminoanthraquinone, III: 2,3-Diaminoanthraquinone, IV: Anthraquinone

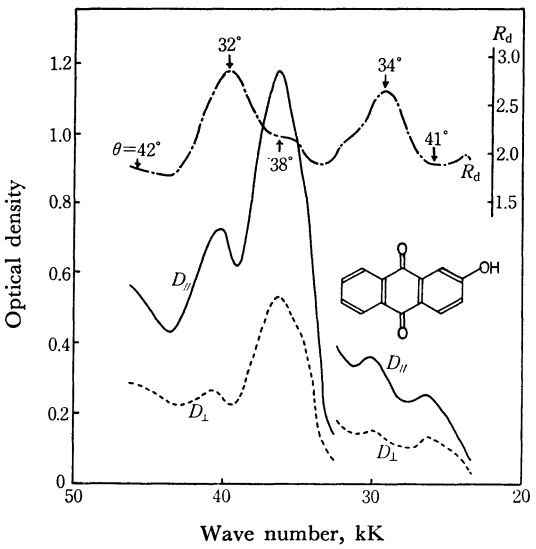

Fig. 2. The polarized absorption spectrum of 2-hydroxyanthraquinone. (R_s=5.8)

Figure 2 shows the polarized absorption spectrum of 2-hydroxyanthraquinone. From the features of the R_d and absorption curves, it is found that the compound has six absorption bands, at 26.3, 30.0, 34.5 (shoulder), 36.2, 40.3, and around 46 kK.

The observed results are compared with the calculated results in Table 1. A band corresponding to the calculated II transition is not found in the polarized absorption spectra. In the case of anthraquinone,[2] the corresponding band is observed around 32 kK. The calculated polarization directions of the III, V, and VI transitions are nearly along the X-axis of the molecule, and that of the IV transition is nearly along the Y-axis (Fig. 3). These results explain well the polarized absorption spectrum of this molecule. As in the cases of anthraquinonesulfonates and α-aminoanthraquinone,[1,2] a band polarized along the long axis of a molecule should have relatively large R_d values. Therefore, it is considered that the 30.0, 36.2, and 40.3 kK bands, with large R_d values, are polarized nearly along the X-(long) axis of the molecule, and that the 26.3, 34.5, and 46 kK bands, with small R_d values, are polarized along the Y-(short) axis.

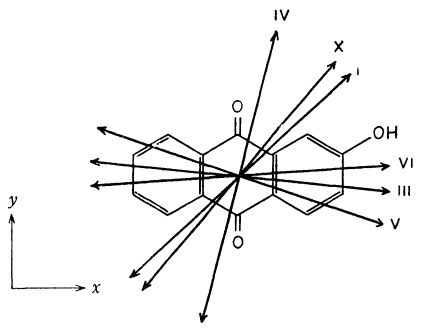

Fig. 3. The calculated polarization directions for 2-hydroxyanthraquinone.

7) N. Mataga and K. Nishimoto, *Z. Phys. Chem. N.F.*, **13**, 140 (1957).

Table 1. Comparison of the observed and the calculated results for 2-hydroxyanthraquinone

	Calcd			Obsd
	Transition energy (kK)	Oscillator strength	Polarization direction[a]	Transition energy (kK)
I	28.3	0.1372	43°	26.3
II	31.2	0.0503	−11°	
III	31.6	0.0384	−6°	30.0
IV	35.0	0.4371	76°	34.5
V	38.0	0.6976	−19°	36.2
VI	40.6	0.3389	4°	40.3
VII	42.2	0.0187	22°	
VIII	44.9	0.0789	77°	
IX	45.2	0.0193	−60°	
X	46.1	0.2473	50°	~46

a) The angle against the X-axis.

Table 2. Comparison of the observed and the calculated results for 2-aminoanthraquinone

	Calcd			Obsd
	Transition energy (kK)	Oscillator strength	Polarization direction[a]	Transition energy (kK)
I	26.5	0.1706	46°	21.7
II	30.8	0.0054	−40°	
III	31.6	0.0877	−6°	29.6
IV	34.7	0.3932	62°	34.6
V	36.9	0.7064	−26°	32.7
VI	40.1	0.2915	22°	40.6
VII	40.9	0.1542	−13°	
VIII	43.0	0.0321	4°	
IX	44.2	0.0199	54°	
X	45.0	0.1029	81°	~46
XI	46.8	0.4183	47°	

a) The angle against the X-axis.

