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Electronic Structures and Spectra of a Novel Diquinone; 1,4 : 5,8-Anthracenediquinone

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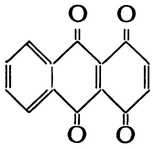
Assignment of the electronic absorption spectrum of 1,4 : 5,8-anthracenediquinone (1,4 : 5,8-ADQ) has been carried out with the aid of magnetic circular dichroism and LCAO MO SCF CI calculations including all valence electrons. The lowest energy absorption region of 1,4 : 5,8-ADQ has been revealed to be composed of the n-π^* transition or transitions. The higher energy absorption region has been concluded to consist of four π-π^* transitions, which are regarded as L_b, L_a, B_a, and B_b in the Platt's notation for anthracene. The above assignment of 1,4 : 5,8-ADQ has been experimentally confirmed with its linear dichroism spectra in stretched polyethylene sheets and its circular dichroism spectra in the β-cyclodextrin solution. The relationship between the absorption spectra of 1,4 : 5,8-ADQ and 1,4-naphthoquinone has been discussed from the experimental and theoretical points of view.

In spite of the extensive studies on the electronic structures, spectra and reactivities of quinones, those on the chemical and physical properties of diquinones have been little known. They are a potential subject of synthetic and theoretical research.

Anthracenediquinone (ADQ) is considered to be a representative of this interesting quinonoid system. Two isomers of para-ADQ illustrated below are **1** for 1,4 : 9,10-ADQ and **2** for 1,4 : 5,8-ADQ. The electronic absorption spectrum of **1** in solution has been interpreted in terms of the n-π^* transition and four π-π^* transitions.[1] The π-π^* electronic absorption occurring in **1** has been theoretically confirmed on the basis of an LCAO MO SCF CI calculation.[2] The synthesis of **2** was reported along with its spectroscopic data,[3] where **2** in *N,N*-dimethylformamide is described to exhibit absorption at 353 nm. The diquinone **2** was also obtained by selenium dioxide oxidation of a photochemical addition product of 2-cyclohexene-1,4-dione with acetylene.[4] A theoretical calculation based on the simple HMO method was given to elucidate the redox potential of **2**.[5]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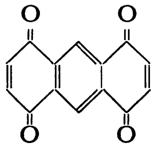
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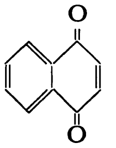
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In this paper, the electronic absorption, magnetic circular dichroism (MCD) spectra[6,7] in solution, and linear dichroism (LD) spectra[8] in stretched polyethylene sheets of **2** are reported in addition to its circular dichroism (CD) spectrum in the β-cyclodextrin (β-CDx) solution, where the observed CD is known as induced circular dichroism (ICD).[9–11] The experimental spectra of **2** are compared with those of 1,4-naphthoquinone, **3**, and discussed in conjunction with LCAO MO SCF CI calculations including all valence electrons (CNDO/S), so as to give a spectroscopic assignment of the characteristic electronic absorption of **2**.

Experimental and Theoretical

The diquinone **2** and **3** were purified by sublimation under reduced pressure after several recrystallizations from dioxane and petroleum ether. Inclusion complexes of quinones with commercially available β-CDx were prepared in the aqueous solutions. The electronic absorption spectra were recorded on a JASCO UVIDEC 510 recording spectrophotometer. The MCD spectra were measured with a JASCO J500C recording circular-dichrometer equipped with a 1.14T electromagnet. All measurements were carried out at room temperature using spectrograde solvents without further purification.

The experimental oscillator strengths, f, and Faraday parameters, B, were evaluated from the observed spectra after resolving the spectrum into its components according to the curve-fitting procedure assuming a Gaussian function, where B was expressed in units of $(\mathrm{Debye})^2\,\mu_B/\mathrm{cm}^{-1}$.**

Polyethylene sheets including quinones were prepared by the usual method[8] and stretched five times. Absorption of the set stretched sheets was recorded both for the electric vectors parallel and perpendicular to the stretching direction. The LD spectra in the wavenumber region higher than 25000 cm^{-1} were obtained from the observed dichroic spectra according to the procedure proposed by Thulstrup *et al.*,[8] neglecting out-of-plane polarized absorption.

