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MCD STUDIES OF o,o'-BRIDGED BIPHENYLS

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The magnetic circular dichroism (MCD) spectra of o,o'-bridged biphenyls were measured, at room temperature, in the wavelength regions of 200 nm to 350 nm. They all showed the Faraday B terms caused by a magnetic coupling of the lower-lying non-degenerate electronic states. A careful inspection of the MCD spectra with the aid of the results of the CNDO calculations led to preferable spectroscopic assignments of the absorption bands of o,o'-bridged biphenyls.

As far as the optical properties of biphenyl and its derivatives are concerned, one of their most characteristic aspects is displayed by an appearance of an intense structureless absorption band with its maximum at the wavelength range of 260-280 nm. This band is known to be very sensitive to the variation of the torsional angle around the central C-C bond of biphenyl, resulting in changes both in the location of the band maximum and its intensity.1) As is seen from Fig. 1, this band shows a marked red shift and an enhancement in its intensity2-4) as the conjugation between the two benzene rings becomes possible by a decrease of the dihedral angle, θ, of biphenyl, and is therefore called the conjugation band.

On the other hand, two other electronic transitions were predicted to be in the longer wavelength region in D_2 or D_{2h} configuration. Usually these transitions are hidden behind the strong conjugation band and either not observed in the absorption spectra or only detected, at most, as a slight shoulder based on the background of the conjugation band.

The purpose of this paper is to use the MCD technique,5) which is known to be a very powerful tool in investigating electronic structures and spectra of molecules and ions in their ground and excited states,6-8) to detect hidden transitions and to clarify spectroscopic assignments of o,o'-bridged biphenyls. The biphenyls studied are biphenyl, fluorene, 9,10-dihydrophenanthrene and 1,2,6,7-tetrahydropyrene which are assumed to belong to the D_2 point group except for fluorene (D_{2h}).

The samples obtained commercially were recrystallized several times from appropriate solvents. All measurements were carried out at room temperature in cyclohexane solution, using a JASCO-20A recording circular dichrograph equipped with an electro-magnet supplying a magnetic field strength of 11.25 kG. We showed the MCD and UV spectra of biphenyl, fluorene, 9,10-dihydrophenanthrene and 1,2,6,7-tetrahydropyrene in Fig. 2, and summarized their spectral features in Table 1.

In Fig. 2a the MCD and UV spectra of biphenyl are shown for a comparison with those of o,o'-bridged biphenyls, in which a seemingly single absorption band with its maximum at 250 nm is split into, at least, two in the MCD spectrum. One of them with well-resolved fine structure is assigned to the $B_3 \leftarrow A$ transition, the conjugation band. The other, in turn, may reasonably be considered to be a band originated from the $B_2 \leftarrow A$ or $B_1 \leftarrow A$, or to be a superimpose of the two.

Figure 2b shows the MCD and UV spectra of fluorene. The UV spectrum of this molecule is courageous for us owing to its well-resolved fine structure in the longest wavelength absorption band. Unfortunately, however, the MCD spectrum is missing in this region. This may be related

