(13 300), 241.0 (72 400); CD (EtOH) λ_{exl} 298 nm ($\Delta\epsilon$ −4.5), 292 (0.0), 288 (+3.0), 283 (0.0), 277 (−5.0), 271 (0.0), 241 (+166.0), 228 (0.0), 217 (−127.3), 201 (0.0).

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Circular Dichroic Power of Chiral Triptycenes

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Abstract: The CD spectra of (5*R*,12*R*)-(−)-1,15-diethynyl-5,12-dihydro-5,12[1',2']benzenonaphthacene (**2**) and (5*S*,12*S*)-(+)-5,12-dihydro-5,12[1',2']benzenonaphthacene-1,15-dicarbonitrile (**3**) were quantitatively calculated on the basis of chiral exciton coupling between three chromophores. The calculated spectra are in excellent agreement with the observed ones, establishing the absolute stereochemistry in a nonempirical manner. In the case of (7*S*,14*S*)-(+)-7,14-dihydro-7,14[1',2']-naphthalenobenzo[*a*]naphthacene (**1**), the complex CD spectrum of which had not been explicable by the simple exciton coupling mechanism, the CD spectrum was computed by the SCF-CI-dipole velocity molecular orbital method including the interchromophoric homoconjugation effect. When the resonance integral ratio $\beta_{\mathrm{hc}}/\beta_{\mathrm{arom}}$ is 32%, the calculated CD curve is in good agreement with the observed one, clarifying the important role of the interchromophoric homoconjugation effect in the circular dichroic power of (+)-**1**.

In the preceding paper,[1] we reported the unequivocal and nonempirical chiroptical determination of the absolute stereochemistry of chiral triptycenes, (5*R*,12*R*)-(−)-1,15-diethynyl-5,12-dihydro-5,12[1',2']benzenonaphthacene (**2**) and (5*S*,12*S*)-(+)-5,12-dihydro-5,12[1',2']benzenonaphthacene-1,15-dicarbonitrile (**3**), achieved by applying the CD exciton chirality method,[2] and also described the complex circular dichroism of (7*S*,14*S*)-(+)-7,14-dihydro-7,14-[1',2']naphthalenobenzo[*a*]naphthacene (**1**) which was not explicable by the simple exciton coupling mechanism.

This paper reports the theoretical calculation results of the CD spectra of diethynylbenzotriptycene (−)-**2** and benzotriptycenedinitrile (+)-**3** obtained by the exciton chirality method.[2] The calculated CD spectra are in excellent agreement with the observed ones, corroborating the previous qualitative configurational assignment. This paper also describes the SCF-CI-dipole velocity molecular orbital calculation results of the UV and CD spectra of chiral tribenzotriptycene (+)-**1**, diethynylbenzotriptycene (−)-**2**, (6*R*,15*R*)-(+)-6,15-dihydro-6,15-ethanonaphtho[2,3-*c*]pentaphene (**4**),[3,4] and (7*R*,14*R*)-(+)-7,14-dihydro-7,14-ethanodibenz[*a*,*h*]anthracene (**5**).[3,5] Good agreement between the calculated and observed curves was obtained, establishing the absolute configurations in a quantitative manner. In the case of tribenzotriptycene (+)-**1**, the SCF-CI-DV molecular orbital calculation clarified the important role of the interchromophoric homoconjugation effect in the circular dichroic power of (+)-**1**.

Methods of Calculation

Molecular Structure. The Cartesian coordinate system for the molecular structure of (7*S*,14*S*)-(+)-tribenzotriptycene **1** was adopted as shown in Figure 1, in which the *z* axis is the C_2 symmetrical axis of the molecule. The coordinates of atoms were calculated[3b] by employing the geometric parameters shown in Figure 1 which were taken from the X-ray crystallographic data of triptycene derivatives.[6]

In the case of the diethynyl compound (−)-**2** and the dinitrile (+)-**3**, the additional parameters for acetylene and nitrile

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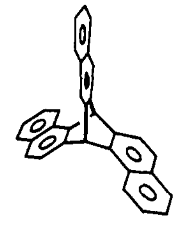
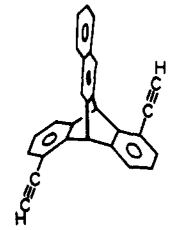
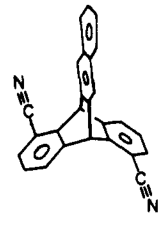


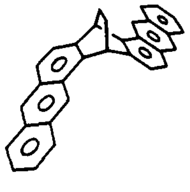
(7S,14S)-(+)-**1**



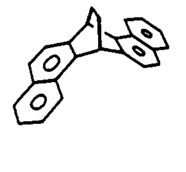
(5R,12R)-(−)-**2**



(5S,12S)-(+)-**3**



(6R,15R)-(+)-**4**



(7R,14R)-(+)-**5**

moieties were adopted as follows: C≡C, 1.21 Å, CC≡, 1.45 Å; C≡N, 1.158 Å; C—CN, 1,419 Å.