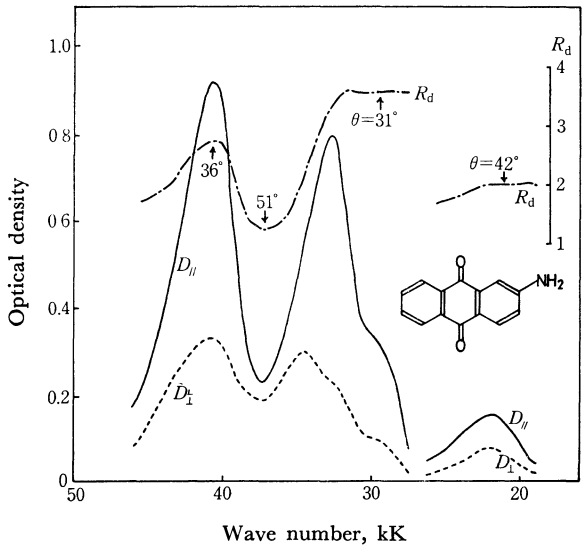

Fig. 4. The polarized absorption spectrum of 2-aminoanthraquinone. (R_s=9.0)

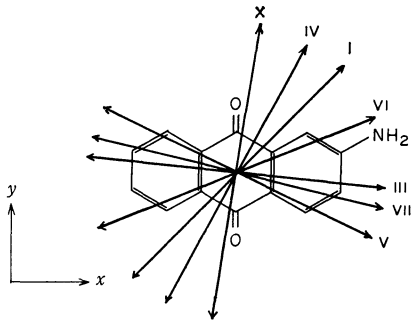

Fig. 5. The calculated polarization directions for 2-aminoanthraquinone.

Judging from the above-mentioned band positions, polarization directions, and relative intensities, the bands at 30.0, 34.5, 40.3, and 46 kK may correspond to the bands of anthraquinone at 30.8, 36.8, 39.7, and 43.4 kK respectively. The corresponding bands have also been found in each spectrum of the α-aminoanthraquinones.

Figure 4 shows the polarized absorption spectrum of 2-aminoanthraquinone. The bands corresponding to those of anthraquinone appear at 29.6, 34.6 (the absorption maximum appears only in the $D_\perp$ curve), 40.7, and around 46 kK (estimated from the R_d curve). The experimental results are summarized in Table 2 and compared with the results of the calculation. Figure 5 shows the calculated polarization directions. We can discuss the polarization directions of the two

Table 3. Comparison of the observed and the calculated results for 2,3-diaminoanthraquinone

	Calcd			Obsd
	Transition energy (kK)	Oscillator strength	Polarization direction	Transition energy (kK)
I	23.9	0.1390	Y	20.0
II	27.9	0.0140	X	
III	31.7	0.1534	X	
IV	34.2	0.7860	X	30.7
V	34.8	0.3320	Y	35.5
VI	37.7	0.0770	Y	
VII	39.9	0.0050	X	
VIII	40.9	0.4345	X	41.0
IX	40.9	0.0026	Y	
X	44.2	0.2574	Y	45.5
XI	45.4	0.2093	Y	

Table 4. The first and fourth excited state wave functions for 2,3-diaminoanthraquinone

$$\Psi_{I} = 0.1137\,\phi_{6,11} - 0.1841\,\phi_{8,11} + 0.9632\,\phi_{10,11} + 0.1006\,\phi_{10,13}$$

$$\Psi_{IV} = 0.1043\,\phi_{6,12} + 0.1079\,\phi_{7,11} - 0.1333\,\phi_{8,12} + 0.6239\,\phi_{9,11} - 0.1092\,\phi_{9,13} - 0.1185\,\phi_{9,15} + 0.6335\,\phi_{10,12} - 0.3669\,\phi_{10,14}$$

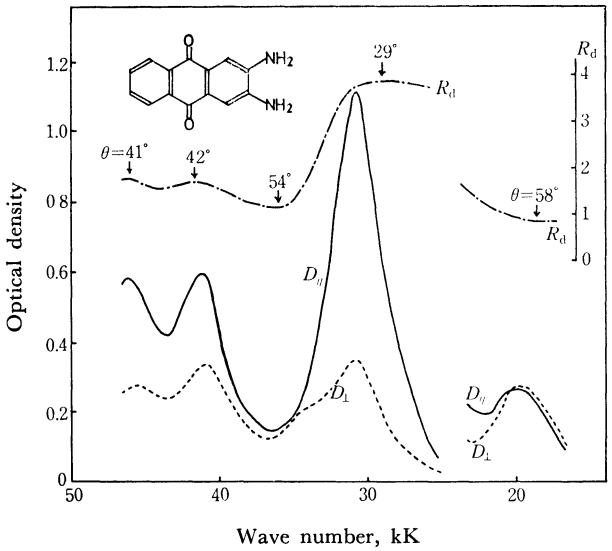

Fig. 6. The polarized absorption spectrum of 2,3-diaminoanthraquinone. (R_s=5.5)

