

THE MAGNETIC CIRCULAR DICHROISM SPECTRUM OF AZULENO[1,2,3-cd]PHENALENE

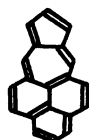
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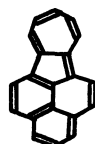
The magnetic circular dichroism (MCD) spectrum of azuleno[1,2,3-cd]phenalene was measured, at room temperature, in the wavelength region of 1000 nm to 200 nm. The compound showed the Faraday B terms in the MCD spectrum caused by a magnetic coupling of the low-lying non-degenerate electronic states. A careful inspection of the MCD spectrum with the aid of its quantum mechanical calculations led to preferable spectroscopic assignments of the complicated absorption bands of azuleno[1,2,3-cd]phenalene.

Azulenophenalene is one of the most interesting non-alternant conjugated hydrocarbon consisting of azulene and phenalene skeletons. One of the three possible isomers of azulenophenalene, azuleno[5,6,7-cd]phenalene (I) has been synthesized firstly by Jutz and his coworkers<sup>1)</sup>. Recently, the synthesis, and chemical and physical properties of the second isomer, azuleno[1,2,3-cd]phenalene (II) have been reported by two of the present authors (I. M and K. N) and their coworkers<sup>2)</sup>.

On the other hand, the magnetic circular dichroism (MCD) technique<sup>3,4)</sup> has been a very powerful tool in investigating the molecular and electronic structures of molecules and ions in their ground and excited states and has been found to be more sensitive than the usual absorption (AB) spectroscopy in such cases as to clarify spectroscopic assignments and detect hidden transitions<sup>5,6,7)</sup>. Recently, Thulstrup et al<sup>8)</sup> have measured the MCD spectrum of I aiming at giving them correct spectroscopic assignments and succeeded in interpreting the absorption spectrum in its longer wavelength region. More recently the photoelectron (PE) and the UV-visible absorption spectra of I and II have also been recorded and interpreted by Gleiter et al<sup>9)</sup>.



