

is needed is an estimate of the cation complexation energy in going from $n = 4$ to $n = \infty$. The $n = 5$ and 6 calculations (Table IV) indicate that a single NH_3 solvation of each NH_3 on the $\text{NH}_4^+(\text{NH}_3)_4$ core will at least produce an $n = 4$ to $n = 8$ stabilization of 4×0.3 eV, or 1.2 eV. In this case the adiabatic ionization potential of $(\text{NH}_4(\text{NH}_3)_4)_6$ in liquid NH_3 (reaction 7) cannot be more than 0.8 eV. Further solvation of the cation will produce additional lowering.³⁶ This argument supports the above conclusion that in liquid ammonia the reaction $(\text{NH}_4)_5 = (\text{NH}_4^+)_5 + (\text{e}^-)_5$ is not far from being isoergic. However, none of these analyses can quantitatively establish the reaction enthalpies of reactions 6 and 7.

Conclusion

We have shown the theoretical origins of the stability of the isolated NH_4 radical. An analysis of its stability on NH_3 com-

plexation for $n > 3$ is still not clear owing to the Rydberg character of this species. Extension of this analysis to liquid NH_3 is possible if one assumes a Rydberg $\text{NH}_4(\text{NH}_3)_4$ bubble structure. This final analysis indicates that NH_4 and $\text{NH}_4^+ + \text{e}^-$ are about isoergic in liquid ammonia even though the ionization potential of NH_4 is 4.7 eV in the gas phase. The final irony of this analysis is that NH_4 radical is predicted to have stability only in the form of intermediate-sized clusters. However, the species is anticipated to play a role in the chemical reactions in liquid ammonia.

Acknowledgment. All computations presented here were done at the CNRS Computing Center (CICRE) at Orsay, France. The authors thank the computing staff at this center for their aid.

Registry No. H_4N^* , 92075-50-8; $(\text{CH}_3)_4\text{N}^*$, 21265-91-8; NH_3 , 7664-41-7.

Absolute Stereostructure of Novel Chiral Troponoid Spiro Compounds as Determined by Theoretical Calculation of CD Spectra

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Abstract: The absolute stereostructures of the chiral troponoid spiro compounds, cyclohepta[1,2-*b*:1,7-*b'*]bis[1,4]benzoxazine (1) and cyclohepta[1,2-*b*:1,7-*b'*]bis[naphth[2,3-*e*][1,4]oxazine] (2), were determined by theoretical calculation of CD spectra. The spiro compounds with a C_2 -symmetrical structure were optically resolved by means of HPLC using a chiral stationary phase of (+)-poly(triphenylmethyl methacrylate). The first-eluted enantiomer of compound 1 exhibits the very intense negative optical rotation $[\alpha]_D -4700^\circ$ and strong CD Cotton effects, indicating that the conjugated π -electron system spread over the whole area of the molecule is strongly twisted. In order to determine the absolute configuration of the twisted π -electron system, the CD spectrum of (15a*S*)-1 was calculated by application of the π -electron SCF-CI-dipole velocity MO method. The calculated CD and UV values are in good agreement with the observed data: calcd CD, λ_{ext} 394 nm, $\Delta\epsilon -106.9$ and λ_{ext} 289 nm, $\Delta\epsilon +76.3$; calcd UV, λ_{infl} 394 nm, ϵ 8000, λ_{max} 284 nm, ϵ 23 500; obsd CD, λ_{ext} 398 nm, $\Delta\epsilon -45.3$ and λ_{ext} 287 nm, $\Delta\epsilon +80.4$; obsd UV, λ_{max} 378 nm, ϵ 7900 and λ_{max} 285 nm, ϵ 23 500. Accordingly, the absolute configuration of (-)-1 was theoretically determined to be 15a*S*. The present conclusion is in line with the X-ray crystallographic results. The absolute configuration of compound (-)-2, a spiro acetal with two naphthalene chromophores, was similarly determined to be 18a*S* by application of the same method: calcd CD, λ_{ext} 403 nm, $\Delta\epsilon -120.0$, λ_{infl} 330 nm, $\Delta\epsilon +38.0$, λ_{ext} 272 nm, $\Delta\epsilon +109.0$; calcd UV, λ_{infl} 402 nm, ϵ 13 700, λ_{max} 316 nm, ϵ 22 200, λ_{max} 255 nm, ϵ 41 000; obsd CD, λ_{ext} 405 nm, $\Delta\epsilon -42.9$, λ_{ext} 319 nm, $\Delta\epsilon +28.9$, λ_{ext} 273 nm, $\Delta\epsilon +103.3$; obsd UV, λ_{max} 390 nm, ϵ 11 500, λ_{max} 308 nm, ϵ 23 900, λ_{max} 262 nm, ϵ 39 100.