Exciton Coupling Circular Dichroic Power of Triple System. In the case of the triple systems of chiral benzotriptycenes **2** and **3**, the excitation energies of component chromophores, i.e., those of the ^1B_b transition of naphthalene and the intramolecular charge transfer or ^1L_a transition of monosubstituted benzene, are almost similar, but not exactly identical with each other. Therefore, the equation of the rotational strength R^k of the kth transition based on the chiral exciton coupling mechanism[2b,3b,7] was modified by adopting the average value of two excitation energies, as follows:[8]

$$R^k = -\pi \sum_{i=1}^{N} \sum_{j>i}^{N} C_{ik}C_{jk}0.5(\sigma_i + \sigma_j)\mathbf{R}_{ij}\cdot(\boldsymbol{\mu}_i \times \boldsymbol{\mu}_j) \qquad (1)$$

$$(k = 1, 2, \ldots, N)$$

where N is the number of chromophores and $N = 3$ in the present case, C_{ik} and C_{jk} are coefficients of the kth wave function, σ_i and σ_j are excitation wavenumbers of chromophores i and j, $\mathbf{R}_{ij}$ is the interchromophoric distance vector from i to j, and $\boldsymbol{\mu}_i$ and $\boldsymbol{\mu}_j$ are electric transition moment vectors of groups i and j.

The exciton interaction energy V_{ij} is calculable by the point dipole approximation method and formulated as follows:

$$V_{ij} = \mu_i\mu_j R_{ij}^{-3}(\mathbf{e}_i \cdot \mathbf{e}_j - 3\,(\mathbf{e}_i \cdot \mathbf{e}_{ij})(\mathbf{e}_j \cdot \mathbf{e}_{ij})) \qquad (2)$$

where $\mathbf{e}_i$, $\mathbf{e}_j$, and $\mathbf{e}_{ij}$ are unit vectors of $\boldsymbol{\mu}_i$, $\boldsymbol{\mu}_j$, and $\mathbf{R}_{ij}$, respectively, and the electric transition dipole moments μ_i and μ_j can be estimated from the integrated peak area of the observed UV spectra, by employing the equation

$$D = \mu^2 = 9.184 \times 10^{-39} \int_0^\infty \epsilon(\sigma)/\sigma \, d\sigma \qquad (3)$$

The resultant CD spectrum was calculated by adopting the Gaussian distribution approximation, because the UV spectra of the two component chromophores, i.e., naphthalene and monosubstituted benzene, are different in shape from each other. Therefore, contribution of the vibrational structure to the shape of CD spectra[2b,3b] was neglected in the present case. The CD curve $\Delta\epsilon(\sigma)$ is formulated as follows:

$$\Delta\epsilon(\sigma) = (0.5(\sigma_i + \sigma_j)/(2.296 \times 10^{-39}\sqrt{\pi}\Delta\sigma)) \times \sum_{k=1}^{N} R^k \exp(-((\sigma - \sigma_k)/\Delta\sigma)^2) \qquad (4)$$

where the standard deviation of the Gaussian distribution $\Delta\sigma$ was approximated by the average $\Delta\sigma$ value of two component transitions. The excitation wavenumber σ_k to the kth excited state is obtainable by solving the secular equation, in which the diagonal and off-diagonal terms are expressed by σ_i ($i = 1, \ldots, N$) and V_{ij} ($i = 1, \ldots, N; j = 1, \ldots, N$), respectively.

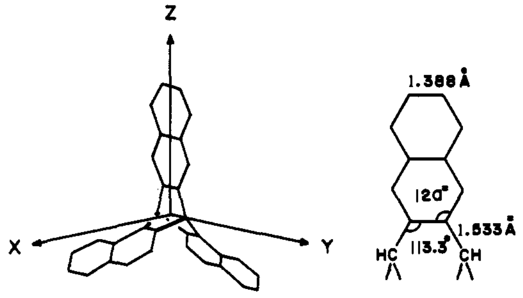


Figure 1. Cartesian coordinate system and geometric parameters of (7*S*,14*S*)-(+)-tribenzotriptycene **1**,