The electronic transition energies, oscillator strengths and Faraday B terms of **2** and **3** were calculated within the framework of the CNDO/S method,[12,13] including CI among singly excited configurations below 10 eV. The values of the bonding parameters for the carbon and the hydrogen atoms were adjusted so that the ionization potentials and the transition energies of benzene and hydrogen molecules are well reproduced.[14] The values of bonding parameter for the oxygen atom and the empirical σ-π separation parameter, κ, were determined so as to reproduce the n-π^* and the first π-π^* transition energies of p-benzoquinone. The quinone ring in **2** was assumed to be identical with that in **3**, while the central six-membered ring was assumed to be a regular hexagon with bond lengths of 1.40 Å. The geometry of **3** was taken from the X-ray diffraction data.[15]

For a molecule possessing non-degenerate states, the theoretical MCD for the transition, a←0, is usually discussed in terms of the Faraday B term. All the atomic integrals in the calcula-

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** B-terms in SI units of 10^{-60} C^2 m^2 T^{-1} can be obtained by multiplying by 5.19.

tion of the *B* terms were evaluated using the Slater AOs, with which the orthogonalized CNDO basis set was expanded by the inverse Löwdin transformation.[16]

Results and Discussion

The electronic absorption spectrum of **2** in dichloromethane is reproduced in Fig. 1. It is characterized by three absorption regions; the first (20000—25000 cm^{-1}) the second (25000—35000 cm^{-1}), and the third (35000—42000 cm^{-1}).

The MCD spectrum of **2** in Fig. 1 reveals a distinct negative extreme at 22200 cm^{-1} in contrast to a discernible shoulder in its electronic absorption spectrum. The first region in the absorption and MCD spectra is considered to arise from an electronic transition or transitions which is or are n-π^* in nature. The n-π^* assignment is partially supported by the solvent effect on the lowest energy absorption and MCD bands. As is clear from Fig. 2, the blue-shift takes place on changing solvents from nonpolar to polar.

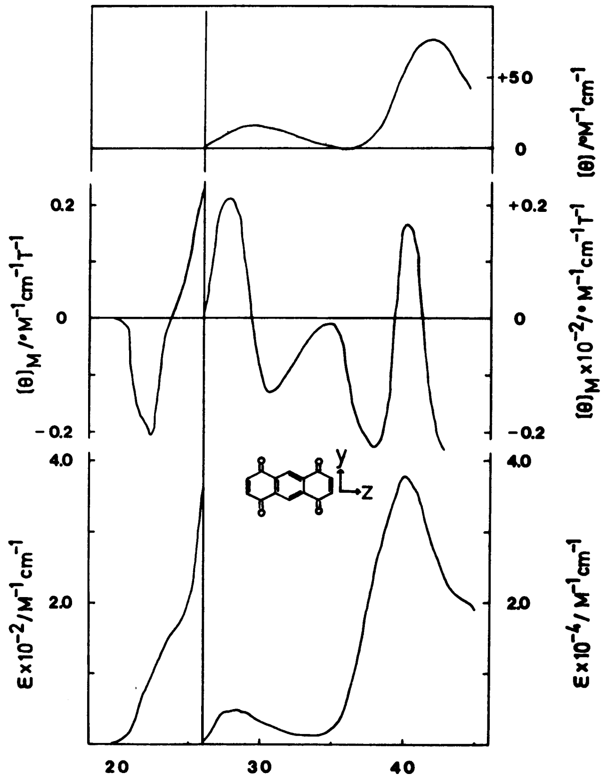

Fig. 1. The magnetic circular dichroism (center) and electronic absorption (bottom) spectra of 1,4 : 5,8-anthracenediquinone in dichloromethane and the circular dichroism (top) spectrum of the β-cyclodextrin complex with 1,4:5,8-anthracenediquinone in water at room temperature.

