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The Dichroic Spectra of Hydroxy Derivatives of Naphthalene, Anthracene, and Phenanthrene in Polyvinylalcohol Sheets[1]

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The dichroic spectra of 1,4-dihydroxynaphthalene, 9-hydroxyanthracene, sodium 9,10-dihydroxyanthracene-2-sulfonate, and 9,10-dihydroxyphenanthrene, which were usually unstable in a liquid solution, were measured in stretched polyvinylalcohol sheets. From a comparison of the results of the dichroic spectra with those of the MO calculations, the polarizations of the electronic bands were determined, and the bands were assigned in terms of the relevant bands of the corresponding unsubstituted aromatic compounds.

The electronic spectra of some hydroxy derivatives of naphthalene and of anthracene have been investigated theoretically and experimentally.[2-4] There have, however, been few reports on the electronic spectra of 1,4-dihydroxynaphthalene, 9-hydroxyanthracene, and 9,10-dihydroxyanthracene. This is also the case for 9,10-dihydroxyphenanthrene. The reason for such a situation is probably that these compounds are very unstable in a liquid solution and it is difficult to determine their absorption spectra by the usual procedure.

It has been well known that these unstable hydroxy aromatic compounds are temporarily formed when 1,4-naphthoquinone, anthrone, anthraquinone, and 9,10-phenanthrenequinone are irradiated by ultraviolet light in solutions. In these cases, the products are very sensitive to oxidation by dissolved oxygen in solution and, hence, change immediately to the original compounds. We have found, however, that the above-mentioned hydroxy aromatic compounds are fairly stable in polyvinylalcohol (PVA) sheets when they are produced in the sheets by photochemical reactions.[5]

Accordingly, in the present paper, the electronic spectra of these compounds will be presented and the assignment of the near-ultraviolet absorption bands will be confirmed by analyses of the dichroic spectra and by theoretical calculations.

Experimental

Materials. All the materials used here were obtained commercially. 1,4-Naphthoquinone and 9,10-phenanthrenequinone were purified by repeated recrystallizations from ethanol. Sodium anthraquinone-2-sulfonate was used in place of anthraquinone, because the latter has poor permeability into PVA sheets. Sodium anthraquinone-2-sulfonate was purified by repeated recrystallizations from an aqueous solution. Anthrone was purified by zone melting using a Shimadzu Zone Refiner CZ-1. The PVA powder used for the preparation of the sheets was used without further purification, and its mean degree of polymerization was 1500.

Preparation of Sample Sheets. To obtain the sample sheets, dried PVA sheets (0.2 mm thick) containing quinones or anthrone in a concentration of 10^{-2}—10^{-3} M were irradiated using a low-pressure mercury lamp as a light source. The quinones and anthrone were completely converted to hydroxy aromatic compounds after a few minutes' photoirradiation. For the measurement of the dichroic spectra, the PVA sheets were stretched prior to the photoirradiation.

Dichroic Spectra. The measurement and analysis of the dichroic spectra were carried out following the method developed by Tanizaki.[6] The spectra were measured with a Shimadzu Spectrophotometer QV-50 equipped with a Glan-Thomson-type calcite polarizer. The notations used in the figures of the dichroic spectra were as follows[4]:

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

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

R_s: Degree of stretching of a sheet.

θ: Orientation angle for the moment of the absorption band. From this, the angle between the transition moments of different bands can be obtained.

MO Calculations

We have used the semi-empirical ASMO SCF CI method, including a variable β approximation.[7] One-center repulsion integrals were evaluated by the Pariser-Parr approximation,[8] in which the ionization potentials and the electron affinities were taken as 11.42 and 0.58 eV respectively for the carbon atom, and as 33.00 and 11.47 eV for the oxygen atom. The two-center repulsion integrals were evaluated by means of the Mataga-Nishimoto equation.[9] 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 included in the CI calculation.

Results and Discussion

1,4-Dihydroxynaphthalene. 1,4-Dihydroxynaphthalene was obtained from 1,4-naphthoquinone by

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* Present address: Shinsei Teppan Co., Ltd., Edogawa-ku, Tokyo.

[2] K. Nishimoto and R. Fujishiro, This Bulletin, **37**, 1660 (1964).

[3] H. Baba and S. Suzuki, *ibid.*, **35**, 683 (1962).

[4] Y. Tanizaki and S. Kubodera, *J. Mol. Spectry.*, **24**, 1 (1967).