CD and UV Calculation by the SCF-CI-Dipole Velocity Molecular Orbital Method. The rotational strength R_{ba} of an excitation ($a \rightarrow b$) by the dipole velocity method[9] is formulated as follows:

$$R_{ba} = 2(\Psi_a|\nabla|\Psi_b)(\Psi_a|\mathbf{r} \times \nabla|\Psi_b)\beta_M{}^2/(\pi\sigma_{ba}) \qquad (5)$$

where ∇ is the del operator, $\mathbf{r}$ is a distance vector, β_M is the Bohr magneton, and σ_{ba} is the excitation wavenumber of the transition $a \rightarrow b$. The z-axis components of the electric and magnetic transition moments, $(\Psi_a|\nabla|\Psi_b)_z$ and $(\Psi_a|\mathbf{r} \times \nabla|\Psi_b)_z$, are expressed by eq 6 and 7, respectively:[9]

$$(\Psi_a|\nabla|\Psi_b)_z = \sum_{\text{bonds}} (C_{ra}C_{sb} - C_{sa}C_{rb})\,\langle\nabla_{rs}\rangle \cos Z_{rs} \qquad (6)$$

$$(\Psi_a|\mathbf{r} \times \nabla|\Psi_b)_z = \sum_{\text{bonds}} (C_{ra}C_{sb} - C_{sa}C_{rb})\langle\nabla_{rs}\rangle \times (X_{rs} \cos Y_{rs} - Y_{rs} \cos X_{rs}) \qquad (7)$$

$$\cos Z_{rs} = (Z_r - Z_s)/R_{rs} \qquad (8)$$

$$X_{rs} = (X_r + X_s)/2 \qquad (9)$$

where C_{ra} is the coefficient of atomic orbital r in the wave function Ψ_a, $\langle\nabla_{rs}\rangle$ is the expectation value of a dipole velocity vector ∇_{rs} which is directed along the bond rs in the direction $r \rightarrow s$, X_r and Z_r are the x and z coordinates of atom r, respectively, and R_{rs} is the length of bond r-s. In a similar way, the x and y components of the electric and magnetic transition moments are calculable.

The dipole strength D_{ba} is formulated as follows:[9]

$$D_{ba} = 2(\Psi_a|\nabla|\Psi_b)^2\beta_M{}^2/(\pi\sigma_{ba})^2 \qquad (10)$$

In the SCF-CI molecular orbital calculation, configuration interaction between maximum 50 singly excited states of low energy was included. The component CD and UV curves were approximated by the Gaussian distribution as in the case of the exciton coupling calculation, and the standard deviation $\Delta\sigma$ values were taken from the observed UV spectra of component chromophores.[1] For example, the $\Delta\sigma$ values of the ^1B_b and ^1L_a transitions of alkyl-substituted naphthalenes employed for the calculation of tribenzotriptycene (+)-**1** are 1751.4 and 2853.5 cm^{-1}, respectively. In the case of diethynylbenzotriptycene (−)-**2** composed of different chromophores, the average $\Delta\sigma$ value of the substituted naphthalenes and ethynylbenzene was adopted.

In the calculation of aromatic hydrocarbons, the following atomic orbital parameters were employed: $W_C = -11.42$ eV, $(rr|rr) = 10.84$ eV, $\beta_{\text{C-C}}(\text{aromatic}) = -2.39$ eV. The del value of the aromatic C-C bond $\langle\nabla_{\text{C-C}}\rangle$ was estimated to be 4,701 × 10^7 cm^{-1} from the observed UV spectra of the ^1B_b transition of anthracene in ethanol. The electronic repulsion integral $(rr|ss)$ between two atoms r and s in one chromophore was estimated by the Nishimoto-Mataga (N-M) equation. In the

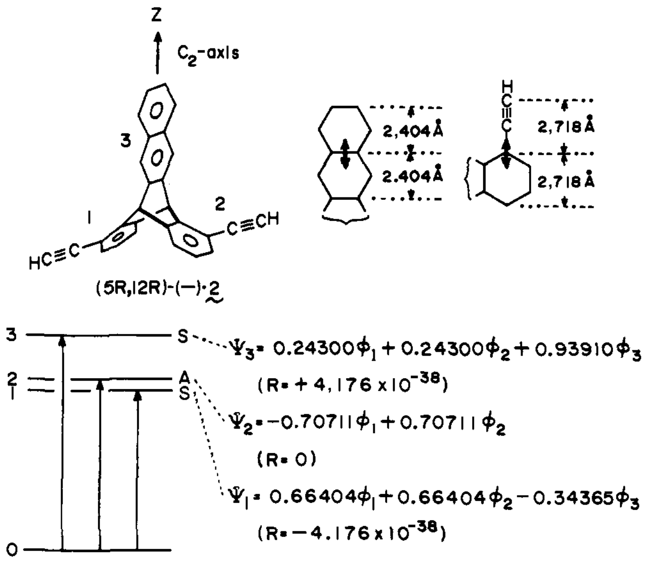


Figure 2. Excitation diagram, wave functions, rotational strengths, and location of excitons of (5*R*,12*R*)-(−)-diethynylbenzotriptycene 2. The wave functions Ψ_1, Ψ_2, and Ψ_3 are symmetrical (S), antisymmetrical (A), and symmetrical (S) around the C_2-symmetrical axis, respectively.

