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Experimental and Theoretical Studies on Magnetic Circular Dichroism and Circular Dichroism of Triptycene Derivatives

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Abstract: The MCD, CD, and UV spectra of substituted triptycenes were measured. Some overlapping absorption bands were separated in the MCD and CD spectra. Spectroscopic assignments were discussed on the basis of the signs of the MCD and CD spectra. Faraday B terms and rotational strengths were calculated using wave functions obtained from the "molecules in molecule" method and the results are in good agreement with experimental data. The absolute configurations of optically active triptycenes determined by the present CD spectral analysis are consistent with those obtained from X-ray crystallographic analysis using the Bijvoet method.

Triptycene, one of the most interesting cage compounds with conjugated systems around its cage, was first synthesized by Bartlett et al.[2] as early as 1942. It contains three benzene rings which are tightly connected at the ortho position by two sp^3-hybridized carbon atoms. If substituent groups are dissymmetrically introduced to the benzene rings of triptycene, the compound becomes optically active. The absolute configurations of optically active triptycenes have been determined using the Bijvoet method of X-ray crystallographic analysis,[3,4] and exciton theoretical analysis of the circular dichroism (CD) spectra.[5-9]

Triptycene derivatives show many absorption bands due to the $\pi \rightarrow \pi^*$ transitions of three benzene rings in the ultraviolet region. However, a detailed explanation of the spectra is not possible because of large overlaps of the absorption bands.

On the other hand, the magnetic circular dichroism (MCD) technique has made remarkable progress in elucidating magnetic moments of the ground and excited electronic states and in clarifying spectroscopic assignments of ions and molecules.[10-13] The molecules with an n-fold axis ($n > 2$) are expected to show Faraday A and C terms resulting from Zeeman splitting of the degenerate ground and excited state, whereas the lower symmetrical molecules exhibit only the Faraday B term due to mixing of the electronic states by the external magnetic fields. Recently, the effect of substituent groups on the signs of the Faraday B terms of substituted benzenes has become of great interest.[14-18] The signs of the MCD spectrum of monosubstituted benzene with electron-donating substituent groups are negative and positive for the first and second transitions, respectively, whereas the situation is reversed for benzene derivatives with electron-accepting groups.[18] From this point of view, it seems interesting to try to interpret the complex absorption spectra of triptycene derivatives using the signs of the MCD bands of constituent benzene derivatives. Although it is a matter of fact that the CD technique is a powerful tool in clarifying the assignments of the absorption bands of optically active triptycenes, the MCD technique should be noted to be useful in such a sense that it is applicable not only to optically active triptycenes, but also to optically inactive or racemic triptycenes. In this work, spectral assignments of the triptycene derivatives are examined not only by analyzing the CD spectrum of optically active triptycenes, but also by comparing the signs of the MCD spectra of triptycene derivatives with those of substituted benzenes. In addition, the Faraday B terms and rotational strengths of substituted triptycenes are calculated by the use of wave functions obtained from the "molecules in molecule" method.[19]

Experimental Section

Synthesis of the samples was described in previous papers.[20] Spectrograde methanol, ethanol, and dioxane were used as solvents. MCD and CD spectra were measured with a JASCO J-20A recording spectropolarimeter, and UV spectra were recorded on a Hitachi EPS-3T recording spectrophotometer. A 12.2-kG electromagnet was used for measurement of the MCD spectra.

Experimental rotational strengths (R) and Faraday B terms were obtained from

$$R = \frac{7.51 \times 10^{-5}}{\nu_{\max}} \int_{\text{band}} [\theta]\, d\nu \qquad (1)$$

$$B = -\frac{1}{33.53\nu_{\max}} \int_{\text{band}} [\theta]_{\mathrm{M}}\, \mathrm{d}\nu \qquad (2)$$

where R and B are expressed in Dβ and in D$^2\beta$/cm^{-1} (β = Bohr magneton), respectively.

Theoretical Section

According to the "molecules in molecule" method,[19] the ground state of substituted triptycene is described by the product of the wave functions of the ground states of three benzene derivatives, Ψ_{io}, namely

$$\Psi_o = \prod_{i}^{3} \Psi_{io} \qquad (3)$$

The kth excited state of substituted triptycene is represented by

$$\Psi_k = \sum_{i}^{3} \sum_{a}^{N_i} C_{k,ia} \Psi_{ia} \prod_{j \neq i}^{3} \Psi_{jo} \qquad (4)$$

where Ψ_{ia} denotes the excited state a in the ith benzene ring, and N_i is the number of excited states of the ith chromophore. The coefficients $C_{k,ia}$ and energies E_k of the excited state k can be obtained by solving the secular equation

$$|V_{ia,jb} - \delta_{ia,jb} E| = 0 \qquad (5)$$

in which $V_{ia,jb}$ is the energy of interaction between the excited state a in the ith chromophore and the excited state b in the jth group, and $\delta_{ia,jb}$ is the Kronecker δ.

The diagonal element, $V_{ia,ia}$, is the transition energy of the $a \leftarrow o$ transition of the ith benzene ring, which is taken from the observed absorption spectra of substituted benzenes in solution. The lowest four or five excited states in each group which correspond to the $^1B_{2u}$, $^1B_{1u}$, and $^1E_{1u}$ states of benzene itself were taken into account, that is, N_i = 4 or 5.