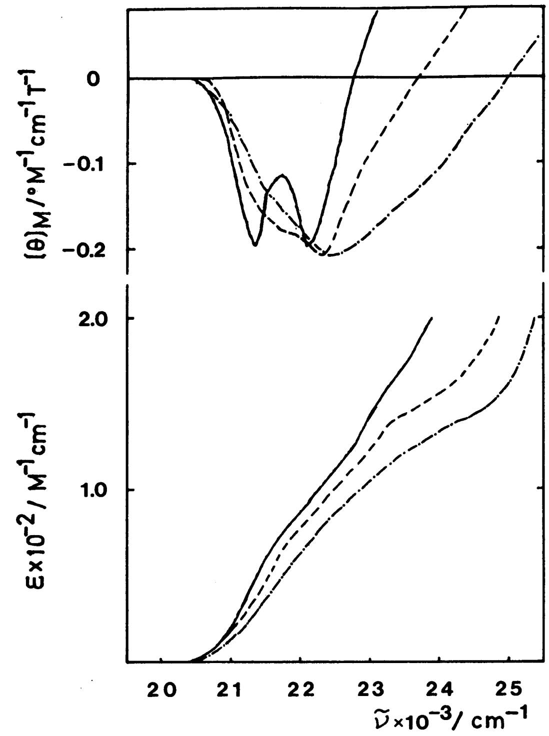

Fig. 2. The magnetic circular dichroism (top) and electronic absorption (bottom) spectra of 1,4:5,8-anthracenediquinone in benzene (——), dichloromethane (-----), and acetonitrile (•—•—) at room temtemperature.

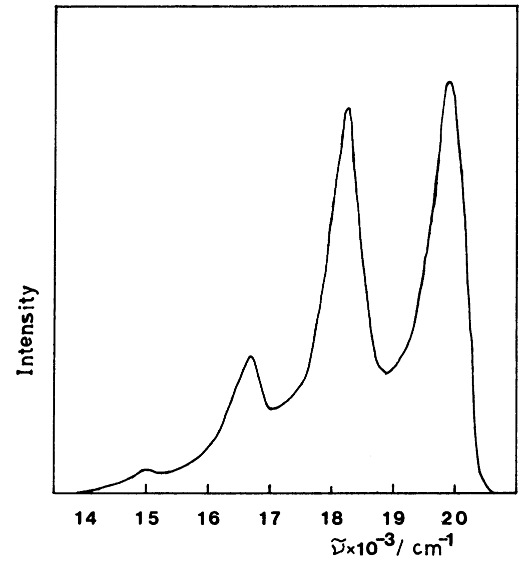

Fig. 3. The phosphorescence spectrum of 1,4:5,8-anthracenediquinone in EPA at 77 K.

The phosphorescence spectrum of **2** was measured in an ether–isopentane–ethanol (EPA) mixture (volume ratio, 5 : 5 : 2) at 77 K, and it is reproduced in Fig. 3. The spectrum exhibits the vibrational structure with spacing of *ca.* 1600 cm^{-1}, which is considered to be due to the carbonyl stretching progression. From the 0-0 band position, which was assumed to be the most intense peak of the spectrum, the lowest triplet level of **2** is estimated to be at 2.45 eV. Provided that the 0-0 band position is at 21350 cm^{-1}, which was assumed to be the lowest wavenumber extreme of the MCD spectrum of **2** in benzene, the energy difference between the lowest singlet and the lowest triplet states is estimated to be 1590 cm^{-1}. The small energy difference and the carbonyl stretching progression suggest that the lowest

TABLE 1. THE CALCULATED AND EXPERIMENTAL TRANSITION ENERGIES, ΔE, OSCILLATOR STRENGTHS, f, AND FARADAY B TERMS, B, FOR 1,4 : 5,8-ANTHRACENEDIQUINONE.

Symmetry	Calculated (CNDO/S)		Experimental (MCD)	
	$\frac{\Delta E\times 10^{-3}}{\mathrm{cm}^{-1}}(f)$	$\frac{B\times 10^{4}}{\mu_B\ \mathrm{D}^2\ \mathrm{cm}}$	$\frac{\Delta E\times 10^{-3}}{\mathrm{cm}^{-1}}(f)$	$\frac{B\times 10^{4}}{\mu_B\ \mathrm{D}^2\ \mathrm{cm}}$
B_{2g} $(\pi^*\leftarrow n)$	20.6 (Forb)	0		
B_{3u} $(\pi^*\leftarrow n)$	20.7 (6×10^{-5})	3.99	22.2 (0.002)	0.05
B_{1g} $(\pi^*\leftarrow n)$	20.8 (Forb)	0		
A_u $(\pi^*\leftarrow n)$	21.0 (Forb)	0		
B_{2u} $(\pi^*\leftarrow \pi)$	30.2 (0.055)	−10.57	27.8 (0.067)	−5.28
B_{1u} $(\pi^*\leftarrow \pi)$	32.9 (0.043)	6.84	30.3 (0.031)	3.73
B_{1u} $(\pi^*\leftarrow \pi)$	40.0 (0.217)	1058.69	37.8 (0.274)	5.19
B_{2u} $(\pi^*\leftarrow \pi)$	40.2 (0.383)	−356.75	40.2 (0.527)	−1.77

phosphorescence state is n-π^* in origin, and in turn that the lowest singlet state is also n-π^* in nature.