Table I. UV Spectral Data[a] of the ^1B_b Transition of 2,3-Dimethylnaphthalene and the Intramolecular Charge Transfer or ^1L_a Transition of Ethynylbenzene and 2-Methylbenzonitrile

	2,3-dimethyl-naphthalene	ethynyl-benzene	2-methylbenzo-nitrile
λ_{max}, nm	226.0	234.0	228.0
ϵ_{max}	92500	15000	14200
σ_0, cm^{-1}	44 247.8	42 735.0	43 859.6
r, Å	1.6647	0.7716	0.7374
$\Delta\sigma$, cm^{-1}	1790.2	2530.5	2503.3

[a] Solvent EtOH.

case of the diethynyl compound (−)-2, the resonance integral and del values of acetylene moiety were calculated by employing the following equations, respectively:

$$\beta = (S/S_{C-C}(\mathrm{arom}))\beta_{C-C}(\mathrm{arom}) \qquad (11)$$

$$\langle\nabla\rangle = (\langle\nabla\rangle_{\mathrm{empir}}(\mathrm{arom})/\langle\nabla\rangle_{\mathrm{theor}}(\mathrm{arom}))\langle\nabla\rangle_{\mathrm{theor}} \qquad (12)$$

where overlap integral S and $\langle\nabla\rangle_{\mathrm{theor}}$ were calculable on the basis of the Slater orbitals.[10,11]

The repulsion integral $(rr|ss)$ of two atoms r and s which belong to different chromophores was also estimated by the N-M equation only on the basis of distance and the angular factor was neglected. The resonance integral value β_{hc} of the interchromophoric homoconjugation was changed until good agreement between the observed and calculated CD curves was obtained. On the other hand, the $\langle\nabla\rangle$ value of the homoconjugation was completely neglected.

Numerical calculations were performed by using the computer ACOS series 77, NEAC 700 system of the Tohoku University Computer Center.

Results and Discussion

Exciton Coupling CD Spectra of the Benzotriptycenes (−)-2 and (+)-3. In the case of the theoretical calculation of chiral exciton coupling in compounds (−)-2 and (+)-3, 2,3-dimethylnaphthalene (6), ethynylbenzene (7), and 2-methylbenzonitrile (8) were adopted as the component chromophores in the triple systems. As indicated in Table I, the ^1B_b transition of 6 and the intramolecular charge transfer or ^1L_a transition of 7 and 8 are different in shape from each other. Namely, the ^1B_b transition of 6 (λ_{max} 226.0 nm, ϵ 92 500, $\Delta\sigma$ 1790.2 cm^{-1}) is stronger and sharper than the intramolecular charge transfer transitions of 7 (λ_{max} 234.0 nm, ϵ 15 000, $\Delta\sigma$ 2530.5 cm^{-1}) and 8 (λ_{max} 228.0 nm, ϵ 14 200, $\Delta\sigma$ 2503.3 cm^{-1}). However, since these transitions are located close to one another, the present intense transitions are ideal for chiral exciton coupling between them.

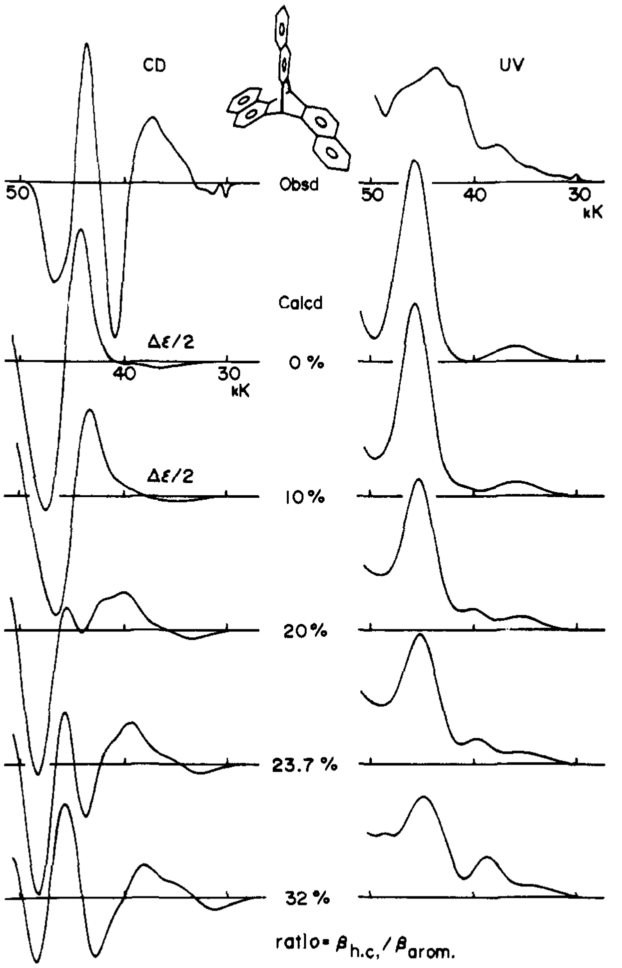


Figure 3. The CD and UV spectra of (7*S*,14*S*)-(+)-tribenzotriptycene 1 obtained by the SCF-CI-DV molecular orbital calculation, in which the value of the interchromophoric homoconjugation resonance integral β_{hc} was gradually changed. The parameter β_{arom} is the resonance integral of a regular aromatic C-C bond (−2.39 eV). The top curves are the observed CD and UV spectra. The amplitudes of the second and third CD curves are illustrated in $\Delta\epsilon/2$ scale.