The Coulombic interaction between the excited states a and b in the different groups, $V_{ia,jb}$ ($i \neq j$), is expressed as

$$V_{ia,jb} = \sum_{k}^{n_i} \sum_{l}^{n_j} q_{ia,k} q_{jb,l} \gamma_{kl} \qquad (6)$$

where n_i and n_j are the number of atoms in the ith and jth chromophores, respectively. The transition density on atom k of the $a \leftarrow o$ transition in the ith group, $q_{ia,k}$, is given by

$$q_{ia,k} = \sqrt{2} \sum_{m}^{\text{occ}} \sum_{n}^{\text{vac}} K_{ia,m \rightarrow n} c_{mk} c_{nk} \qquad (7)$$

where $K_{ia,m \rightarrow n}$ is the coefficient of a configuration in which one electron is excited from the mth molecular orbital to the nth molecular orbital in the excited state a of the ith benzene ring, and c_{mk} is the LCAO-MO coefficient of the kth atomic orbital in the mth molecular orbital. The first and second sums in eq 7 are taken over the occupied and vacant MO's, respectively. The value of the transition density, $q_{ia,k}$, is calculated by the use of wave functions obtained from the Pariser–Parr–Pople (PPP) approximation.[21] The electron repulsion integral between atoms k and l in the different chromophores, γ_{kl}, is evaluated from the Nishimoto–Mataga equation[22] including the effect of tilting of the $2p_z$ AO's according to the procedure proposed by Grinter.[23]

The rotational strength and the Faraday B term of a transition $k \leftarrow o$ are given by[24-26,10-13]

$$R_{o \rightarrow k} = \mathrm{Im}\langle o|\boldsymbol{m}|k\rangle \cdot \langle k|\boldsymbol{\mu}|o\rangle \qquad (8)$$

$$B_{o \rightarrow k} = \mathrm{Im}\left\{\sum_{l \neq o} \frac{\langle l|\boldsymbol{\mu}|o\rangle}{E_l - E_o} \cdot \langle o|\boldsymbol{m}|k\rangle \times \langle k|\boldsymbol{m}|l\rangle + \sum_{l \neq k} \frac{\langle k|\boldsymbol{\mu}|l\rangle}{E_l - E_k} \cdot \langle o|\boldsymbol{m}|k\rangle \times \langle l|\boldsymbol{m}|o\rangle\right\} \qquad (9)$$

where $\boldsymbol{\mu}$ and $\boldsymbol{m}$ denote the magnetic and electric moment operators, respectively. The Faraday B terms calculated for noncentric molecules using a limited basis set are origin dependent.[16,27] In this work, origin is set at the center of charge of the ground state of the triptycene derivatives according to the proposal by Caldwell and Eyring.[16] In order to avoid the origin dependence of the calculated rotational strength, the electric moments were calculated using the dipole velocity operator, ∇.[28]

The matrix elements of the electric and magnetic moment operators are obtained to be

$$\langle o|\boldsymbol{m}|k\rangle = -\frac{e\hbar^2}{m} \sum_{i}^{3} \sum_{a}^{N_i} C_{k,ia} \nabla_{ioa} / (E_k - E_o) \qquad (10)$$

$$\langle o|\boldsymbol{\mu}|k\rangle = -\sqrt{-1}\beta \sum_{i}^{3} \sum_{a}^{N_i} C_{k,ia} (\boldsymbol{r} \times \nabla)_{ioa} \qquad (11)$$

$$\langle k|\boldsymbol{m}|l\rangle = -\frac{e\hbar^2}{m} \sum_{i}^{3} \sum_{a}^{N_i} \sum_{b}^{N_i} C_{k,ia} C_{l,ib} \nabla_{iab} / (E_l - E_k) \qquad (12)$$

$$\langle k|\boldsymbol{\mu}|l\rangle = -\sqrt{-1}\beta \sum_{i}^{3} \sum_{a}^{N_i} \sum_{b}^{N_i} C_{k,ia} C_{l,ib} (\boldsymbol{r} \times \nabla)_{iab} \qquad (13)$$

where ∇_{iab} and $(\boldsymbol{r} \times \nabla)_{iab}$ are the matrix elements of the ∇ and $\boldsymbol{r} \times \nabla$ operators, respectively, between states a and b in the ith group. These quantities were calculated at the center of charge of the ground state of the triptycene derivatives using wave functions determined on the basis of the PPP method.

The effects of the charge-transfer configurations between the benzene rings are neglected in the present calculations because of the relatively small overlap of the molecular orbitals among the benzene rings. The parameters used in the PPP procedure were determined in the same way as described in our previous paper.[18]

Calculations were carried out using the NEAC 2200 computer in the computer center of Tohoku University.

Results and Discussion

The MCD, CD and UV spectra of (−)-2,7-diaminotriptycene and (+)-2-chloro-7-methoxytriptycene are shown in Figures 1 and 2. Since these compounds contain only electron-donating substituent groups, the first negative and the second positive MCD bands can be assigned to the transitions corresponding to the $^1B_{2u} \leftarrow {}^1A_{1g}$ and $^1B_{1u} \leftarrow {}^1A_{1g}$ transitions of benzene, respectively. They are both forbidden in benzene itself, but allowed in substituted benzenes and in substituted triptycenes because of the symmetry reduction. However, it seems convenient to discuss the transition in triptycenes with respect to that of parent hydrocarbons. Therefore, the assignments are hereafter referred to those of benzene itself.

