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The Magnetic Circular Dichroism of the Conjugated *O*- and *S*-Heterocycles

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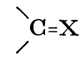
The MCD spectra of the monobenzo and dibenzo derivatives of thiophene and furan are reported; especially in dibenzofuran, two electronic origins are revealed in its lowest energy absorption band. The quantum-mechanical calculations of the transition energies and the Faraday parameters elucidate the experimental data to a fair extent, suggesting similarities in the electronic structures of the lower-lying excited states of furan and thiophen derivatives.

The oxygen (sulfur) atom is incorporated into a conjugated system so as to form ether (thioether) or ketone (thioketone). Sulfur heterocycles of the former type have attracted the attention of many authors because of their characteristic chemical and physical properties.

=C-X-C=



$>C=X$

X=O, S

Johnstone *et al.*[1] have measured the UV and photoelectron spectra of molecules containing several sulfur atoms located in the five-membered ring part of the structure, and have tried to elucidate the observed spectra within the framework of semi-empirical SCF–MO–CI calculations, retaining both the one-center and two-center core integral terms as variable parameters. They have found reasonable values which reproduce the observed electronic spectra. The photoelectron spectra of planar sulfur heterocycles, such as benzothiophene, thienothiophene, and benzothiadiazole have been reported by Clark *et al.*[2] The ionization potentials calculated by the extended Hückel and the PPP method, without 3d atomic orbitals in the basis set, give good agreement with the experimental data; this suggests that sulfur 3d-orbital participation must be very small. The singlet-singlet absorption spectra of six-membered heterocyclic compounds were studied by the use of the PPP method in order to make spectroscopic assignments in the UV region.[3]

The UV spectra of thiophenes seem to have thus far been discussed in conjunction with those of furans, leading to a similarity and correspondence between their electronic transitions. Recently, however, Bree *et al.*[4] have measured the single-crystal absorption spectra of dibenzofuran and shown that the lowest absorption band, which seems to correspond to that of dibenzothiophene, consists of two electronic transitions; one is polarized along the short axis, and the other, along the long axis. Although this point has been further investigated by Tanaka,[5] the vibrational structure has complicated the resolution of the band into its two electronic components.

On the other hand, the magnetic circular dichroism (MCD) technique[6] has been recognized to be a powerful tool for investigating the electronic structures of molecules and their ions in their ground and excited states.[7] In addition, the MCD technique often reveals hidden transitions or resolves heavily overlapping bands into their components. However, although simple organic compounds and their ions have been extensively studied,[8] the MCD technique has not been applied to organic sulfur compounds except for thiophene.[9,10] Håkansson and Nordén[9,10] have demonstrated the existence of two transitions with opposite MCD in the UV-spectral region of thiophene.

In this paper, the electronic structures of thiophene, furan, and their benzo derivatives are investigated from the viewpoint of MCD spectroscopy. On the basis of the UV and MCD spectral data and the results of the PPP calculation, the electronic states of these compounds will be discussed.

Experimental

The thiophene, furan, benzo[*b*]thiophene, benzofuran, dibenzothiophene, and dibenzofuran were purified by repeated distillation or sublimation after recrystallization. Cyclohexane, ethanol, and heptane were used as solvents; all were of a spectral grade.

The MCD spectra were measured with a JASCO J-500C recording spectropolarimeter using an electromagnet, while the UV spectra were recorded on a HITACHI EPS-3T recording spectrophotometer. The magnetic-field strength was calibrated with freshly prepared potassium hexacyanoferrate(III) and was 1.169T.

The observed spectrum was resolved into its components according to the curve-fitting procedure assuming a Gaussian function. The error in estimating the area under the curve was less than ±5%. The experimental oscillator strengths, *f*, and Faraday B terms, *B*, were extracted according to the following equations:

$$f = 4.3792 \times 10^{-9} \times \tilde{\nu}_0 \times \int \frac{\varepsilon(\tilde{\nu})}{\tilde{\nu}} \mathrm{d}\tilde{\nu}, \tag{1}$$

$$B = \frac{1}{33.5294} \times \int \frac{[\theta]_{\mathrm{M}}(\tilde{\nu})}{\tilde{\nu}} \mathrm{d}\tilde{\nu}, \tag{2}$$

where f and B were expressed in units of cgs and (debye)$^2\beta$/cm^{-1} (β=Bohr magneton) respectively.