[5] The products are almost unchanged as long as the PVA sheets are kept dry.

[6] Y. Tanizaki and N. Ando, *Nippon Kagaku Zasshi*, **78**, 542 (1957); Y. Tanizaki, This Bulletin, **32**, 75 (1959); Y. Tanizaki, T. Kobayashi, and N. Ando, *ibid.*, **32**, 1362 (1959); Y. Tanizaki, *ibid.*, **38**, 1798 (1965).

[7] K. Nishimoto and L. S. Forster, *Theoret. Chim. Acta*, **3**, 407 (1965); **4**, 155 (1966).

[8] R. Pariser and R.G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).

[9] N. Mataga and K. Nishimoto, *Z. Physik. Chem.*, *Neue Folge*, **13**, 140 (1957).

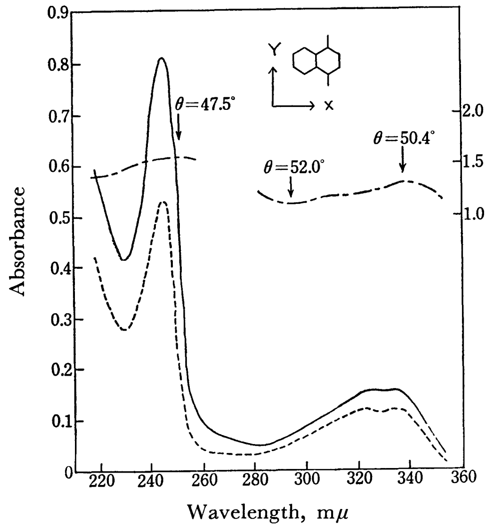

Fig. 1. Dichroic spectra of 1,4-dihydroxynaphthalene. $R_s=10$, ——: $D_\parallel$, ----: $D_\perp$, — —: $R_d(=D_\parallel/D_\perp)$

photoirradiation in a PVA sheet. The dichroic spectra are shown in Fig. 1. The features of the absorption curve were similar to that measured previously by Spruit.[10)]

The intense band at 246 mμ has the highest R_d value; hence, the transition moment of this band is considered to be inclined to the stretched direction of the sheet (hereafter, such a band will be denoted as "a ∥ band", and the band whose transition moment is perpendicular to the ∥ band will be denoted as "a ⊥ band"). The R_d values in the region of 280—360 mμ were relatively small and varied to some extent, having a maximum and a minimum. From this behavior of the R_d curve, it may be deduced that there are two bands closely overlapping in this wavelength region. The tendency of the R_d value to increase with an increase in the wavelength indicates that the longer-wavelength one of the overlapped bands is a ∥ band, while the shorter-wavelength one is a ⊥ band.

According to the consideration of the symmetry of this molecule, an isolated band should be polarized along the X- or Y-axis of the molecule, so the sum of the orientation angles of two differently polarized bands can be expected to give a right angle if the bands are not overlapped with other bands. However, the observed orientation angles of the ∥ band at 246 mμ and of the ⊥ band at around 300 mμ were 47.5° and 52.0° respectively, and their sum (99.5°) was too large for the orthogonality of the direction of polarizations. This non-orthogonality is attributable to the large value of the apparent orientation angle of the 246 mμ band. A weak ⊥ band can, therefore, be predicted to be hidden under the 246 mμ band. However, the presence of this ⊥ band is not detected from the absorption curve.

Next, let us compare the experimental results described above with the calculated electronic transitions. The results of the calculations are presented in Table 1. The observed 246 mμ (∥) band can be safely said to correspond to the III transition (X-polarized). Hence, the ∥ and ⊥ band in the dichroic spectra can be said to be polarized along the X- and Y-axes of the molecule respectively. Therefore, the ∥ and the ⊥ bands observed in the long wavelength region are due to the I (X) and II (Y) transitions respectively. The ⊥ band hidden under the 246mμ band may correspond to the IV transition (Y).

Table 1. The result of the MO calculation on the electronic transition of 1,4-dihydroxynaphthalene

	Transition energy, eV (mμ)[a)]	Polarization[b)]	Oscillator strength
I	3.53 (351)	X	0.1007
II	3.61 (344)	Y	0.2013
III	4.83 (257)	X	0.5051
IV	5.04 (246)	Y	0.1324
V	5.44 (228)	Y	0.0148
VI	5.49 (226)	X	0.8593

a) Only the transitions appeared above 220 mμ were listed.
b) The molecular axes were shown in Fig. 1.