The CD exciton chirality method for determination of absolute configuration on the basis of a chiral exciton coupling mechanism has been extensively applied to various chiral natural and synthetic organic compounds.² The exciton method, however, is not always applicable to all kinds of organic compounds. For example, 1,8a-dihydro-3,8-dimethylazulene is one of such difficult cases, to which the CD exciton chirality method is not directly applied. For such a compound with a twisted conjugated π -electron system, the theoretical calculation of CD spectra by the π -electron SCF-CI-dipole velocity MO method²⁻⁵ is useful for determination

of absolute stereostructures. In fact, we have succeeded in determining the absolute stereochemistry of optically active 1,8a-dihydro-3,8-dimethylazulene, a natural product isolated from the cell culture of the liverwort *Calypogeia granulata* Inoue as a labile biosynthetic intermediate for 1,4-dimethylazulene, by the theoretical calculation of CD spectra.⁶ The CD curve calculated for 1,8a-dihydroazulene with a twisted conjugated tetraene system was in a good agreement with the observed spectrum, leading to the unequivocal determination of absolute configuration.

In this report, we describe the determination of the absolute stereostructure of novel troponoid spiro compounds 1 and 2 with a twisted conjugated π -electron system which is spread over the whole area of the molecules, by application of the π -electron

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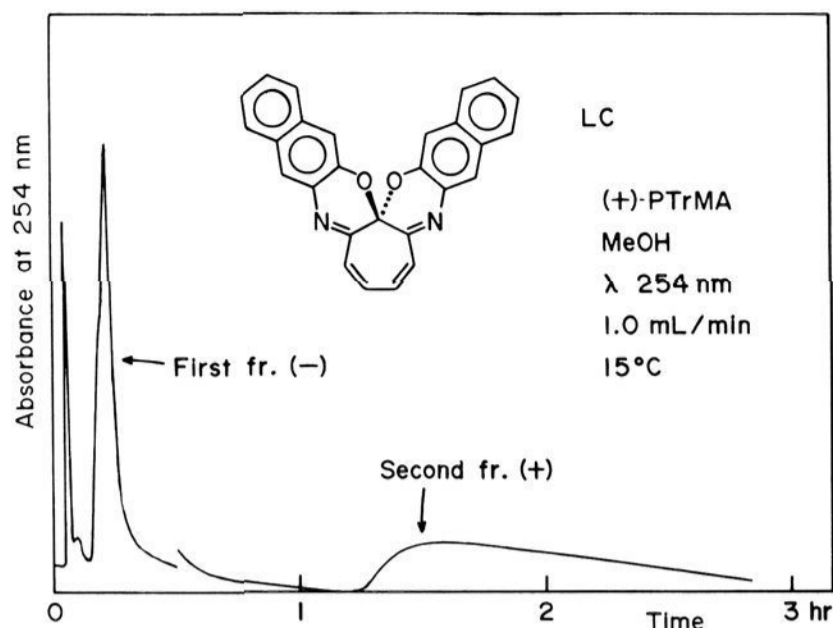
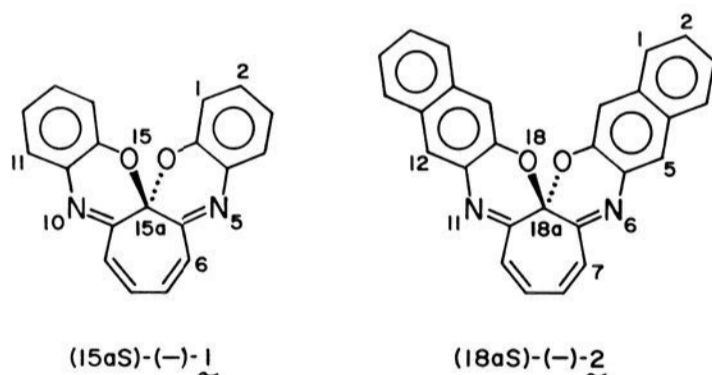


Figure 1. HPLC optical resolution of **2** on a (+)-poly(triphenylmethyl methacrylate) column.