In the CD spectrum of (−)-2,7-diaminotriptycene (Figure 1), the $^1B_{2u} \leftarrow {}^1A_{1g}$ transitions of the two aniline groups show a negative-positive band pair at 33 700 and 37 300 cm^{-1}, while a positive-negative couplet is observed in the region of the $^1B_{1u} \leftarrow {}^1A_{1g}$ transitions. In the CD spectrum of (+)-2-chloro-7-methoxytriptycene (Figure 2), the $^1B_{2u} \leftarrow {}^1A_{1g}$ transitions of the anisole and chlorobenzene chromophores exhibit a positive-negative couplet at 35 600 and 38 200 cm^{-1}, and the $^1B_{1u} \leftarrow {}^1A_{1g}$ transition of the anisole group causes a negative CD band at 41 300 cm^{-1}. The intense CD bands of these compounds observed in the higher wavenumber region (44 000–50 000 cm^{-1}) are mainly induced by the coupling of the $^1E_{1u}$ states of three benzene rings.

The MCD, CD, and UV spectra of (−)-2,7-dicarboxytriptycene are shown in Figure 3. The first positive MCD band at 33 800 cm^{-1} and the second negative MCD band at 42 600 cm^{-1} are ascribed to the $^1B_{2u} \leftarrow {}^1A_{1g}$ and $^1B_{1u} \leftarrow {}^1A_{1g}$ transitions, respectively, of the benzoic acid group. The former shows negative CD bands at 32 900 and 35 400 cm^{-1}, while the latter causes a positive CD band at 41 300 cm^{-1}. The weak positive CD band at 39 100 cm^{-1} may be assigned to the $^1B_{2u} \leftarrow {}^1A_{1g}$ transition of the unsubstituted benzene ring. The

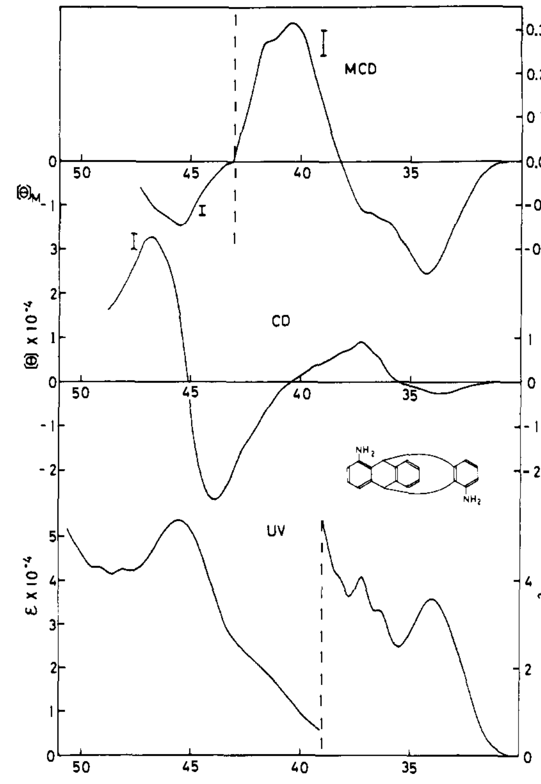

Figure 1. MCD, CD, and UV spectra of (−)-2,7-diaminotriptycene (optical purity 16%) in methanol solution at room temperature.

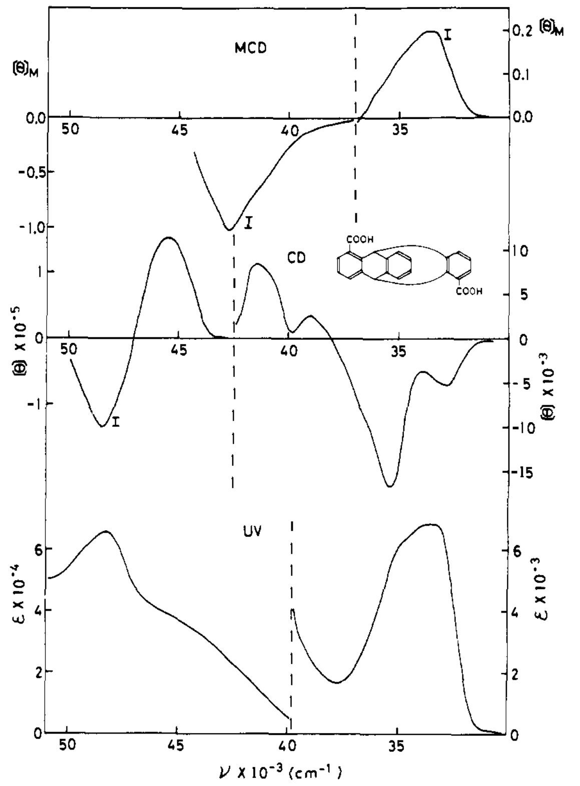

Figure 3. MCD, CD, and UV spectra of (−)-2,7-dicarboxytriptycene in ethanol solution at room temperature.