Theoretical Calculations

The excitation energies, the oscillator strengths, and the Faraday *B* values of the furans and thiophenes have been calculated within the framework of the PPP approximation,[11] including configuration interaction (CI) among the 28 singly excited configurations. The one-center core and repulsion integrals have been evaluated from the valence-state ionization potentials and electron affinities using the table of Hinze and Jaffé.[12] For the sulfur atom, the one-center core and repulsion integrals are −16.27 eV and 10.78 eV respectively. The two-center core and repulsion integrals have been evaluated by the use of the Wolfsberg-Helmholz[13] and Nishimoto-Mataga[14] equations respectively. The proportionality constant, κ, in the

Wolfsberg-Helmholz equation has been chosen to be 0.7602 so as to reproduce the observed extrema of the MCD spectra of thiophene.

In the absence of degeneracy, a quantum mechanical expression for the Faraday B value associated with an electronic transition a←0 is:

$$B_{0a} = \frac{1}{3} Im \left\{ \sum_{b \neq 0} \frac{\hat{\mu}_{b0}}{\nu_{b0}} \cdot \hat{m}_{0a} \times \hat{m}_{ab} + \sum_{b \neq a} \frac{\hat{\mu}_{ab}}{\nu_{ab}} \cdot \hat{m}_{0a} \times \hat{m}_{b0} \right\}, \quad (3)$$

where $\hat{\mu}_{ij}$ and $\hat{m}_{ij}$ represent the off-diagonal matrix elements of the magnetic- and electric-moment operators respectively, whereas Im stands for taking the imaginary part of the bracketed expression of the above equation. The denominator ν_{ij} is the energy difference between the i and j states. The atomic orbitals used in the calculation are the Slater AO's χ, with which the basis set, χ^{λ}, in the PPP procedure is expanded in terms of the overlap integral, S, according to this equation:[15)]

$$\chi^{\lambda} = \chi S^{-1/2}. \quad (4)$$

The molecular geometries of furan and thiophene were taken from microwave results,[16,17)] and those of dibenzofuran and dibenzothiophene, from the X-ray diffraction data.[18,19)] In benzofuran and benzo[*b*]-thiophene, the nuclear arrangements were assumed to be those of furan and thiophene for the five-membered ring, while the bondlengths in the six-membered ring were taken to be equal, 1.40 Å.

Results and Discussion

The UV and MCD spectra of furans and thiophenes are reproduced in Figs. 1—5. In each figure, the full line shows the observed spectrum, while the broken lines stand for the curves after the curve-fitting procedure.

Thiophene and Furan. In the spectral region corresponding to the lowest energy-absorption band of thiophene, there have been observed two MCD bands; one is negative at a higher energy, while the other is positive, as is shown in Fig. 1. It is clear that there are at least two π-π^* electronic origins in this region, as has already been pointed out by Håkansson and Nordén.[9,10)] In their calculation, based on the PPP method, these two oppositely directed MCD bands have nearly equal transition energies and Faraday B values which are too large to reproduce the experimental values. This comes from the small energy gap between the lowest two excited states predicted in their calculation. On the contrary, it should be noted that the experimental B values are larger for the higher-energy band than for the lower-energy band, even though cancellation is taken into account.

In Table 1 the theoretical results for thiophene are summarized and listed along with the experimental data. The lowest energy transition is predicted to be $B_2 \leftarrow A_1$, with its transition moment directed along the long axis, while the second is $A_1 \leftarrow A_1$, with its transition moment directed along the short axis. The theoretical oscillator strengths and Faraday B values seem to reproduce well the relative magnitudes of the experimental data. Especially the splitting of the first and second excited states is calculated to be 3500 cm^{-1}, in fairly good agreement with the observed