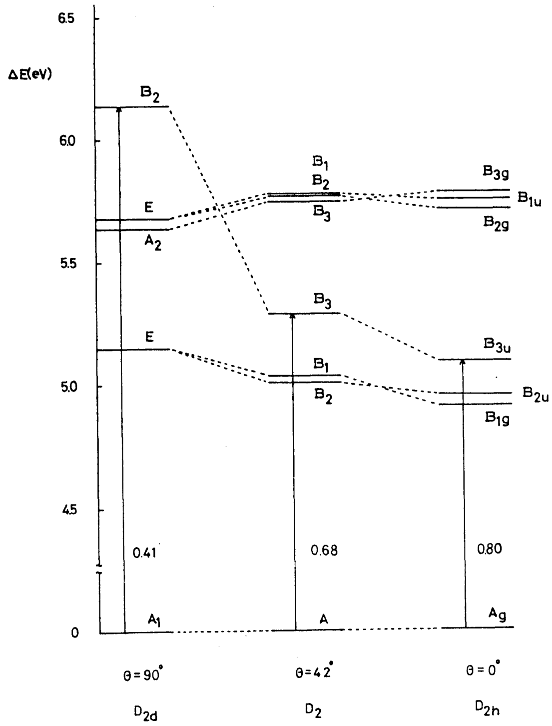


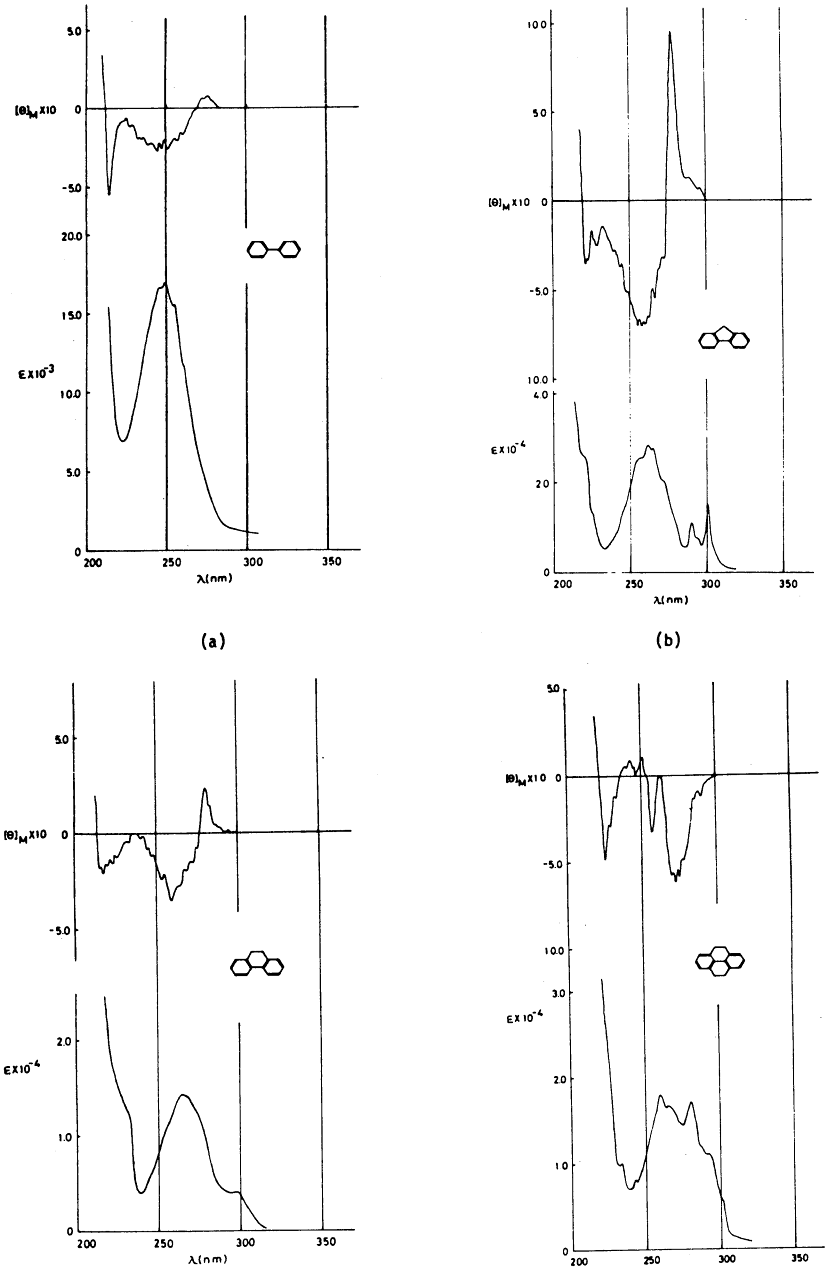
Fig.1. Lower excited states of biphenyl predicted within the framework of the CNDO method. A transition corresponding to the conjugation band is indicated by an arrow in each configuration along with its calculated oscillator strength.

Table 1. MCD Spectral Features of o,o'-Bridged Biphenyls

Compound	$\lambda^{UV}_{max.}$(nm)	$\lambda^{MCD}_{max.(min.)}$(nm)	$[\theta]^{*}_{M}\times 10$	Transition
Biphenyl	——	——	——	$B_2 \leftarrow A$
	249	276	+0.8	$B_1 \leftarrow A$
		244	-2.7	$B_3 \leftarrow A$
	——	214	-5.5	$B_3 \leftarrow A$
Fluorene	300	——	——	$B_{1g} \leftarrow A_g$
	262	278	+9.5	$B_{2u} \leftarrow A_g$
		258	-7.5	$B_{3u} \leftarrow A_g$
	220(s)**	221	-3.3	$B_{3u} \leftarrow A_g$
9,10-Dihydro-phenanthrene	298	——	——	$B_2 \leftarrow A$
	265	280	+2.8	$B_1 \leftarrow A$
		259	-3.3	$B_3 \leftarrow A$
	230(s)**	218	-2.5	$B_3 \leftarrow A$

* $[\theta]_M$ in deg cm^2 G^{-1} mol^{-1}.

** shoulder band



(a) (b)

(c) (d)

Fig. 2. The MCD(top) and UV(bottom) spectra of biphenyl(a), fluorene(b), 9,10-dihydrophenanthrene(c) and 1,2,6,7-tetrahydropyrene(d) at room temperature.

to the fact that fluorene has a forced coplanar ($\theta=0^\circ$) or near coplanar configuration because of a single methylene bridge over o,o'-position of biphenyl. From a group theoretical consideration it is clarified that the lowest excited state B_{1g} can never cause a magnetic coupling with any other states. A sharp positive MCD band with its maximum at 278 nm is assigned to the electronic transition $B_{2u} \leftarrow A_g$ which is scarcely discernible in the UV spectrum. The MCD band corresponding to the conjugation band is appeared as a negative peak at 258 nm.

The MCD and UV spectral features of 9,10-dihydrophenanthrene (Fig. 2c) are the same, as a whole, as those of fluorene. A sharp positive peak at 280 nm corresponds to the electronic transition $B_1 \leftarrow A$ which is hidden behind the strong conjugation band and appeared, at about 275 nm, as a gentle shoulder in the UV spectrum. A negative MCD peak at 259 nm is the conjugation band. As is in the case of fluorene, the longest wavelength MCD band is also missing in this molecule.

The MCD spectrum of 1,2,6,7-tetrahydropyrene (Fig. 2d) is so complicated that a plausible explanation cannot be given. The shortest wavelength negative MCD band which is appeared in common in each spectrum is ascribed to a higher electronic transition $B_3 \leftarrow A$ because of its immovability of the location. This is in good agreement with the theoretical prediction.

It is shown that the hidden transitions of biphenyl and o,o'-bridged biphenyls which have been predicted to be in the wavelength region of 240-280 nm are clearly observed in their MCD spectra leading to give them preferable assignments ($B_1 \leftarrow A$ for D_2 configuration and $B_{2u} \leftarrow A_g$ for D_{2h}).

The similarity of the MCD spectra of o,o'-bridged biphenyls to those of biphenyl itself leads to conclude that the methylene bridge can never cause an appreciable change in the electronic structures of biphenyl skeleton, while substituents such as -OH and $-NH_2$ are known to give rise to a sign-inversion of the corresponding MCD band and an appearance of a new band which is considered to be an intra-molecular charge-transfer (CT) band.[9)]

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