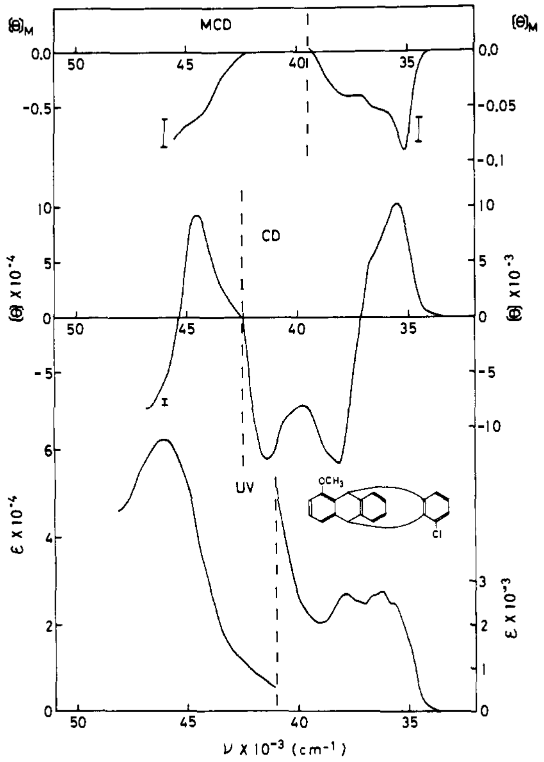

Figure 2. MCD, CD, and UV spectra of (+)-2-chloro-7-methoxytriptycene in dioxane solution at room temperature.

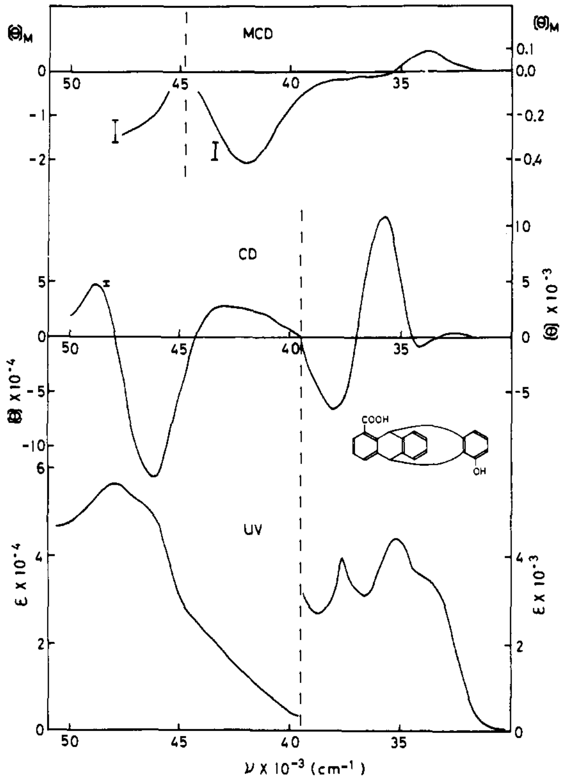

Figure 4. MCD, CD, and UV spectra of (+)-2-hydroxy-7-carboxytriptycene in ethanol solution at room temperature.

strong positive CD band at 45 400 cm^{-1} and the negative CD band at 48 500 cm^{-1} are interpreted as arising from the coupling among the $^1E_{1u}$ states.

The MCD, CD, and UV spectra of (+)-2-hydroxy-7-carboxytriptycene are shown in Figure 4. The first positive MCD band at 33 800 cm^{-1} and the negative MCD band at 42 000 cm^{-1} are attributed to the $^1B_{2u} \leftarrow {}^1A_{1g}$ and $^1B_{1u} \leftarrow {}^1A_{1g}$ transitions, respectively, of the benzoic acid group. Two weak CD bands are observed in the lowest wavenumber region (32 000–34 500 cm^{-1}). One of them corresponds to the $^1B_{2u}$

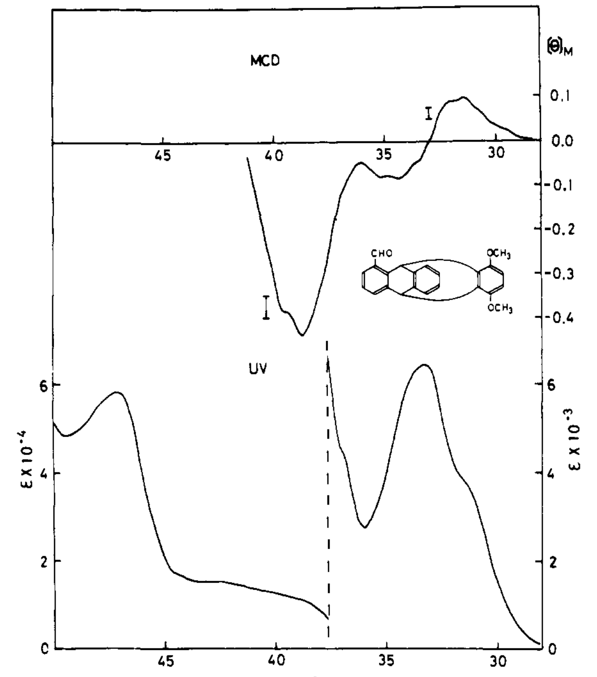

Figure 5. MCD and UV spectra of (±)-2,5-dimethoxy-7-formyltriptycene in ethanol solution at room temperature.