SCF-CI-DV MO method. Cyclohepta[1,2-*b*:1,7-*b*]bis[1,4]-benzoxazine (**1**) and cyclohepta[1,2-*b*:1,7-*b*]bis[naphth[2,3-*e*]-[1,4]oxazine] (**2**), synthesized^{7,8} starting from 3-bromo-2-methoxytropone, are spiro acetal compounds with C_2 -symmetrical structure. Therefore, they can exist in a dissymmetrical form. In fact, compounds **1** and **2** were optically resolved⁹ into enantiomers by means of HPLC using a column with a chiral stationary phase of (+)-poly(triphenylmethyl methacrylate); see Figure 1. The chiroptical properties and absolute stereochemistry of these compounds are quite interesting because of their novel structure with a strongly twisted π -electron system. The twist of the π -electron systems generates very large values of optical rotation of compounds **1**, $[\alpha]_D -4700^\circ$, and **2**, $[\alpha]_D -4360^\circ$, which are comparable to those of various helicenes.¹⁰ Therefore, compounds **1** and **2** occupy a leading position in the class of an inherently dissymmetrical chromophore system. Hence, it is of significance to study if the absolute stereostructure of these novel compounds can be determined by theoretical calculation of CD spectra on the basis of the π -electron SCF-CI-DV MO method, in order to clarify the scope and limitation of the applicability of the present CD method.



Methods of Calculation

Molecular Structure. The molecular geometries of (15a*S*)-**1** and (18a*S*)-**2** were calculated at first by the method of the molecular mechanics (MMPI).¹¹ However, the conformation of **1** obtained was a little different, in dihedral angles, from that obtained by the X-ray crystallographic studies⁹ of 3,12-dichlorocyclohepta[1,2-*b*:1,7-*b*]bis[1,4]benzoxazine (**6**). So, the crystallographic atomic coordinates of **6** were directly used for compound **1**. The Cartesian coordinate system for the molecular structure of (15a*S*)-**1** was adopted as shown in Figure 5. In the

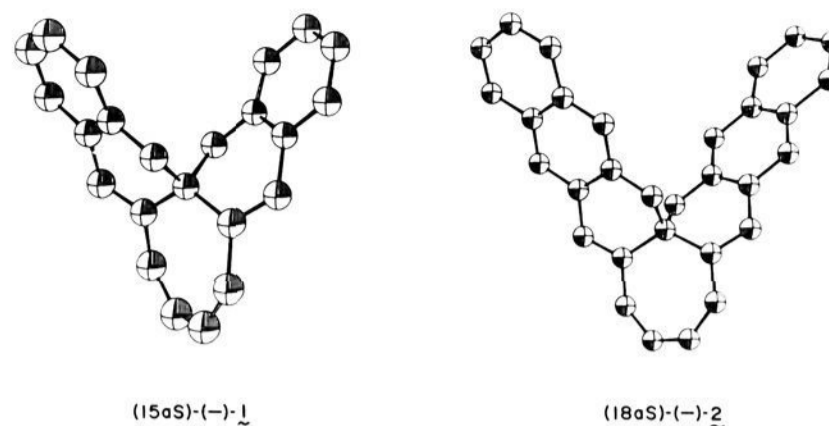


Figure 2. Stereoscopic view of chiral troponoid spiro compounds: for (15a*S*)-(-)-**1**, adapted from the X-ray data of 3,12-dichlorocyclohepta[1,2-*b*:1,7-*b*]bis[1,4]benzoxazine;⁹ for (18a*S*)-(-)-**2**, calculated by the molecular mechanics using the X-ray data of 3,12-dichlorocyclohepta[1,2-*b*:1,7-*b*]bis[1,4]benzoxazine.

case of compound **2**, the part of cyclohepta[1,2-*b*:1,7-*b*]bis[1,4]benzoxazine was taken from the X-ray data, and the remaining parts of the naphthalene rings were calculated by molecular mechanics. The stereoscopic views of (15a*S*)-**1** and (18a*S*)-**2** are illustrated in Figure 2.