Because of the centrosymmetric nature of the naphthalene chromophore, it is reasonable to locate the point dipole moment in the center of the chromophore. Similarly, the point dipole of the ethynylbenzene or benzonitrile chromophore was located in the middle point of the line connecting the carbon or nitrogen atom of the triple bond and the benzene carbon in the para position (Figure 2).

In the case of the diethynyl compound (−)-2, the exciton wave functions indicated in Figure 2 were obtained by solving the secular equation of three dimensions. It is noteworthy that the second transition is optically inactive. The second transition is antisymmetrical against rotation around the C_2-symmetrical axis. Therefore, the wave function Ψ_2 of the second excited state excludes the excitation wave function ϕ_3 of the naphthalene chromophore. Since the remaining two transitions of ethynylbenzene chromophores are completely parallel to each other, the rotational strength R is nil. Thus, the second transition is optically inactive. The first and third transitions give the conservative rotational strength as shown in Figure 2. The same is true in the case of the dinitrile (+)-3.

Table II. Calculated and Observed CD Cotton Effects of Chiral Benzotriptycenes by the Exciton Chirality Method

compd	obsd		calcd	
	UV, λ, nm (ε)	CD, λ, nm (Δε)	$R \times 10^{38}$ [a]	CD, λ, nm (Δε)
(−)-**2**	241.0 (75 000)	245.5 (−138.2)	−4.176	240.0 (−135.5)
			0.0	
		215.0 (+113.6)	+4.176	221.0 (+135.3)
(+)-**3**	241.0 (72 400)	241.0 (+166.0)	+5.824	236.0 (+136.2)
			0.0	
		217.0 (−127.3)	−5.824	219.0 (−136.2)

[a] In cgs units.

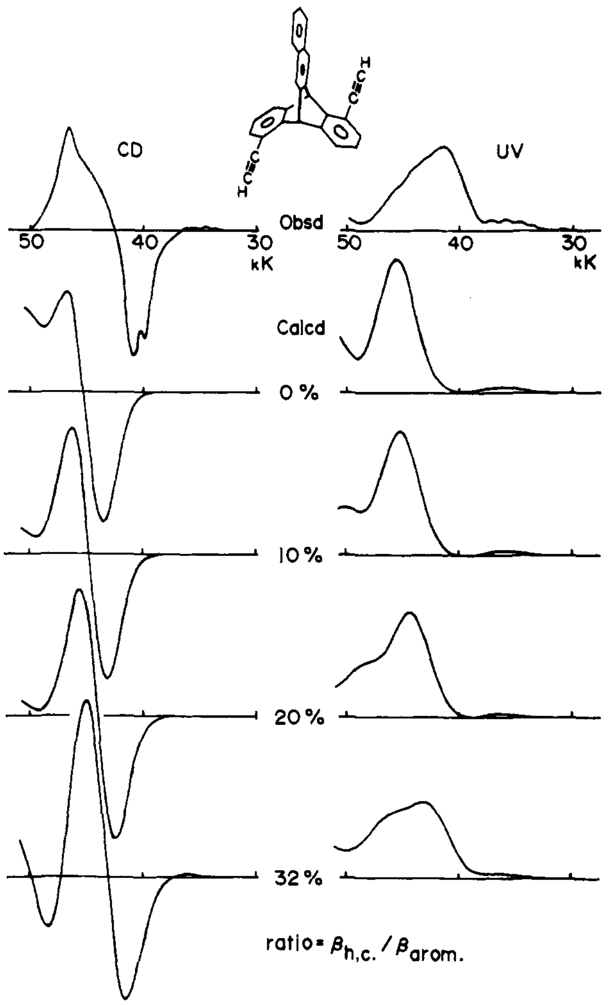


Figure 4. The CD and UV spectra of (5*R*,12*R*)-(−)-**2** obtained by the SCF-CI-DV molecular orbital calculation, in which the value of the interchromophoric homoconjugation resonance integral was changed.