By the use of Platt's notation, we can assign the observed bands as follows. The 246 mμ band is the ^1B_b band, and the ∥ band and the ⊥ band appearing in the region of 280—360 mμ are the ^1L_b and the ^1L_a bands respectively. Consequently, the order of the positions of the bands for 1,4-dihydroxynaphthalene (the ^1B_b, ^1L_a, and ^1L_b bands as the wavelengths increase) is same as those for the other hydroxynaphthalenes studied by Tanizaki and Kubodera.[4)] However, the ^1B_b and the ^1L_a bands of 1,4-dihydroxynaphthalene appeared at longer wavelengths than the corresponding bands of the other α-hydroxynaphthalenes (1-, 1,5-1,8-derivatives),[4)] and it was remarkable that the fine structure disappeared in the ^1L_a and the ^1L_b bands of 1,4-dihydroxynaphthalene.

9-Hydroxyanthracene. 9-Hydroxyanthracene was obtained from anthrone by photoinduced tautomeriza-

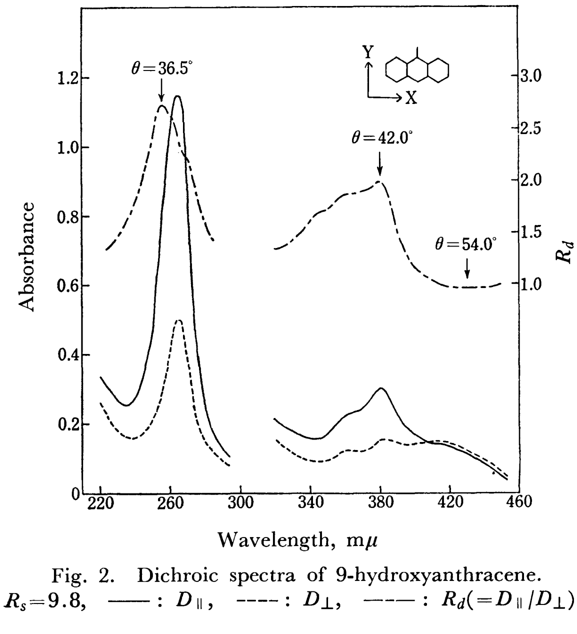

Fig. 2. Dichroic spectra of 9-hydroxyanthracene. $R_s=9.8$, ——: $D_\parallel$, ----: $D_\perp$, — —: $R_d(=D_\parallel/D_\perp)$

[10)] C. J. T. Spruit, *Rec. Trav. Chim.*, **68**, 309 (1949).

tion.[11] Its absorption spectrum in a PVA sheet closely resembles that measured by Baba and Takemura[12] with a rapid-scan spectrophotometer in the region above 320 mμ. The dichroic spectra of 9-hydroxyanthracene are shown in Fig. 2. It may be seen in the figure that the intense 266 mμ band has a large R_d value, so it is a $\parallel$ band. On the other hand, the relatively weak bands with three peaks appearing in the region of 340—460 mμ have medium and small R_d values, so it is clear that there are two bands in this region; the longer-wavelength one is a $\perp$ band, and the shorter-wavelength one is a $\parallel$ band. Since the sum of the orientation angles of this $\perp$ band at 420 mμ and the $\parallel$ band at 266 mμ is 90.5°, the orthogonality of the transition moments between these bands is almost satisfied. Thus, the absorption band in the region above 410 mμ consists of the pure $\perp$ band. On the other hand, the band in the region of 340—410 mμ consists of this $\perp$ band and a $\parallel$ band, because the R_d values in this wavelength region are too small in comparison with that of the 266 mμ band to be that of a pure $\parallel$ band.

Consequently, it was found that 9-hydroxyanthracene showed three absorption bands above 220 mμ; these bands may be interpreted as those of anthracene shifted to red by hydroxy groups. Concerning the electronic transitions of anthracene, the polarizations of the bands have already been investigated by Zimmermann and Joop,[13] and Craig and Hobbins.[14] According to their results, the intense 250 mμ band is polarized to the long axis of the molecule (X-axis) and assigned to the ^1B_b band, while the relatively weak band at longer wavelength is polarized to the short axis (Y-axis) and assigned to the ^1L_a band. The ^1L_b band of anthracene was not appreciably observed, but this band is considered to be hidden under the ^1L_a band. The absorption bands of 9-hydroxyanthracene can easily be interpreted on the basis of this assignment. At first, the 266 mμ band ($\parallel$) can be said to correspond to the ^1B_b band of anthracene (X-axis); consequently, the polarization of a $\parallel$ band is determined to be along the long axis of the molecule (X-axis). Therefore, the $\perp$ band in the region of 340—460 mμ is polarized to the short axis of the molecule (Y-axis); hence, this band can be said to correspond to the ^1L_a band of anthracene. Furthermore. it is apparent that the X-polarized ^1L_b band is present in the region of 340—410 mμ.