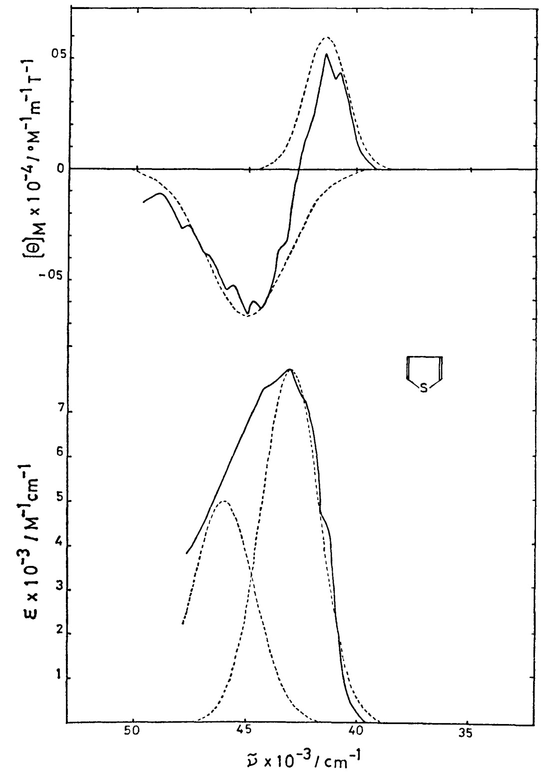


Fig. 1. The MCD (upper) and absorption (lower) spectra of thiophene in cyclohexane at room temperature.

TABLE 1. THE OBSERVED AND CALCULATED SINGLET-SINGLET π-π^* TRANSITION ENERGIES, $\tilde{\nu}$, OSCILLATOR STRENGTHS, f, AND FARADAY PARAMETERS, B, FOR THIOPHENE AND FURAN

Molecule	Calculated				Observed			
	$\tilde{\nu} \times 10^{-3}$ / cm^{-1}	f	$B \times 10^5$ / β Debye^2 cm	Transition symmetry	$\tilde{\nu}^{UV} \times 10^{-3}$ / cm^{-1}	f	$\tilde{\nu}^{MCD} \times 10^{-3}$ / cm^{-1}	$B \times 10^5$ / β Debye^2 cm
Thiophene[a)]	42.6	0.433	−20.37	$B_2 \leftarrow A_1$	43.0	0.115	41.5	−101.6
	46.1	0.002	28.00	$A_1 \leftarrow A_1$	46.0	0.066	45.0	199.4
Furan[b)]	41.7	0.299	4.86	$B_2 \leftarrow A_1$	48.5	0.300	47.0	30.0
	45.8	0.000	1.38	$A_1 \leftarrow A_1$				

a) The experimental values after curve analysis. b) The experimental values from B. Nordén, R. Håkansson, P. B. Pedersen, and E. W. Thulstrup, *Chem. Phys.*, **33**, 355 (1978).

value, 3000 cm^{-1}.

Nordén *et al.* observed a negative MCD band at 47000 cm^{-1} and also an onset of the positive MCD band in the energy region higher than 50000 cm^{-1} for the broad absorption spectrum of furan, which suggests that there are two electronic transitions.[10]

Our calculated results for furan are included in Table 1. In the lower-energy region two π-π^* transitions assigned to $B_2 \leftarrow A_1$ and $A_1 \leftarrow A_1$ are predicted. The sign of the B value associated with the first transition is positive, in agreement with the experimental results. As for the excitation energies, however, the theoretical values are in disagreement with the experimental values.

Benzo[b]thiophene and Benzofuran. The UV and MCD spectra of benzo[*b*]thiophene are illustrated in Fig. 2. In the highest energy region, two negative peaks are observed at *ca.* 44000 cm^{-1} and *ca.* 46000 cm^{-1} in the MCD spectrum. It seems to be interesting to consider whether they are due to the vibrational structure or to different electronic origins. We ascribed these bands to the latter, because the PPP method calculation indicates that there are two π-π^* electronic transitions in this energy region. Accordingly, the MCD and UV spectra are resolved into four components, assuming Gaussian functions. Then, corresponding to four absorption bands of benzo[b]-thiophene, four MCD bands are observed; their signs are all negative except that of the lowest energy band, at 34500 cm^{-1}.