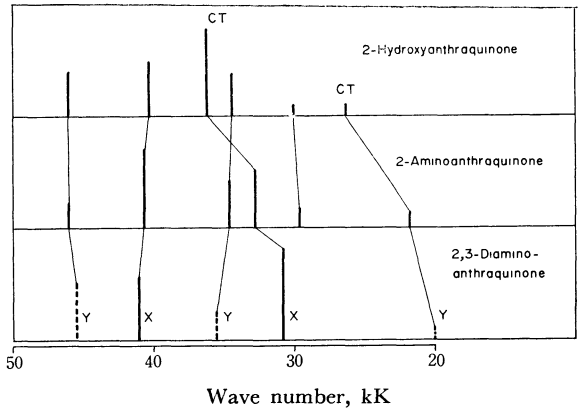

Fig. 7. Correlation diagram of the observed results.

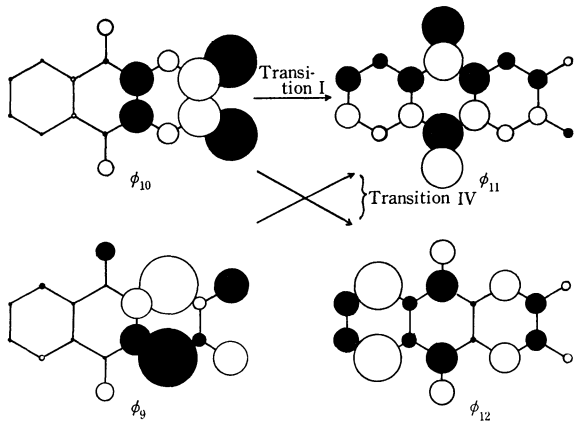

Fig. 8. Coefficients of the wave functions for 2,3-diaminoanthraquinone.

extra bands quantitatively, since the 21.7 kK band is isolated from the other bands and since the 32.7 kK band is not influenced in its polarization direction, because the intensities of the adjacent bands are very weak. The relative polarization direction of the 21.7 kK band with respect to that of the 32.7 kK band can be evaluated from the orientation angles as either 11° (=42°−31°) or 73° (=42°+31°). As has been shown above, the theoretical calculation shows the latter angle to be more reasanable.

The polarized absorption spectrum of 2,3-diaminoanthraquinone is shown in Fig. 6. The compound is assumed to belong to the C_{2v} point group; hence, the polarization direction of each band should be along the X- or Y-axis of the molecule. The extra bands of compound are found at 30.7 and 20.0 kK, and their orientation angles are 29° and 58° respectively. These bands are polarized perpendicularly to each other, because the sum of the orientation angles are approximately a right angle (29°+58°=87°). Since the

compound seems to orient in a manner similar to the cases of anthraquinonesulfonates and α-aminoanthraquinones,[1,2] that is, since the molecule orients its X-axis preferentially along the stretching direction of the sheet, the 30.7 kK band, with relatively large R_d values, is considered to be polarized along the X-axis, and 20.0 kK band, along the Y-axis. The experimental results obtained above are compared with the theoretical results in Table 3.

The results for the three compounds are compared in Fig. 7 as a correlation diagram. As may be seen from the figure, both of the two extra bands shift to the lower wave numbers with an increase in the electron-donating power of the substituent (OH→ NH_2) or with an increase in the number of the substituents. On the other hand, the positions of bands corresponding to the bands of anthraquinone are not significantly affected by the substitution. These tendencies can also be seen in the calculated results.

Table 4 presents the first and fourth excited state wave functions, which correspond to the two extra bands for 2,3-diaminoanthraquinone. The ψ_I is approximately represented by $\psi_{10,11}$ and the ψ_{IV}, by $\psi_{9,11}$ and $\psi_{10,12}$. The coefficients of the wave functions associated with the excitations are shown pictorially in Fig. 8. As may be seen from the figure, the charge migration from the amino to the carbonyl groups takes place in these excitations. Therefore, the I and IV transitions may be assigned to the intramolecular charge-transfer types. Similar results were obtained for 2-hydroxy- and 2-aminoanthraquinones.