Numerical Calculation of CD and UV Spectra. The CD and UV spectra of (15a*S*)-**1** and (18a*S*)-**2** were calculated by the π -electron SCF-CI-dipole velocity MO method.²⁻⁵ In the calculation, configuration interactions between all singly excited states were included, and the following standard values of atomic orbital parameters were used: $W(C) = -11.16$ eV, $(rr|rr)(C) = 11.13$ eV, $\beta(C-C, 1.388 \text{ \AA}) = -2.32$ eV, $\langle \nabla \rangle(C-C, 1.388 \text{ \AA}) = 4.70 \times 10^7 \text{ cm}^{-1}$; $W(N) = -14.12$ eV, $(rr|rr)(N) = 12.34$ eV, $(C-N) = -2.32$ or -2.55 eV, $\langle \nabla \rangle(C-N) = 4.70$ or $5.17 \times 10^7 \text{ cm}^{-1}$; $W(O) = -33.00$ eV, $(rr|rr)(O) = 21.53$ eV, $(C-O) = -2.11$ or -2.59 eV, $\langle \nabla \rangle(C-O) = 6.00$ or $7.35 \times 10^7 \text{ cm}^{-1}$. The electric repulsion integral $(rr|ss)$ was estimated by the Nishimoto-Mataga equation. The resonance integral and del values were calculated by employing the following equations, respectively;

$$\beta = [S/S(C-C, 1.388 \text{ \AA})]\beta(C-C, 1.388 \text{ \AA}) \cos \theta \quad (1)$$

$$\langle \nabla \rangle = \frac{[\langle \nabla \rangle(\text{empir}, 1.388 \text{ \AA})/\langle \nabla \rangle(\text{theor}, 1.388 \text{ \AA})]\langle \nabla \rangle(\text{theor}) \cos \theta}{(2)}$$

where θ is the dihedral angle.

The component CD and UV bands were approximated by the Gaussian distribution

$$\Delta\epsilon(\sigma) = \sum \Delta\epsilon_k \exp[-((\sigma - \sigma_k)/\Delta\sigma)^2] \quad (3)$$

$$\epsilon(\sigma) = \sum \epsilon_k \exp[-((\sigma - \sigma_k)/\Delta\sigma)^2] \quad (4)$$

where $2\Delta\sigma$ is the $1/e$ width of the bands. The $\Delta\sigma$ value of 3040 cm^{-1} was taken from the observed UV spectrum of compound **1**.

The numerical calculations were carried out on the NEC ACOS-1000 computer at the Computer Center of Tohoku University.

Results and Discussion

Synthesis and Chromatographic Optical Resolution of Spiro Compounds. The synthesis of cyclohepta[1,2-*b*:1,7-*b*]bis[1,4]benzoxazine (**1**), a troponoid spiro compound with C_2 -symmetrical structure, starting from 3-bromo-2-methoxytropone (**3**) and 2-aminophenol, already has been reported by one group of the authors.^{7,8} In general, for the determination of absolute configuration of organic compounds by means of CD spectroscopy, use of the exciton coupling between 1B_b transitions of two naphthalene chromophores is quite effective, as exemplified in the case of 2,2'-spirobiphenylindan systems.¹² Namely, the exciton coupling between two strong transitions gives rise to intense exciton split Cotton effects, which enable one to determine the absolute stereostructure in an unambiguous manner.² Taking into account

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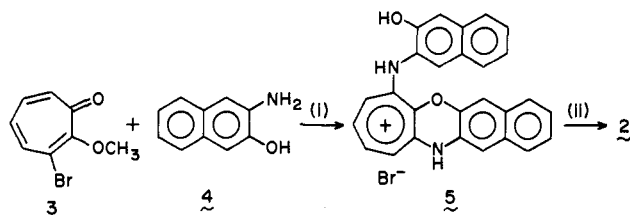
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Table I. Calculated and Observed UV and CD Spectra of Chiral Troponoid Spiro Compounds

compd	calcd (π -SCF-CI-DV MO)		obsd (MeOH)	
	UV, λ_{\max} , nm (ϵ)	CD, λ_{ext} , nm ($\Delta\epsilon$)	UV, λ_{\max} , nm (ϵ)	CD, λ_{ext} , nm ($\Delta\epsilon$)
(15aS)-(-)-1	394 sh (8 000) 284 (23 500)	394 (-106.9) 289 (+76.3)	378 (7 900) 285 (23 500)	398 (-45.3) 287 (+80.4)
(18aS)-(-)-2	402 sh (13 700) 316 (22 200) 255 (41 000)	403 (-120.0) 330 sh (+38.0) 272 (+109.0)	390 (11 500) 308 (23 900) 262 (39 100)	405 (-42.9) 319 (+28.9) 273 (+103.3)