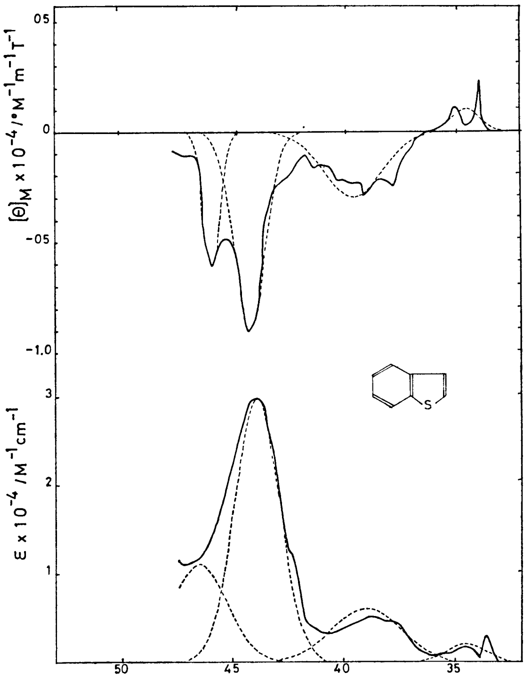


Fig. 2. The MCD (upper) and absorption (lower) spectra of benzo[b]thiophene in ethanol at room temperature.

The theoretical results for benzo[b]thiophene are listed in Table 2, along with the experimental data. Calculation gives the transition energies at 33000, 38600, 45300, and 47200 cm^{-1}, in good agreement with the observed values of 34500, 39000, 43900, and 46500 cm^{-1} respectively. Benzo[*b*]thiophene belongs to the point group C_s, and these four transitions are assigned to $A' \leftarrow A'$ polarized on the molecular plane. The predicted B values seem to agree well with the extracted values both in sign and magnitude. Unfortunately, however, the calculation gives a negative B value associated with the fourth transition, while the experiment gives a positive value. The further inclusion of the CI neglected in this calculation may improve this disagreement.

As is shown in Fig. 3, the UV and MCD bands are blue-shifted in benzofuran. Only two bands are observed for benzofuran in the UV region, although there are four bands for benzo[*b*]thiophene. These two bands, however, in the lower-energy region are similar to those of benzo[*b*]thiophene with respect to the spectral-band shape and the absorption coefficient. At energies higher than 46000 cm^{-1}, a strong absorption band with a negative MCD is observed. As a result, it is expected that the MCD sign sequence of benzofuran is +, −, −, which is the same as that of benzo[*b*]thiophene, and benzofuran seems to show a band system similar to that of benzo[*b*]thiophene in the whole UV spectral region.

The calculation predicts that benzofuran has positive and negative MCD bands for the first and the second transitions respectively. The absolute values of the Faraday B term and the oscillator strength associated

Table 2. The observed and calculated singlet-singlet π-π^* transition energies, $\tilde{\nu}$, oscillator strengths, f, and Faraday parameters, B, for benzo[*b*]thiophene and benzofuran

Molecule	Calculated				Observed			
	$\tilde{\nu} \times 10^{-3}$ / cm^{-1}	f	$B \times 10^5$ / β Debye^2 cm	Transition symmetry	$\tilde{\nu}^{UV} \times 10^{-3}$ / cm^{-1}	f	$\tilde{\nu}^{MCD} \times 10^{-3}$ / cm^{-1}	$B \times 10^5$ / β Debye^2 cm
Benzothiophene	33.0	0.001	−20.22	$A' \leftarrow A'$	34.5	0.019	34.5	−12.9
	38.6	0.565	85.91	$A' \leftarrow A'$	39.0	0.103	39.5	76.5
	45.3	0.501	81.59	$A' \leftarrow A'$	43.9	0.330	44.2	107.7
	47.2	0.130	−92.14	$A' \leftarrow A'$	46.5	0.098	45.9	38.0
Benzofuran	32.8	0.001	−11.90	$A' \leftarrow A'$	36.6	0.020	37.0	−71.8
	38.6	0.474	66.52	$A' \leftarrow A'$	41.5	0.193	41.6	188.5
	44.9	0.374	71.61	$A' \leftarrow A'$	—	—	—	(positive)
	47.2	0.041	22.47	$A' \leftarrow A'$	—	—	—	