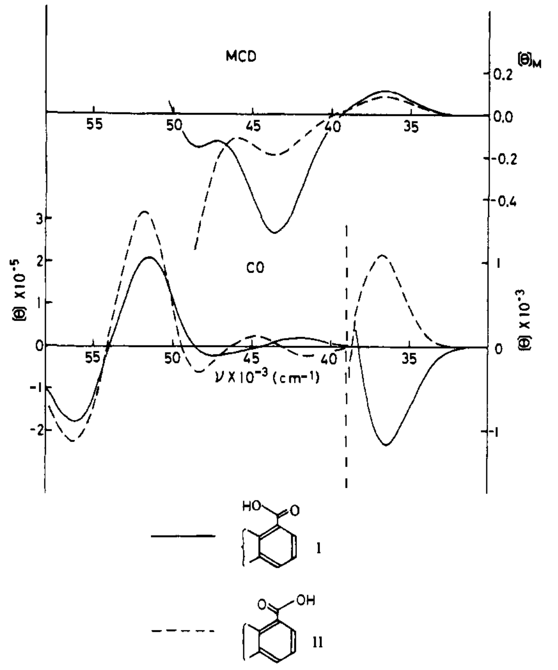

Figure 6. Calculated MCD and CD spectra of (−)-2,7-dicarboxytriptycene. The solid and broken lines denote the calculated curves of forms I and II, respectively.

$\leftarrow {}^1A_{1g}$ transition of the benzoic acid group, but the origin of another one was not determined. The positive CD band at 35 700 cm^{-1} and the negative CD band at 38 100 cm^{-1} are regarded as the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transitions of the phenol and unsubstituted benzene chromophores, respectively. In the region of the ${}^1E_{1u} \leftarrow {}^1A_{1g}$ transitions, two intense CD bands are observed at 46 200 and 48 900 cm^{-1}.

The MCD and UV spectra of (±)-2,5-dimethoxy-7-formyltriptycene are shown in Figure 5. The first positive MCD band at 31 500 cm^{-1} and the second negative MCD band in the region of 33 000-36 000 cm^{-1} are assigned to the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transitions of the benzaldehyde and *p*-dimethoxybenzene groups, respectively. The large negative MCD band at 38 800 cm^{-1} originated from the ${}^1B_{1u} \leftarrow {}^1A_{1g}$ transition of the benzaldehyde group. It should be noted that the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition of benzaldehyde observed at 35 800 cm^{-1} is shifted to 31 500 cm^{-1} in (±)-2,5-dimethoxy-7-formyltriptycene.

We have also measured the MCD and CD spectra of (−)-2-methoxy-7-acetoxytriptycene, (±)-2,5-dimethoxy-7-aminotriptycene, (−)-3-chloro-7-carboxytriptycene, (−)-4-chloro-7-carboxytriptycene, and (±)-5-methoxy-7-carboxytriptycene, and determined the spectral assignments of these compounds in an analogous way. The results are available as supplementary material.[29]

In the case of triptycene derivatives containing a benzoic acid group, rotational isomers of the carboxyl group shown in the bottom of Figure 6 must be considered. The MCD and CD spectra calculated for forms I and II of (−)-2,7-dicarboxytriptycene are shown in Figure 6. The sign of the calculated CD curve of form I (—) coincides with experimental data, whereas the theoretical curve of form II (- - -) cannot explain the signs of the observed CD spectrum in the lower wavenumber region. Therefore, form I was assumed in the calculation of the Faraday *B* terms and rotational strengths of the other triptycene derivatives with a benzoic acid group.

Tables I-III show the observed and calculated transition energies, rotational strengths, and Faraday *B* terms of (−)-2,7-diaminotriptycene, (+)-2-chloro-7-methoxytriptycene, and (+)-2-hydroxy-7-carboxytriptycene. The calculated results and the spectral data of the remaining compounds are

Table I. Observed and Calculated Transition Energies (cm^{-1}), Rotational Strengths (Dβ), and Faraday *B* Terms ($10^{-5}\beta D^2$/cm^{-1}) of (−)-2,7-Diaminotriptycene (Optical Purity 16%)

MCD					CD				
ν_{obsd}[a]	B_{obsd}	B_{calcd}	ν_{calcd}	R_{calcd}	R_{obsd}	ν_{obsd}[b]	Assignment		Symmetry
34 300	85.0	54.1	34 900	−0.408	−0.014	33 700	NH_2-Ph	${}^1B_{2u}$	B
		22.4	35 300	0.397	0.046	37 300	NH_2-Ph	${}^1B_{2u}$	A
		0.0	39 400	0.0			H-Ph	${}^1B_{2u}$	A
		3.3	42 500	0.329			NH_2-Ph	${}^1B_{1u}$	A
40 400	−73.9	−181.1	43 200	−0.115	−0.116	43 900	NH_2-Ph	${}^1B_{1u}$	B
		83.0	48 900	0.061			H-Ph	${}^1B_{1u}$	B
		6.7	49 400	−0.223			NH_2-Ph	${}^1E_{1u}$	A
45 500	Positive	572.2	49 800	−1.284			NH_2-Ph	${}^1E_{1u}$	B
		645.8	50 700	1.624	0.164	46 800	NH_2-Ph	${}^1E_{1u}$	A
		−918.8	51 100	1.080			NH_2-Ph	${}^1E_{1u}$	B
		1561.0	55 800	−1.103			H-Ph	${}^1E_{1u}$	A
		−1902.1	55 900	−0.227			H-Ph	${}^1E_{1u}$	B

[a] Wavenumber at the MCD peak. [b] Wavenumber at the CD peak.