I

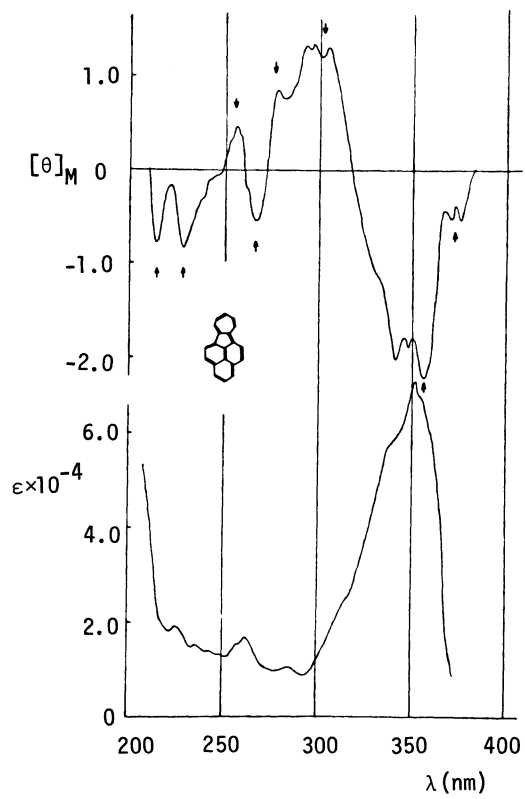
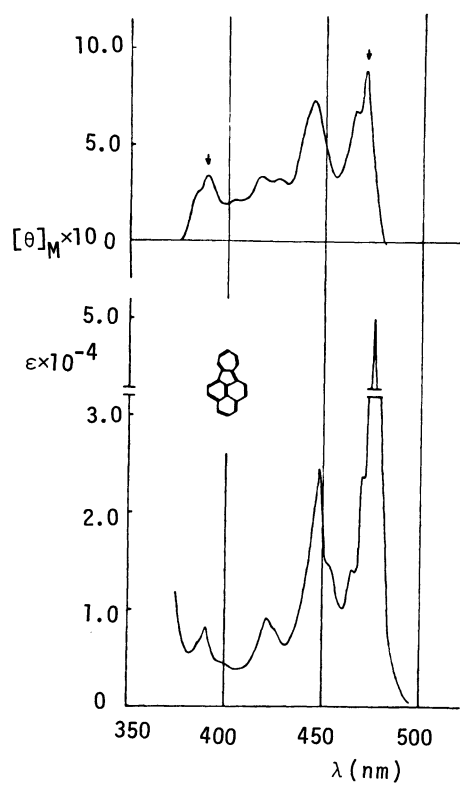
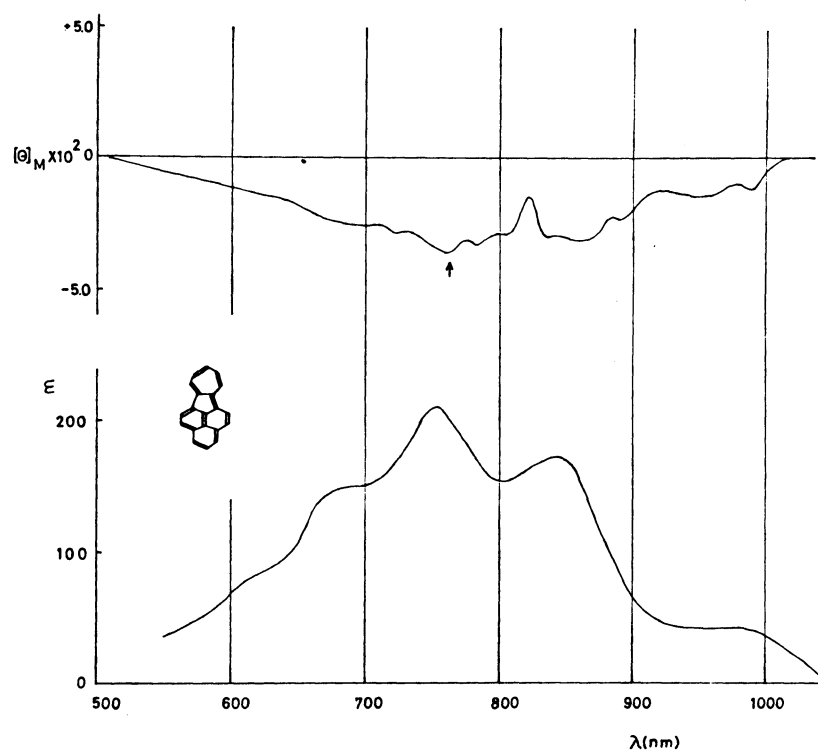


II

It seems to be valuable to report here the MCD spectrum of the second isomer, azuleno[1,2,3-cd]phenalene, along with its quantum mechanical calculations.

All measurements were carried out at room temperature in cyclohexane for the spectral range of 200-500 nm and in methanol for that of 500-1000 nm, using a JASCO-20A recording spectropolarimeter equipped with an electro-magnet supplying magnetic field strength of 12.25 kG. The MCD and AB spectra of II are displayed in Figs. 1-3.

Although assuming the highest point group ( $C_{2v}$ ) to which II belongs, no degeneracy will be



found in its ground or excited electronic states. Therefore the MCD of II should be considered to be due to the sole contribution from the Faraday B term,

$$B_{O \rightarrow a} = \text{Im} \left[ \sum_{b \neq O} \frac{\hat{m}_{bO} \cdot \hat{\mu}_{Oa} \times \hat{\mu}_{ab}}{W_b - W_O} + \sum_{b \neq a} \frac{\hat{m}_{ab} \cdot \hat{\mu}_{Oa} \times \hat{\mu}_{bO}}{W_b - W_a} \right] \dots\dots\dots (1)$$

where  $\hat{\mu}_{ab}$  and  $\hat{m}_{ab}$  represent the off-diagonal matrix elements of electric and magnetic moment operators, respectively, whereas Im stands for taking the imaginary part of the bracketed expression of eq. (1). As is pointed out by several authors<sup>10-12)</sup>, however, the difficulty arises from an infinite sum in eq. (1) over all molecular electronic states  $|b\rangle$ 's with energies  $W_b$ 's. Since in a practical treatment of eq. (1) the sum is so severely truncated that  $B_{O \rightarrow a}$  is origin dependent. To avoid this origin dependency we set the origin at the center of charge distribution of the molecule in its ground state<sup>10)</sup>. The energies and wavefunction used in evaluating the Faraday B terms are obtained within the framework of the PPP<sup>13)</sup> approximation, where 30 singly excited configurations are taken into account in the CI calculations.