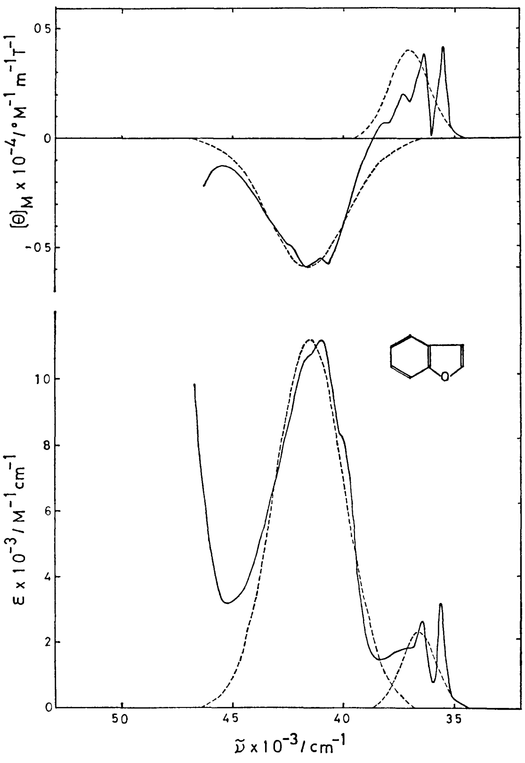


Fig. 3. The MCD (upper) and absorption (lower) spectra of benzofuran in ethanol at room temperature.

with the first transition are smaller than those associated with the second one, which is in good agreement with the experimental values. For the second and the third transitions, it is found that the relative magnitude of the theoretical values for benzofuran is similar to that for benzo[*b*]thiophene. The calculation seems to show the similarity between benzofuran and benzo[*b*]thiophene, as does the experiment.

Dibenzothiophene and Dibenzofuran. Figure 4 shows the observed and resolved spectra for dibenzothiophene. The MCD spectrum is considered to consist of five main bands, with extrema at 32000, 35500, 38800, 42100, and 44000 cm^{-1}. Accordingly, the observed UV spectrum is resolved into three components in the spectral range of 37000—46000 cm^{-1}, so as to give five absorption bands as a whole. In both the UV and MCD spectra the lowest energy band is assumed to be single.

The UV and MCD spectra of dibenzofuran are reproduced in Fig. 5. Apart from the blue-shifts of the bands, the observed UV spectrum of dibenzofuran seems to have the same profile as that of dibenzothiophene, provided that a shoulder at 43700 cm^{-1} in Fig. 5 corresponds to the third absorption band in dibenzothiophene.

On the other hand, the MCD spectrum of dibenzofuran shows a complicated band system different from that of dibenzothiophene; especially in the lowest energy absorption region, the MCD spectrum shows a fine structure with an alternating sign. These positive and negative MCD bands may be ascribed to either electronic or vibrational origins. In general, prominent sign-alternation is observed in the MCD

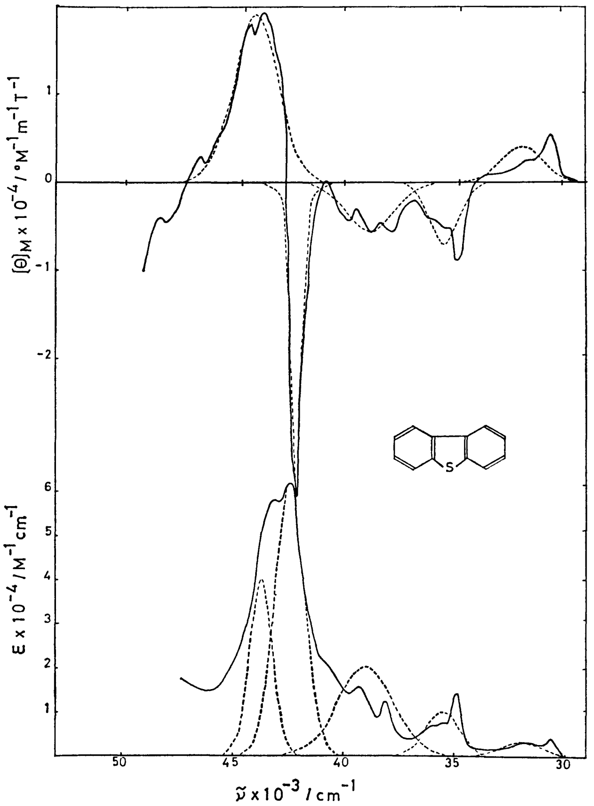


Fig. 4. The MCD (upper) and absorption (lower) spectra of dibenzothiophene in heptane at room temperature.