Table II. Observed and Calculated Transition Energies (cm^{-1}), Rotational Strengths (Dβ), and Faraday B Terms ($10^{-5}\beta$D^2/cm^{-1}) of (+)-2-Chloro-7-methoxytriptycene

MCD				CD				
ν_{obsd}[a]	B_{obsd}	B_{calcd}	ν_{calcd}	R_{calcd}	R_{obsd}	ν_{obsd}[b]	Assignment	
35 200	17.3	28.2	37 100	0.031	0.038	35 600	CH$_3$O-Ph	$^1B_{2u}$
		13.6	38 300	−0.015	−0.051	38 200	Cl-Ph	$^1B_{2u}$
		0.0	39 400	0.0			H-Ph	$^1B_{2u}$
		−66.9	46 100	−0.104	−0.041	41 300	CH$_3$O-Ph	$^1B_{1u}$
		−84.2	47 400	0.077	0.214	44 400	Cl-Ph	$^1B_{1u}$
Positive (42 500-45 500 cm^{-1})		19.4	49 000	−0.008			H-Ph	$^1B_{1u}$
		965.5	50 600	1.085			CH$_3$O-Ph	$^1E_{1u}$
		−502.9	50 700	−0.049	−0.258	46 700	CH$_3$O-Ph	$^1E_{1u}$
		323.6	51 500	−0.786			Cl-Ph	$^1E_{1u}$
		−248.4	52 100	−0.875			Cl-Ph	$^1E_{1u}$
		−324.7	56 500	0.121			H-Ph	$^1E_{1u}$
		−60.5	57 100	0.484			H-Ph	$^1E_{1u}$

[a] Wavenumber at the MCD peak. [b] Wavenumber at the CD peak.

Table III. Observed and Calculated Transition Energies (cm^{-1}), Rotational Strengths (Dβ), and Faraday B Terms ($10^{-5}\beta$D^2/cm^{-1}) of (+)-2-Hydroxy-7-carboxytriptycene

MCD				CD				
ν_{obsd}[a]	B_{obsd}	B_{calcd}	ν_{calcd}	R_{calcd}	R_{obsd}	ν_{obsd}[b]	Assignment	
					0.0011	32 600		
33 800	−15.7	−19.1	36 500	0.008	−0.0012	34 200	HOOC-Ph	$^1B_{2u}$
		19.1	37 100	0.016	0.036	35 700	HO-Ph	$^1B_{2u}$
		0.0	39 400	0.0	−0.021	38 100	H-Ph	$^1B_{2u}$
42 000	96.2	58.1	43 300	−0.098			HOOC-Ph	$^1B_{1u}$
		−89.8	47 500	0.018	0.160	43 000	HO-Ph	$^1B_{1u}$
		−5.0	48 900	−0.002			H-Ph	$^1B_{1u}$
		37.9	50 300	0.401			HOOC-Ph	$^1E_{1u}$
		256.7	50 500	0.547			HOOC-Ph	$^1E_{1u}$
		103.8	51 000	−0.361	−0.453	46 200	HOOC-Ph	
		366.8	51 500	−0.843			HO-Ph	$^1E_{1u}$
		−218.5	51 900	−0.532			HO-Ph	$^1E_{1u}$
		249.3	56 300	0.193	0.122	48 900	H-Ph	$^1E_{1u}$
		−434.5	56 700	0.588			H-Ph	$^1E_{1u}$

[a] Wavenumber at the MCD peak. [b] Wavenumber at the CD peak.

Table IV. Changes in the Calculated Faraday B Terms, ΔB_x, ΔB_y, and ΔB_z, Caused by Moving the Origin by 1 Å along the x, y, and z Axes, Respectively ($10^{-5}\beta$D^2/cm^{-1})

(−)-2,7-Diaminotriptycene				(+)-2-Chloro-7-methoxytriptycene			
B_{calcd}	ΔB_x	ΔB_y	ΔB_z	B_{calcd}	ΔB_x	ΔB_y	ΔB_z
54.1	1.28	0.0	0.0	28.2	−0.03	−1.90	−0.15
22.4	0.0	0.0	0.0	13.6	−0.10	0.98	0.05
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3.3	0.0	0.0	0.0	−66.9	−0.35	−0.15	−0.66
−181.1	−0.66	0.0	0.0	−84.2	−0.58	0.12	0.67
83.0	−0.13	0.0	0.0	19.4	−0.02	0.0	0.10
6.7	0.0	0.0	0.0	965.5	−0.93	−16.89	−1.32
572.2	1.04	0.0	0.0	−502.9	−2.00	0.74	−1.44
645.8	0.0	0.0	0.0	323.6	−0.13	10.49	0.20
−918.8	5.26	0.0	0.0	−248.4	−0.95	0.07	−0.59
1561.0	0.0	0.0	0.0	−324.7	−2.66	0.0	−0.25
−1902.1	1.86	0.0	0.0	−60.5	0.29	2.44	0.17

summarized in the supplementary material.[29] The calculated Faraday B terms of triptycene derivatives are in excellent agreement with the experimental values both in sign and magnitude. Although the theoretical rotational strength of the first weak transition of (+)-2-hydroxy-7-carboxytriptycene has the wrong sign, the agreement between the theoretical and experimental rotational strengths is satisfactory, as a whole.