In the present work, a symmetry allowed $B_{3u}\leftarrow A_g$ transition is assigned to the observed lowest energy absorption and MCD bands. This seems to require a further confirmation, however.

The MCD spectrum exhibits a positive extreme at 27800 cm^{-1} and a negative extreme at 30300 cm^{-1} in the second absorption region, suggesting that two electronic origins are included in the corresponding spectral region. Both bands are roughly equal in magnitude, but opposite in sign. In the third region, the MCD spectrum manifests two electronic transitions which have never been resolved in the absorption spectrum due to overlapping.

The CD spectrum of the inclusion complex of **2** with β-CDx is shown in Fig. 1. No ICD for the first absorption region has been observed, due to the low solubility of **2** in water. The inclusion complex exhibits only two positive CD extrema, corresponding to the second and third absorption regions. If the long axis of the guest molecule is parallel to the seven-fold symmetry axis of β-CDx (an axial inclusion), the transition polarized along the z-axis gives positive CD and the transition polarized along the y-axis gives negative CD.[9–11] Therefore, the observed positive extreme in the CD spectrum originates from the transition polarized along the z-axis. In general, the positive CD band in inclusion complexes tends to appear larger than the negative one.[17] The negative CD component expected to come from the transition polarized along the y-axis seems to be compensated by the larger positive CD component.

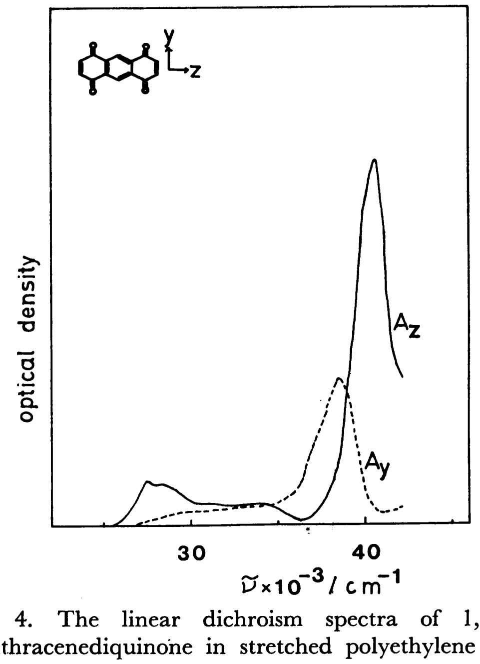

Fig. 4. The linear dichroism spectra of 1,4:5,8-anthracenediquinone in stretched polyethylene sheets at room temperature (redution factors $d^0_{\parallel}=1.02$, $d^0_{\perp}=0.77$). The solid and broken lines stand for the absortion components polarized along the z- and y-axis respectively.

The LD spectra of **2** in the y-direction, A_y, and z-direction, A_z, are illustrated in Fig. 4, which were obtained from the experimental dichroic spectra using the reduction factors of $d^0_{\perp}=0.77$ and $d^0_{\parallel}=1.02$ respectively. The reduction factors, $d^0_{\perp}$ and $d^0_{\parallel}$, were estimated on the assumption that the z- and y-polarized absorption bands have their maxima at 40800 and 35700 cm^{-1} respectively.

According to the present calculation, the lowest two π-π^* transitions take place at 30200 and 32900 cm^{-1} with their directions of polarization along the z- and y-axis respectively. Theoretical B values associated with these transitions are negative for the lower energy transition and positive for the higher, in agreement with the experiment. Therefore, the positive and negative bands are considered to be assigned to the predicted B_{2u} and B_{1u} states respectively. The assignment is further supported by the LD spectra which show the two components polarized along the z-axis in the lower energy region and along the y-axis in the higher. Thus, in the second region there are two π-π^* transitions, where the lower energy transition is polarized along the z-axis and the higher energy one along the y-axis.