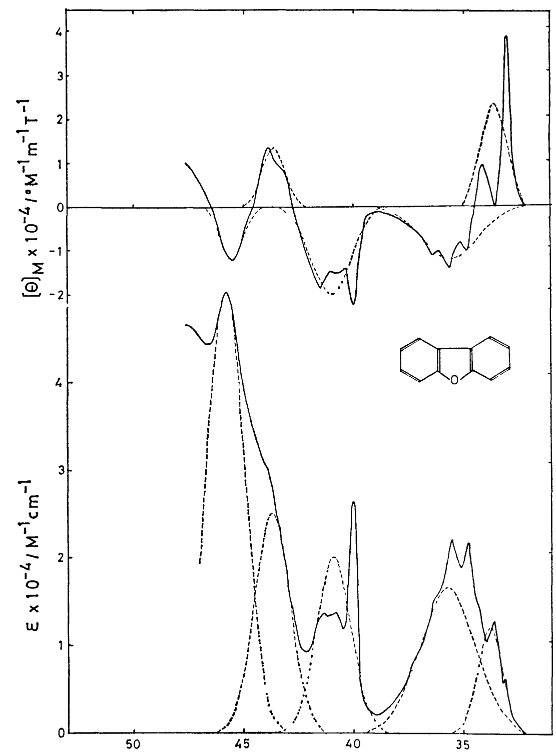


Fig. 5. The MCD (upper) and absorption (lower) spectra of dibenzofuran in cyclohexane at room temperature.

TABLE 3. THE OBSERVED AND CALCULATED SINGLET-SINGLET π-π^* TRANSITION ENERGIES, $\tilde{\nu}$, OSCILLATOR STRENGTH, f, AND FARADAY PARAMETERS, B, FOR DIBENZOTHIOPHENE AND DIBENZOFURAN

Molecule	Calculated				Observed			
	$\tilde{\nu}\times10^{-3}$/cm^{-1}	f	$B\times10^5$/βDebye^2 cm	Transition symmetry	$\tilde{\nu}^{UV}\times10^{-3}$/cm^{-1}	f	$\tilde{\nu}^{MCD}\times10^{-3}$/cm^{-1}	$B\times10^5$/βDebye^2 cm
Dibenzothiophene	32.6	0.001	−79.60	$A_1\leftarrow A_1$	32.0	0.031	32.0	−87.8
	34.1	0.040	6.60	$B_2\leftarrow A_1$				
	35.9	0.749	170.68	$B_2\leftarrow A_1$	35.5	0.084	35.5	95.6
	45.7	0.066	35.61	$A_1\leftarrow A_1$	39.0	0.280	38.8	112.5
	46.7	0.673	1588.92	$B_2\leftarrow A_1$	42.4	0.463	42.1	163.4
	46.9	1.111	−1444.46	$A_1\leftarrow A_1$	43.7	0.222	44.0	−321.2
Dibenzofuran	33.6	0.000	−18.70	$A_1\leftarrow A_1$	33.8	0.073	33.6	−298.9
	34.5	0.004	−3.93	$B_2\leftarrow A_1$	35.7	0.231	35.6	321.4
	38.5	0.683	104.84	$B_2\leftarrow A_1$	40.9	0.172	41.0	320.7
	45.8	0.080	54.72	$A_1\leftarrow A_1$	43.7	0.220	43.6	−116.8
	46.7	0.689	261.23	$B_2\leftarrow A_1$	45.8	0.441	45.5	101.8
	47.0	0.470	22.21	$B_2\leftarrow A_1$	47.2[a]	—	—	—

a) "UV Atlas of Organic Compounds," Verlag Chemie, Weinheim, Butterworths, London (1967).

spectra for symmetry-forbidden but vibronically-allowed transitions, such as the $B_{2u}\leftarrow A_{1g}$ transition of benzene.[20] In order to examine the existence of symmetry-forbidden transitions, the INDO/S calculations[21] were carried out for dibenzofuran. However, neither n-π^*, σ-π^* nor π-σ^* electronic transitions were predicted in the energy region lower than 40000 cm^{-1}. The possibilities of the electronic origins due to n-π^*, σ-π^*, and π-σ^* transitions, and, in turn, the possibility of the vibrational origin, seem to be quite small. The positive and negative MCD bands in the lowest energy region are ascribed to two π-π^* electronic transitions. Considering this in conjunction with the positive onset of the MCD spectrum in the highest energy region, dibenzofuran can be said to show a band system consisting of six main bands (see the resolved UV and MCD spectrum in Fig. 5).