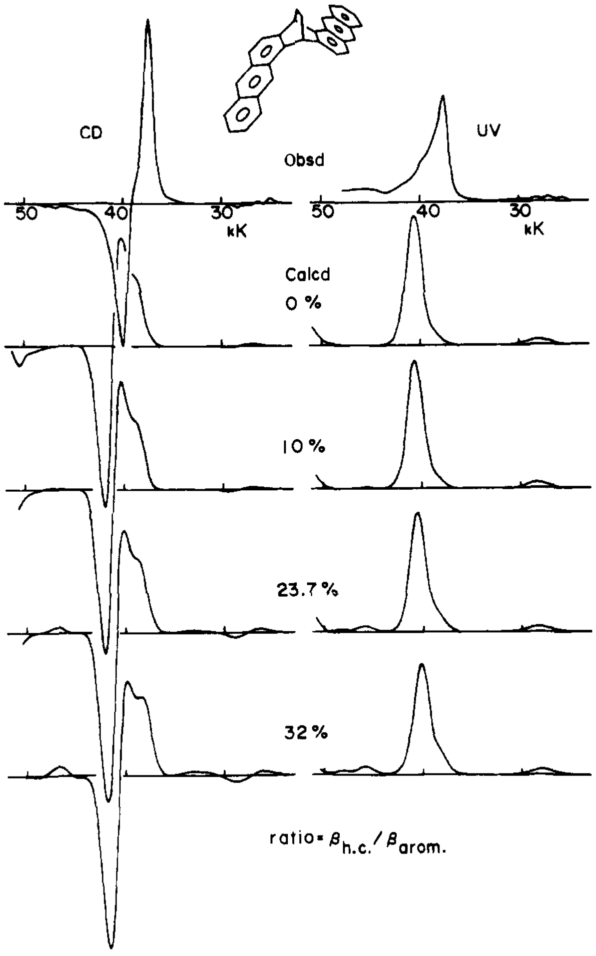


Figure 5. The CD and UV spectra of (6*R*,15*R*)-(+)-**4** obtained by the SCF-CI-DV molecular orbital calculation, in which the value of the interchromophoric homoconjugation integral was changed.

The CD spectrum curve of compound (−)-**2** was numerically calculated by employing eq 4 and the parameters listed in Table I. The calculated values of CD Cotton effects, λ_{ext} 240.0 nm ($\Delta\epsilon$ −135.5) and 221.0 (+135.3), are in excellent agreement with the observed values, λ_{ext} 245.5 nm ($\Delta\epsilon$ −138.2) and 215.0 (+113.6) (Table II). Thus, the present theoretical calculation results establish the (5*R*,12*R*) absolute stereochemistry of the diethynyl compound (−)-**2** in a nonempirical manner.

Similarly, as indicated in Table II, the splendid agreement between the calculated and observed CD exciton Cotton effects of (+)-**3** leads to the unequivocal and nonempirical determination of the (5*S*,12*S*) absolute configuration of the dinitrile (+)-**3** in line with the X-ray results.

SCF-CI-Dipole Velocity Molecular Orbital Calculation of the CD and UV Spectra of Tribenzotriptycene (+)-1 and Diethynylbenzotriptycene (−)-2. As discussed in the preceding paper, the complex CD curve of tribenzotriptycene (+)-**1** was not explicable by the simple chiral exciton coupling mechanism. Therefore, the SCF-CI molecular orbital calculation of the CD activity was performed by the use of the dipole velocity method, in which the resonance integral value β_{hc} of the interchromophoric homoconjugation was gradually changed.

The del value $\langle\nabla\rangle$, a key parameter of the dipole velocity molecular orbital method, is theoretically calculable on the basis of the Slater orbital.[11] In the case of the aromatic C-C bond with a length of 1.388 Å, the calculated value is 4.175×10^7 cm^{-1}. On the other hand, the empirical value estimated from the excitation wavenumber and the dipole strength of the β band of benzene was reported[12] to be 6.44×10^7 cm^{-1}. Because of the semiempirical nature of the Pariser-Parr-Pople

Table III. Observed and Calculated UV and CD Spectra of Chiral Triptycenes and Related Compounds by the SCF-CI-DV Molecular Orbital Method

compd	obsd UV, λ, nm (ε)	obsd CD, λ, nm (Δε)	ratio,[a] %	calcd UV, λ, nm (ε)	calcd CD, λ, nm (Δε)
(+)-**1**		317.0 (−24.6)	32		320.5 (−29.0)
	264.5 (35 800)	267.5 (+160.8)		259.0 (39 800)	261.8 (+78.4)
		244.5 (−381.9)			232.5 (−142.0)
	229.0 (113 800)	229.0 (+344.9)		223.2 (98 700)	218.3 (+226.2)
		213.0 (−246.4)			205.7 (−157.3)
(−)-**2**	278.0 (10 300)	290.0 (+3.5)	20	277.8 (2 300)	279.3 (+0.6)
	241.0 (75 000)	245.5 (−138.2)		225.2 (92 900)	235.8 (−136.8)
		215.0 (+113.6)			219.3 (+139.0)
(+)-**4**	371.2 (11 200)	397.2 (+26.4)	23.7	357.1 (11 900)	381.7 (+13.5)
		352.8 (−14.5)			347.2 (−24.2)
	267.2 (268 600)	268.0 (+931.3)		247.5 (299 200)	250.0 (+515.2)
		249.7 (−720.8)			239.2 (−858.4)
(+)-**5**		304.5 (+25.5)	20		295.9 (+12.1)
	283.5 (11 100)	283.0 (−35.6)		279.3 (6700)	261.8 (−4.3)
	232.3 (98 200)	237.0 (+326.5)		220.3 (123 500)	223.2 (+236.6)
		224.0 (−180.5)			211.0 (−106.3)

[a] Ratio = β_{hc}/β_{arom}, and β_{arom} = −2.39 eV.