The calculated Faraday B terms linearly depend on the origin in the present cases. Table IV shows the changes in the calculated Faraday B terms of (−)-2,7-diaminotriptycene and (+)-2-chloro-7-methoxytriptycene caused by shifting the origin by 1 Å along the x, y, and z axes (Figure 7). The calculated Faraday B terms so weakly depend on the origin that the sign and the order of magnitude of the B_{calcd} values are not

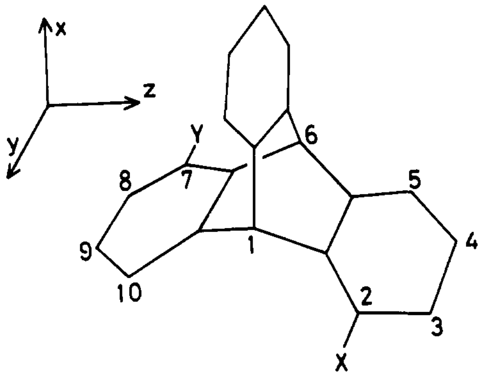

Figure 7. The absolute configuration of (−)-2,7-disubstituted triptycene.

significantly affected by moving the origin within the skeleton of triptycene derivatives.

The absolute configuration of (−)-2,7-disubstituted triptycene determined by the present theoretical analysis of the CD spectrum (1*S*,6*S*) is shown in Figure 7. It can be also concluded from the comparison of the calculated rotational strengths with the experimental data[29] that (+)-2,5-dimethoxy-7-aminotriptycene, (−)-3-chloro-7-carboxytriptycene, and (−)-4-chloro-7-carboxytriptycene have 1*R*,6*S*, 1*S*,6*S*, and 1*S*,6*R* absolute configurations, respectively. These configurations are in agreement with those[20] determined by chemical correlation with compounds whose absolute configurations have been determined[3,4] using the Bijvoet method of X-ray crystallographic analysis.

Let us consider the case in which CD is mainly induced by the coupling of states *a*, in the *i*th and *j*th chromophores. The rotational strength for the lower energy component of a pair of transitions, $a \leftarrow o$, is expressed as[8]

$$R_{o\rightarrow a}{}^{-} = -\frac{\pi}{c}\nu_{oa}\boldsymbol{m}_{ioa} \times \boldsymbol{m}_{joa}\cdot(\boldsymbol{R}_i - \boldsymbol{R}_j) - \frac{1}{2}\,\mathrm{Im}\{\boldsymbol{m}_{ioa}\cdot\boldsymbol{\mu}_{joa} + \boldsymbol{m}_{joa}\cdot\boldsymbol{\mu}_{ioa}\} \quad (14)$$

where $\boldsymbol{R}_i$ and $\boldsymbol{R}_j$ are the vectors pointing from the origin fixed in the molecule to the local origins in the *i*th and *j*th groups, O_i and O_j, respectively.

If the local origins, O_i and O_j are chosen so that μ_{ioa} and μ_{joa} vanish, only the first term in eq 14 remains. According to the PPP approximation, the local magnetic moment, μ_{ioa}, of the $^1B_{2u} \leftarrow {}^1A_{1g}$ transition of aniline vanishes at a point away from the center of the benzene ring toward the para carbon atom. The orientation of the electric transition moment for the lowest transition of (−)-2,7-diaminotriptycene is shown in Figure 8a. It is clearly seen from Figure 8a that $\boldsymbol{m}_{ioa} \times \boldsymbol{m}_{joa}\cdot(\boldsymbol{R}_i - \boldsymbol{R}_j)$ has a positive sign and that the first transition of (−)-2,7-diaminotriptycene shows a negative CD band.

Then, another explanation is considered. If the local origins, O_i and O_j, are set at the centers of the benzene rings, the first term in eq 14 vanishes. In this case, CD is considered to arise from the coupling of the local electric moment, $\boldsymbol{m}_{ioa}$, and the local magnetic moment, μ_{joa}, in the different groups. Figure 8b shows that Im $\boldsymbol{m}_{ioa}\cdot\boldsymbol{\mu}_{joa}$ and Im $\boldsymbol{m}_{joa}\cdot\boldsymbol{\mu}_{ioa}$ have positive signs and the lowest transition of (−)-2,7-diaminotriptycene exhibits a negative CD band.

If the electric moments in eq 14 are evaluated by the dipole velocity method, calculations by these two treatments lead to the same results. Thus, the sign of the lowest CD band of (−)-2,7-diaminotriptycene can be explained by the simple coupling models of the local electric and magnetic moments. The similar explanations may be applied to the short-axis polarized component of the $^1E_{1u} \leftarrow {}^1A_{1g}$ transitions.

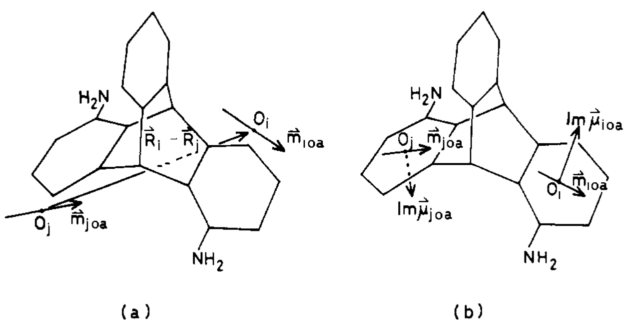

Figure 8. (a) The coupling of the electric moments, $\boldsymbol{m}_{ioa}$ and $\boldsymbol{m}_{joa}$, in the lowest transition of (−)-2,7-diaminotriptycene, when the local origin is set at the point in which μ_{ioa} and μ_{joa} vanish. (b) The coupling of the electric moment, $\boldsymbol{m}_{ioa}$, and the magnetic moment, Im μ_{joa}, in the lowest transition of (−)-2,7-diaminotriptycene, when the local origin is set at the center of the benzene ring.