These experimental results are compared with the results of the MO calculations in Table 2. The V transition (265 mμ) can be said to correspond unequivocally to the observed 266 mμ band. There are four transitions (I—IV) in the longer wavelength region of the V transition; however, two of them correspond to the observed ^1L_a and ^1L_b bands. From a consideration of the position, the polarization, and the oscillator strength, the I and II transitions may be said to correspond to the ^1L_a and the ^1L_b bands respectively.

Table 2. The result of the MO calculation on the electronic transition of 9-hydroxyanthracene

	Transition energy, eV (mμ)[a]	Polarization[b]	Oscillator strength
I	3.22(385)	Y	0.2900
II	3.38(367)	X	0.0520
III	4.08(304)	X	0.0221
IV	4.65(267)	Y	0.0002
V	4.67(265)	X	2.0347
VI	4.75(261)	X	0.2683
VII	5.05(246)	Y	0.0106
VIII	5.32(233)	Y	0.0045

a) Only the transitions appeared above 220 mμ were listed.
b) The molecular axes were shown in Fig. 2.

Sodium 9,10-Dihydroxyanthracene-2-sulfonate. This was obtained from sodium anthraquinone-2-sulfonate by a photochemical reduction.[15,16] Since a sodium sulfonate group has only a slight influence on the electronic spectrum of an aromatic compound, the observed dichroic spectra shown in Fig. 3 may be regarded as those of 9,10-dihydroxyanthracene. The patterns of the absorption curve and of the R_d curve were very similar to those of 9-hydroxyanthracene; hence, each band can be assigned like that of 9-hydroxyanthracene. That is, the intense band at 272 mμ is the ^1B_b band and is polarized along the X-axis, and the longer- and the shorter-wavelength parts of the relatively weak band in the region of 340—460 mμ are determined to be the ^1L_a and the ^1L_b bands respectively.

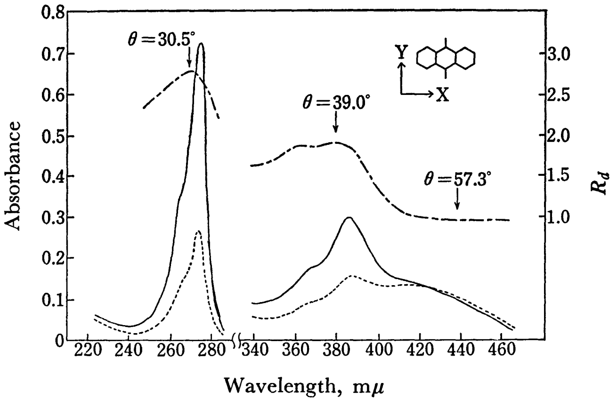

Fig. 3. Dichroic spectra of sodium 9,10-dihydroxyanthracene-2-sulfonate.

$R_s=4.5$, ——: $D_{\parallel}$, ----: $D_{\perp}$, —-—: $R_d(=D_{\parallel}/D_{\perp})$

The results of the MO calculations for 9,10-dihydroxyanthracene are shown in Table 3. The observed ^1L_a, ^1L_b, and ^1B_b bands can be said to correspond to the I, II, and V transitions respectively.

9,10-Dihydroxyphenanthrene. This was obtained from 9,10-phenanthrenequinone by photochemical

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Table 3. The result of the MO calculation on the electronic transition of 9,10-dihydroxyanthracene

	Transition energy, eV (mμ)[a]	Polarization[b]	Oscillator strength
I	2.96(419)	Y	0.2820
II	3.22(385)	X	0.1831
III	3.63(342)	forbidden	
IV	4.58(271)	forbidden	
V	4.61(269)	X	1.8888
VI	4.87(255)	Y	0.0760
VII	4.93(251)	forbidden	
VIII	5.23(237)	Y	0.0018
IX	5.37(231)	forbidden	
X	5.63(220)	X	0.3625

a) Only the transitions appeared above 220 mμ were listed.
b) The molecular axes were shown in Fig. 3.