The negative and positive MCD bands in the third absorption region are assigned to the $B_{1u}\leftarrow A_g$ and $B_{2u}\leftarrow A_g$ transitions predicted at 40000 and 40200 cm^{-1} respectively. The calculated B values for the both transitions are too large to reproduce experimental values, however. This arises from the small energy difference between two states predicted in the present calculation. The assignment is supported by the LD spectra (Fig. 4) which exhibit the y-component at the lower energy region and the z-component at the higher.

Table 2. The calculated and experimental transition energies, ΔE, oscillator strengths, f, and Faraday B terms, B, for 1,4-naphthoquinone

Symmetry	Calculated (CNDO/S)		Experimental (MCD)	
	$\frac{\Delta E \times 10^{-3}}{\text{cm}^{-1}}(f)$	$\frac{B \times 10^4}{\mu_B\ \text{D}^2\ \text{cm}}$	$\frac{\Delta E \times 10^{-3}}{\text{cm}^{-1}}(f)$	$\frac{B \times 10^4}{\mu_B\ \text{D}^2\ \text{cm}}$
B_1 ($\pi^* \leftarrow n$)	19.1 (1×10^{-6})	4×10^{-3}	22.8 (3×10^{-4})	0.01
A_2 ($\pi^* \leftarrow n$)	19.7 (Forb)	0		
A_1 ($\pi^* \leftarrow \pi$)	32.9 (0.028)	−4.77	28.8 (0.026)	−4.49
B_2 ($\pi^* \leftarrow \pi$)	36.0 (0.030)	3.17	32.0 (0.046)	2.36
A_1 ($\pi^* \leftarrow \pi$)	41.1 (0.110)	18.88	40.0 (0.261)	−4.66
B_2 ($\pi^* \leftarrow \pi$)	41.9 (0.171)	−13.31	— —	+

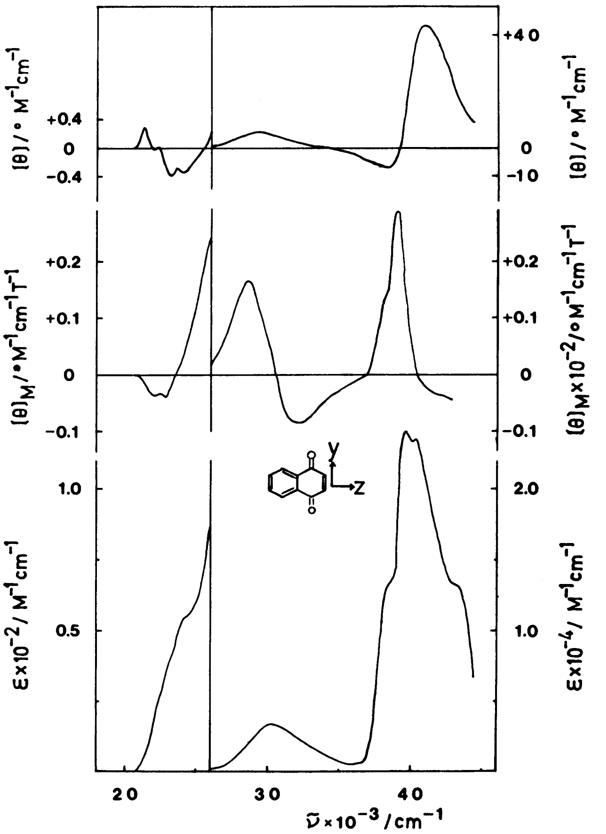

Fig. 5. The magnetic circular dichroism (center) and electronic absorption (bottom) spectra of 1,4-naphthoquinone in dichloromethane and the circular dichroism (top) spectrum of β-cyclodextrin complex with 1,4-naphthoquinone in water at room temperature.

Taking the theoretical and experimental results into consideration, the third absorption region is concluded to consist of two π-π^* transitions: One is polarized along the y-axis and the other along the z-axis.

The electronic absorption spectrum of **3** in Fig. 5 is divided into three characteristic spectral regions. The first region of the absorption and MCD spectra is considered to come from the n-π^* transitions, which are predicted to take place at the lowest energy region (see Table 2). The ICD spectrum in this region exhibits two extrema at 21280 and 23260 cm^{-1}, which are considered to be either electronic or vibrational in origin.