Conclusions

Measurements of the MCD and CD spectra make it possible to distinguish the individual electronic transitions which are strongly overlapping in the absorption spectra. The signs of the MCD bands of the triptycene derivatives are closely related to those of constituent benzene derivatives, which lead to reasonable assignments of their absorption spectra. The experimental rotational strengths and Faraday *B* terms obtained from the CD and MCD spectra are in good agreement with those calculated using wave functions determined on the basis of the "molecules in molecule" method combined with the PPP approximation. The origin dependence of the calculated Faraday *B* term is found to be insignificantly small, and shifting the origin within the carbon skeleton of the molecule does not have much influence on the sign and the order of magnitude of the calculated Faraday *B* term. The absolute configurations of triptycene derivatives obtained from the present work are consistent with those determined by chemical transformation and X-ray crystallographic analysis using the Bijvoet method.

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Supplementary Material Available: MCD, CD, and UV spectra of (−)-2-methoxy-7-acetoxytriptycene, (±)-2,5-dimethoxy-7-aminotriptycene, (−)-3-chloro-7-carboxytriptycene, (−)-4-chloro-7-carboxytriptycene, and (±)-5-methoxy-7-carboxytriptycene, and tables of the experimental and theoretical Faraday *B* terms and rotational strengths of (−)-2-methoxy-7-acetoxytriptycene, (+)-2,5-dimethoxy-7-aminotriptycene, (−)-2,7-dicarboxytriptycene, (−)-3-chloro-7-carboxytriptycene, (−)-4-chloro-7-carboxytriptycene, (±)-2,5-dimethoxy-7-formyltriptycene, and (±)-5-methoxy-7-carboxytriptycene (12 pages). Ordering information is given on any current masthead page.

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Use of Dispersion-Induced Circular Dichroism (DICD) in Spectroscopic Assignment: Applications to Copper(II) Complexes

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Abstract: A new spectroscopic method (DICD) is discussed which permits the direct observation of electronic transitions which are either magnetic or electric dipole allowed. The method is furthermore capable of discriminating between these two types of excitations. The importance of this in the assignment of magnetic dipole transitions is discussed, especially with regard to the d–d excitations of transition metal complexes. The method involves the measurement of the CD spectrum of the (achiral) complex in solution with some nonassociating chiral solute or in a chiral solvent. Application of the method to the assignment of the d–d transitions of Cu(II) complexes is discussed.

1. Introduction

Intensities of absorption lines in conventional absorption spectroscopy are determined almost exclusively by the electric dipole transition moments of the observed transitions and are therefore direct functions of the electric dipole selection rules. Intensity measurements are thus useful for making spectral assignments. Even transitions which are to first-order electric dipole forbidden usually appear in absorption through some mechanism such as vibronic coupling, whereby a small effective electric dipole transition moment is induced through mixing with other electronic states. Intensity contributions from magnetic dipole transition moments are generally swamped even by the contributions of relatively small vibronically-induced electric moments. It is for this reason that magnetic dipole selection rules are of little use in assigning direct absorption bands.

There are numerous systems where a mechanism for measuring the magnetic transition moments would yield valuable information for spectral assignments. Consider, for example, the d–d transitions of metal complexes. These are invariably electric dipole forbidden to first order, but many of them are magnetic dipole allowed. It therefore seems somewhat incongruous to use absorption intensity measurements based on electric dipole transition moments for their assignment.

Is there then some mechanism available for estimating magnetic transition moments? The answer lies in CD techniques. CD measurements depend directly on magnetic transition moments, but are unfortunately restricted to chiral species. MCD has extended CD techniques to the study of achiral molecules, especially in the solid state. This has proved a useful tool in studying degeneracies, but again terms depending on magnetic transition moments are usually swamped by electric dipole terms. Recent theoretical studies[2,3] have, however, led to the development of a new technique which, like MCD, extends CD techniques to the study of achiral complexes, but depends directly on the magnetic transition moment. Referred to as DICD (dispersion-induced circular dichroism), the resultant CD spectrum has measurable peaks only if the transition is *either* electric *or* magnetic dipole allowed. Unlike the direct absorption spectrum, d–d transitions which are magnetic dipole allowed appear through the magnetic dipole contribution, any electric dipole contributions from the small vibronically-induced electric moments being negligible. Electric contributions to DICD arise only when the transition is electric dipole allowed in first order.

DICD is the circular dichroism induced at transition frequencies of achiral species due to the long-range dispersive interactions with other chiral species (all species being orientationally uncorrelated). The effect was first noted in a number of experimental papers,[4,5] and has since been put on a sound theoretical basis.[2,3] It is probably fair to say that the DICD of inorganic complexes is at present further advanced theoretically than it is experimentally. It is the purpose of this paper to encourage narrowing the gap by illustrating the utility of the DICD effect in potentially assigning magnetic dipole transitions. Note that in DICD, the chiral species effectively acts as a source of a chiral electric field which acts on the achiral species. This may be compared with MCD, where a chiral magnetic field is used.

The DICD of the Cu(II) ion is looked at in detail for a number of reasons. The assignment of the d–d transitions for a number of Cu(II) complexes is still uncertain, so that this system poses a challenge to the new technique; Cu(II) complexes have a range of stereochemistries,[7] so that the DICD symmetry rules may be put to the test for a range of molecular symmetries; the d^9 configuration (for which electron repulsion/correlation effects are minimal) leads to a relatively