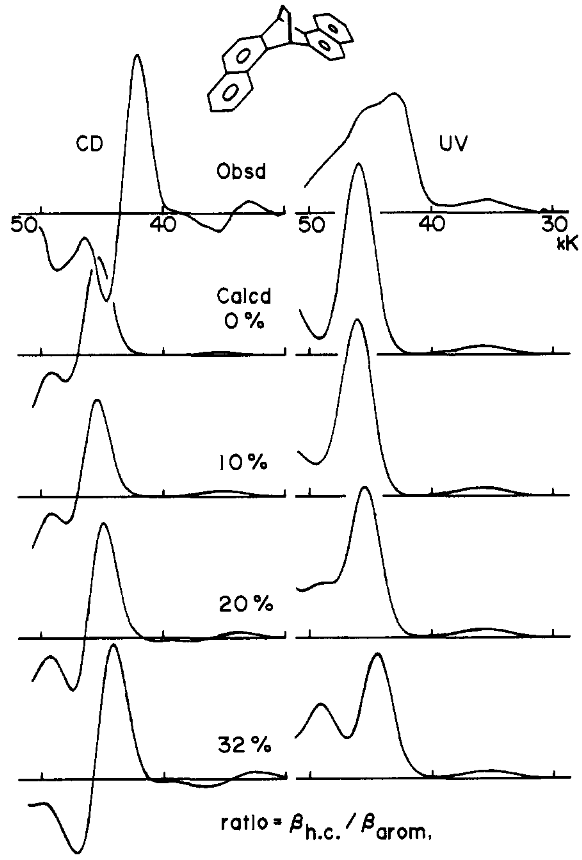


Figure 6. The CD and UV spectra of (7*R*, 14*R*)-(+)-**5** obtained by the SCF-CI-DV molecular orbital calculation, in which the value of the interchromophoric homoconjugation resonance integral was changed.

molecular orbital method, the empirical del value was adopted for the present CD calculation. However, the $\langle \nabla_{C-C} \rangle$ value of 6.44 × 10^7 cm^{-1} is too large to explain the absorption intensity of the observed UV spectra of several aromatic compounds. For example, the calculated UV intensity of tribenzotriptycene (+)-**1** was twice as large as the observed one. Therefore, instead of the β band of benzene, the ^1B_b transition of anthracene was chosen for estimating the empirical del value, because the ^1B_b transition of anthracene around 250 nm is very intense (ε 2 × 10^5) and is isolated from other transitions. These factors benefit easy and reliable determination of the empirical del value. From the observed dipole strength, D_{obsd} = 8,789 × 10^{-35} cgs unit, of the ^1B_b transition of anthracene in ethanol, the $\langle \nabla_{C-C} \rangle$ (aromatic) value of 4.701 × 10^7 cm^{-1} was obtained by eq 10 and adopted hereinafter.

The numerically calculated[13] CD and UV spectra of tribenzotriptycene (+)-**1** are illustrated in Figure 3, where top ones are the observed curves. When the interchromophoric resonance is neglected, i.e., β_{hc} = 0, the calculated CD curve exhibits two intense Cotton effects of positive first and negative second signs in the ^1B_b transitional region. This situation corresponds to the case of chiral exciton coupling reflecting the combination of two positive and one negative exciton chiralities between the three ^1B_b transition moments.

As the integral β_{hc} gradually increases the CD spectrum becomes complex and when β_{hc}/β_{arom} = 32% (β_{arom} = −2,39 eV), good agreement between the observed and calculated curves was obtained (Table III).[14,15] Namely, the calculated CD spectrum exhibits four intense Cotton effects of +/−/+/− signs in the region above 34 × 10^3 cm^{-1}, in line with the observed one, although the calculated amplitude is smaller than the observed one. The weak negative Cotton effect around 32 × 10^3 cm^{-1} is also reproducible by the present calculation (Table III). Moreover, the calculation of the UV curve satisfactorily reproduces the new absorption band of medium intensity around 38 × 10^3 cm^{-1} as shown in Figure 3 and Table III. Thus, the interchromophoric homoconjugation effect plays an important role in the circular dichroism of tribenzotriptycene (+)-**1**, and the (7*S*, 14*S*) absolute stereochemistry of (+)-**1** was established by the SCF-CI-DV molecular orbital calculation.