The PPP method predicts two π-π^* electronic transitions in the lowest energy region for dibenzofuran. The $A_1\leftarrow A_1$ and $B_2\leftarrow A_1$ transitions are encountered at 33600 cm^{-1} and 35600 cm^{-1}; they are assigned to the first and second MCD bands at 33800 cm^{-1} and 35700 cm^{-1} respectively. The calculation gives the same results as for the single-crystal absorption spectra with regard to the polarization of these transitions.[4,5] For the remaining four transitions, the assignments are given in Table 3.

The theoretical results for dibenzothiophene are summarized and listed in Table 3, which shows that two π-π^* transitions are predicted in the lowest energy region; one is at 32600 cm^{-1} and the other, at 34100 cm^{-1}. For comparison, a schematic diagram of the states for dibenzothiophene and dibenzofuran is given in Fig. 6. A very close similarity is found for the predominant configuration which contributes to the excited state in question. In conclusion, six π-π^* electronic transitions are theoretically predicted in the UV spectral region of dibenzothiophene.

It seems reasonable to consider that there exists a similarity between dibenzofuran and dibenzothiophene as to the π-π^* electronic transitions, because both the molecules are iso-π-electronic; nevertheless, the observed UV and MCD spectra of the former consist of six main bands while those of the latter consist of five main bands.

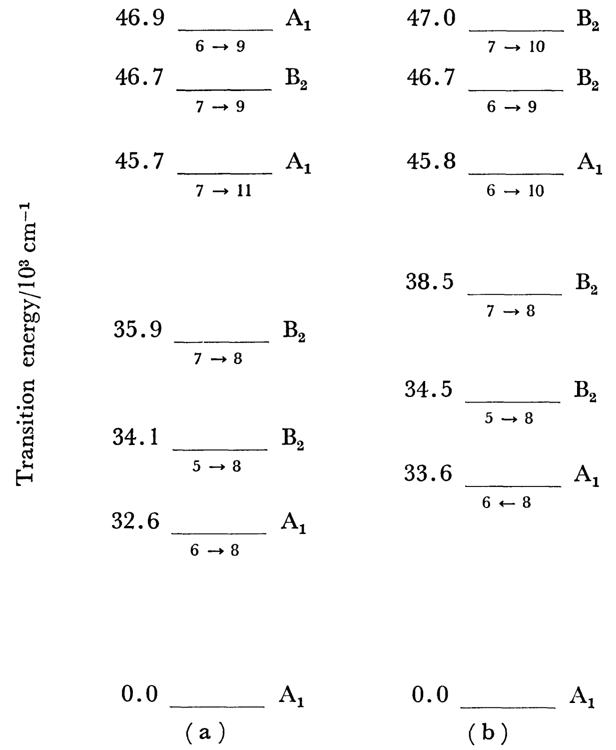


Fig. 6. The calculated lower lying excited states in dibenzothiophene(a) and dibenzofuran(b). The numbers under the bars stand for the main singly excited configuration contributing to the CI state.

Accordingly, it appears that there is one more transition in the lowest spectral region of dibenzothiophene as well as of dibenzofuran. This may be partially verified by the PPP calculation, which predicts two closely separated π-π^* transitions in dibenzothiophene. One of the two transitions in dibenzothiophene, however, is considered to be so weak as not to be observed or as to be hidden by the neighbouring transition, which was difficult to resolve even in the present MCD work.

Concluding Remarks

The lowest absorption band of dibenzofuran is confirmed, by the analysis of the MCD spectra and the PPP calculation, to be a super position of the two π-π^* electronic transitions, which is consistent with the results of the single-crystal experiments by Bree *et al.*[4] and Tanaka.[5] For dibenzothiophene, the lowest absorption band is expected to consist of two transitions, although the present work was not successful in resolving these transitions.

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