Table 1 Calculated Singlet-Singlet Transition Energies  $\Delta E$ (eV), Oscillator Strengths  $f$  and the Faraday Parameters B/D ( $\beta/\text{cm}^{-1}$ ).

Symmetry	$\Delta E(f)$	Calculated B/D $\times 10^5$	$\Delta E^*$	Observed B/D $\times 10^5$
$B_2 \leftarrow A_1$	1.47(0.019)	+ 62.4	1.60 <sup>**</sup>	+ 87.8 <sup>**</sup>
$A_1 \leftarrow A_1$	2.70(0.74)	- 10.1	2.66	- 14.4
$B_2 \leftarrow A_1$	3.81(0.073)	- 14.5	3.21	- 21.8
$A_1 \leftarrow A_1$	3.87(1.74)	+ 17.8	3.57	+ 14.4
$B_2 \leftarrow A_1$	4.00(0.050)	+ 128	3.35	positive
$A_1 \leftarrow A_1$	4.12(0.262)	- 78.7	4.17	- 66.6
$B_2 \leftarrow A_1$	4.23(0.017)	- 187		
$A_1 \leftarrow A_1$	4.39(0.016)	- 5.17	4.50	negative
$B_2 \leftarrow A_1$	4.49(0.015)	+ 15.1	4.70	+ 18.4
$B_2 \leftarrow A_1$	4.73(0.341)	- 17.5	4.88	- 15.0
$A_1 \leftarrow A_1$	4.90(0.111)	- 20.8	5.48	positive
$B_2 \leftarrow A_1$	5.41(0.411)	+ 2.43		
$A_1 \leftarrow A_1$	5.60(0.038)	+ 95.9		
$A_1 \leftarrow A_1$	5.84(0.006)	- 30.2	5.84	negative
$B_2 \leftarrow A_1$	5.89(0.002)	+ 232		

\* Experimental values taken from the peaks or troughs, which are indicated in Figs. 1 ~ 3 by arrows, of the MCD spectra.

\*\* Values in the methanol solution.

In Table 1 the calculated transition energies, oscillator strengths, B/D values (D is a dipole strength) are listed along with their experimental values. The observed values of transition energies are taken from the MCD spectrum, not from the AB spectrum. This is because

the overlapped bands in the AB spectrum are well resolved in the MCD spectrum, especially in the shorter wavelength region. The B/D values are extracted from the observed MCD and AB spectra by use of the method of moment<sup>4)</sup>.

The longest wavelength MCD band in Fig.1 corresponding to the broad weak absorption band in visible region is considered to arise from a single electronic origin and corresponding to the predicted transition with the lowest energy,  $B_2 \leftarrow A_1$  transition polarized along the short axis. The calculated B/D value is in good agreement with the experimental data both in sign and in magnitude.

It is seen from Fig.2 that the positive MCD band with fine structure is observed in the wavelength region of 350-500 nm. The vibrational spacings observed in this spectrum are recognized to be ca.  $1400\text{ cm}^{-1}$ . As for the MCD band at 390 nm, however, it seems to be not reasonable to give it a vibronic origin. This band is assigned to the third electronic transition which is predicted to be polarized along the short axis, and to have a negative B/D value in agreement with the experimental value.

The well resolved MCD spectrum in the shorter wavelength region (Fig.3) seems to be very courageous for us: some hidden transitions buried in the strong band with its maximum at 350 nm in the AB spectrum are clearly resolved in the MCD spectrum as negative ( $\sim 370\text{ nm}$ ) and positive ( $\sim 300\text{ nm}$ ) peaks. The structured negative MCD band centered at 350 nm is considered to be a single electronic origin, while the positive MCD band at  $\sim 300\text{ nm}$  seems to be a result of a superimposition of two or three electronic transitions.

It is concluded that the complicated electronic spectrum of azuleno[1,2,3-cd]phenalene was well resolved in the MCD spectrum leading to give them reasonable spectroscopic assignments.

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