In a similar way, the CD and UV spectra of diethynylbenzotriptycene (−)-**2** were computed. When β_{hc}/β_{arom} = 20%, good agreement between the observed and calculated curves was obtained as shown in Figure 4, establishing the (5*R*, 12*R*) absolute configuration of (−)-**2** in a quantitative manner (Table III). In this case, it is noteworthy that the basic pattern of the CD Cotton effects around 42 × 10^3 cm^{-1}, i.e., negative first and positive second signs, remains unchanged irrespective of variation of the β_{hc} value. This result indicates that the circular dichroism of (−)-**2** is relatively insensitive to variation of the interchromophoric homoconjugation resonance integral. In other words, the interchromophoric homoconjugation effect is negligible, which corroborates the applicability of the exciton chirality method to the circular dichroism of (−)-**2**. Thus, diethynylbenzotriptycene (−)-**2** is an ideal compound for the CD exciton chirality method.

Similarly, the interchromophoric homoconjugation effect has no influence on the exciton circular dichroism of the bisanthracene **4** and bisnaphthalene **5** compounds, In the case of (+)-**4,** the pattern of the two Cotton effects of positive first and negative second signs around 40×10^3 cm^{-1} which are due to the ^1B_b transition of anthracene chromophores is little affected by variation of the ratio β_{hc}/β_{arom} (Figure 5). When the ratio is 23.7%, the calculated CD spectrum including the weak positive and negative Cotton effects in the ^1L_a transitional region is in good agreement with the observed one (Table III). Similarly, in the case of (+)-**5,** when the ratio β_{hc}/β_{arom} is 20%, good agreement was obtained as shown in Figure 6 and Table III.

From the present calculation results of compounds (+)-**1,** (−)-**2,** (+)-**4,** and (+)-**5,** the resonance integral β_{hc} of the interchromophoric homoconjugation in triptycene systems[16] was estimated to be 20–30% of the resonance integral of a regular aromatic C–C bond (Table III). This value (−0,478 to −0.717 eV) is reasonable in comparison with the previously reported value (−0.916 eV)[17] and the theoretical value (−0.567 eV) calculated by eq 11.

In conclusion, the SCF-CI-DV molecular orbital calculations including the interchromophoric homoconjugation effect satisfactorily reproduced the CD spectra of the chiral triptycenes and related compounds, establishing the absolute stereochemistries in a quantitative manner.

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(13) In the case of triptycene systems, although two combination modes of the three atomic orbitals of interchromophoric homoconjugation are possible as a basic set of wave function, both cases give the identical result.
(14) In the present CD calculation, increase of the β_{hc} value beyond 32% of β_{arom} caused a considerable extent of red shift of the Cotton effects, in disagreement with the observed curve.
(15) The origin independence of the calculated CD spectra of (+)-**1** by the SCF-CI-DV molecular orbital method including the interchromophoric homoconjugation effect was ascertained by the actual numerical calculation, in which the origin was shifted from the original point illustrated in Figure **1**.
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Conformation of Dimethyl Tartrate in Solution. Vibrational Circular Dichroism Results

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Abstract: Data on the temperature dependence of the O–H stretching VCD and the vicinal hydrogen NMR for dimethyl tartrate are interpreted as demonstrations of restricted conformational mobility of this molecule in dilute CCl_4 solution. New VCD for the C=O stretch is presented and is shown to be interpretable with the degenerate coupled oscillator model. Only one rotamer about the central C–C bond is found to be consistent with the observed VCD and NMR data.

Introduction

Vibrational circular dichroism (VCD) is a new technique with great potential for stereochemical analysis of chiral molecules in solution. VCD data have now been shown to be experimentally accessible in a wide variety of systems.[1] The major impediment to the utilization of this data for determination of molecular geometry is development of a reliable method of interpretation. To this end, theories dependent on vibrational analysis have been proposed[2] and applied with limited success.[3]

We have previously used a simple model for VCD, degenerate coupled oscillator (DCO) theory,[3b,4] to interpret the OH stretching VCD in dimethyl tartrate.[5] Our use of this theory follows Holzwarth and Chabay[4] in that we assume that the oscillators are achiral and become optically active only through their coupling. The resultant VCD is bisignate and dependent only on geometrical factors. This assumption ignores the intrinsic optical activity of each oscillator, which is expected to be quite small from evidence we shall give. This interpretation of the OH VCD was subsequently questioned and an alternative explanation proposed that assumed that the intrinsic VCD of the OH groups on two different conformers gave rise to the observed bisignate VCD.[6]

In this paper we present new data on the temperature dependence of the O—H stretching VCD, on the previously inaccessible C=O stretching VCD, and on the ^{1}H NMR of the vicinal CH groups of dimethyl tartrate. In addition, new VCD data for deuterated dimethyl tartrate and for dimethyl malate is discussed. Coupling of these three results leads us to propose that this molecule has two possible dominant conformers but only one rotamer about the central C-C bond in CCl_4 solution. This then becomes the first application of VCD for stereochemical analysis.

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