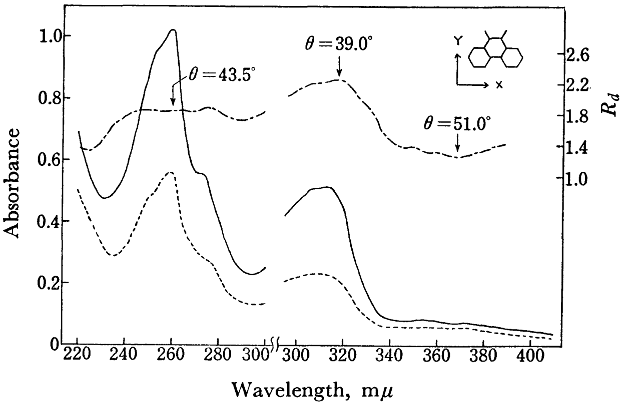

Fig. 4. Dichroic spectra of 9,10-dihydroxyphenanthrene. $R_s=9.0$, ——: $D_{\parallel}$, ----: $D_{\perp}$, —-—: $R_d(=D_{\parallel}/D_{\perp})$

reduction.[17] The dichroic spectra are shown in Fig. 4. From the behavior of the R_d curve, it can be deduced that the bands at 260 mμ and at 314 mμ are polarized in the same direction (∥ bands). However, the R_d values of the 260 mμ band are somewhat smaller than those of the 314 mμ band. This suggests the presence of a ⊥ band near the 260 mμ band.

A very weak band appears above 340 mμ. The polarization of this band is perpendicular to the transition moment of the 314 mμ band, because the sum of the orientation angles of these band makes a right angle; that is, this weak band is a ⊥ band.

These experimental results are compared with the theoretical results in Table 4. The most intense ∥ band, at 260 mμ, undoubtedly corresponds to the calculated transition VI, which is polarized along the X-axis of the molecule and which has the largest oscillator strength in the region above 220 mμ. Therefore, the ∥ bands may be considered to be polarized to the X-axis. Although there is no transition around 314 mμ in the present calculation, the II transition presumably corresponds to the observed 314 mμ band, judging from the direction of the polarization and the oscillator strength. Between the II and VI transition, there are two Y-polarized transitions, III ($f=0.0676$) and V ($f=0.400$), at 285 mμ and 267 mμ. The lower R_d values of the 260 mμ band as compared with those of the 314 mμ band are ascribable to the presence of the Y-polarized bands corresponding to the III and V transitions. However, it can not be decided in the present study whether the shoulder at about 275 mμ corresponds to the V transition or whether it is the vibrational structure of the 260 mμ band. The ⊥ band appearing above 340 mμ may be considered to be due to the I transition, judging from its position, its intensity, and its polarization.

Table 4. The result of the MO calculation on the electronic transition of 9,10-dihydroxyphenanthrene

	Transition energy, eV (mμ)[a]	Polarization[b]	Oscillator strength
I	3.32(374)	Y	0.0459
II	3.58(346)	X	0.4001
III	4.35(285)	Y	0.0676
IV	4.44(280)	X	0.0160
V	4.64(267)	Y	0.4000
VI	4.78(259)	X	1.1400
VII	5.11(243)	X	0.0452
VIII	5.42(229)	Y	0.0823
IX	5.59(222)	X	0.4076

a) Only the transitions appeared above 220 mμ were listed.
b) The molecular axes were shown in Fig. 4.

The results obtained above were compared with those on the absorption bands of phenanthrene. The electronic spectrum of phenanthrene has been studied in detail.[18–20] The two bands at 258 mμ and at 300 mμ have been found to be polarized along the X-axis and have been assigned to the ^1B_b and the ^1L_a bands respectively. Thus, the 260 mμ and the 314 mμ bands of 9,10-dihydroxyphenanthrene may be considered to be the ^1B_b and the ^1L_a bands respectively. The very weak band of phenanthrene around 330 mμ ($\log \varepsilon = 2.2$) may be interpreted as being due to the symmetry-forbidden ^1L_b transition. In the case of 9,10-dihydroxyphenanthrene, the ⊥ band appearing above 340 mμ (the I transition) may correspond to the ^1L_b band of phenanthrene. In contrast to the case of phenanthrene, the I transition of 9,10-dihydroxyphenanthrene is symmetry-allowed, $f=0.0459$.

The authors wish to thank Dr. T. Hoshi of Aoyama Gakuin University for his help in the MO calculations.

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