The positive and negative MCD bands in the second region are considered to be assigned to the theoretically predicted A_1 and B_2 states respectively. The assignment is supported by the LD spectra in Fig. 6, where the lower energy transition is polarized along the z-axis and the higher energy one along the y-axis.

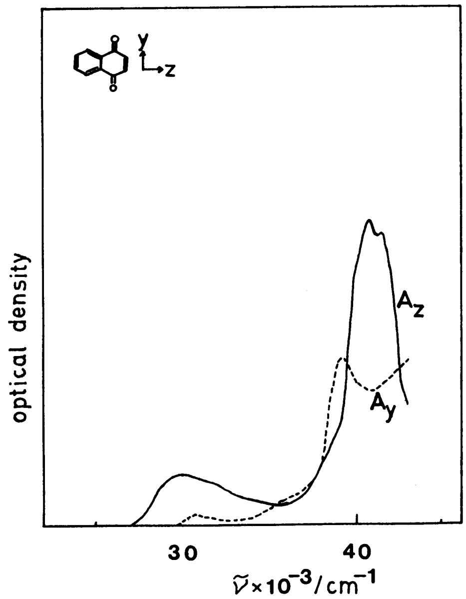

Fig. 6. The linear dichroism spectra of 1,4-naphthoquinone in stretched polyethylene sheets at room temperature (redution factors $d^0_{\parallel} = 1.07$, $d^0_{\perp} = 0.69$). The solid and broken lines stand for the absorption components polarized along z- and y-axis respectively.

The LD and ICD spectra show that the third absorption region consists of two π-π^* transitions, where the lower energy transition is polarized along the y-axis and the higher energy one along the z-axis. On the contrary, the present CNDO/S calculation predicts the $A_1 \leftarrow A_1$ (41100 cm^{-1}) and $B_2 \leftarrow A_1$ (41900 cm^{-1}) transitions with the transition moments directed along the z- and y-axis respectively. The theoretical result is in disagreement with the experimental result. The latter, however, is consistent with that of Kuboyama and his coworkers.[18]

The spectral profile of **2** and **3** in the wavenumber region higher than 26000 cm^{-1} seems to be related to the skeletal π-π^* transitions in the annelated aromatics. The singly excited configurations contributing dominantly to the lowest $B_{2u} \leftarrow A_g$ and $B_{1u} \leftarrow A_g$ transitions in the second region of **2** are respectively due to the

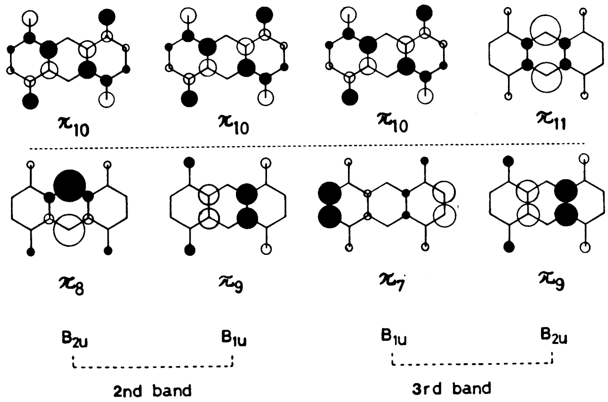

Fig. 7. The bonding π-MOs (bottom) and anti-bonding π-MOs (top) associated with the π-π^* electronic transitions in 1,4: 5,8-anthracenediquinone.

$\pi_8 \rightarrow \pi_{10}$ and $\pi_9 \rightarrow \pi_{10}$, and illustrated in Fig. 7. The two configurations are correlated to the L_b and L_a bands in anthracene. Further, the B_{1u} and B_{2u} states included in the third absorption region of **2** are B_b and B_a respectively, in nature.

Concluding Remarks

The assignment of the electronic absorption spectra of **2** has been carried out. The first absorption region is considered to arise from the n-π^* electronic transition or transitions. The absorption region higher than 25000 cm^{-1} is concluded to consist of four π-π^* transitions.

The present CNDO/S calculation seems to reproduce the absorption and MCD spectra of **2** and **3** fairly well. As has been seen above, however, the agreement between the theoretical and experimental is considered to be less satisfactory in the higher energy region than in the lower energy region.

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