Scheme 1^a

^a(i) 120 °C in *n*-butyl alcohol for 5 days; (ii) 3 M aq NaOH/methanol.

the present nature of CD Cotton effects, we synthesized cyclohepta[1,2-*b*:1,7-*b'*]bis[naphth[2,3-*e*][1,4]oxazine] (2), a troponoid spiro compound with two naphthalene chromophores, in a similar way to the case of compound 1; condensation of 3-bromo-2-methoxytroponone (3) and 3-amino-2-naphthol (4) by heating at 120 °C for 5 days gave 7-(*N*-3-(2-hydroxy)naphthalenyl-amino)cyclohepta[*b*]naphth[2,3-*e*][1,4]oxazine hydrobromide (5) in a 22% yield as the most polar product: mp 150–151 °C from methanol (Scheme I). The salt was then autoxidized by allowing the methanol solution containing 3 M aqueous NaOH solution to stand at room temperature, giving the naphthalene analogue 2 in a 73% yield; mp 253–255 °C from benzene. The structure of compound 2 was secured by the 270-MHz ¹H NMR and mass spectra.

For optical resolution of compounds 1 and 2, we adopted a direct HPLC method using a column with a chiral stationary phase of (+)-poly(triphenylmethyl methacrylate). One of us already reported that the column was very effective for optical resolution of organic compounds having aromatic groups.¹³ This method proved successful and both racemates 1 and 2 were optically resolved under a reverse phase condition with methanol as eluent. Enantiomers were completely separated as exemplified in the case of compound 2 (Figure 1). Each enantiomer thus obtained was further purified by standard chromatography or by recrystallization in order to remove a contaminant of the chiral polymer.

Chiroptical Properties of Spiro Compounds. The first-eluted fractions gave levorotatory enantiomers (-)-1, [α]_D -4700° (*c* 0.0018, MeOH), and (-)-2, [α]_D -4360° (*c* 0.003255, MeOH), respectively. The optical rotation values are very large and comparable to those of various helicenes.¹⁰ These phenomena suggest that the conjugated π -electron systems which are spread over the whole area of molecules are strongly twisted. In fact, the CD spectra also show intense CD Cotton effects as shown in Figures 3 and 6.

The UV spectrum of (-)-1 exhibits two π - π^* transitions: λ_{\max} 378 nm (ϵ 7900) and 285 (23 500). In the region of the corresponding transitions, the CD spectrum shows negative and positive Cotton effects: λ_{ext} 398 nm ($\Delta\epsilon$ -45.3) and 287 (+80.4). In addition, a relatively weak positive Cotton effect appears as a shoulder around 325 nm, while the corresponding second UV transition band is completely buried in the neighboring intense absorption band (Figure 3). On the other hand, in the case of (-)-2, the second transition is clearly observable both in the UV and CD spectra (Figure 6). The UV spectrum of (-)-2 exhibits

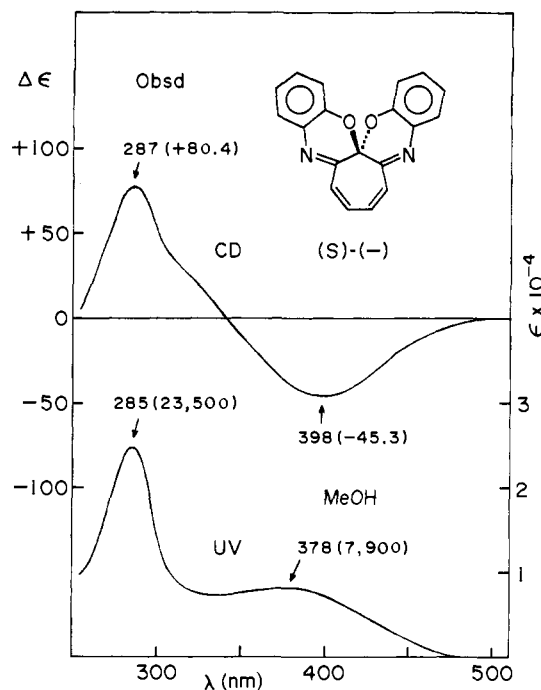


Figure 3. CD and UV spectra of (15aS)-(-)-cyclohepta[1,2-*b*:1,7-*b'*]bis[1,4]benzoxazine (1) in methanol.⁹

three π - π^* transitions: λ_{\max} 390 nm (ϵ 11 500), 308 (23 900), and 262 (39 100). The CD spectrum also shows three major Cotton effects: λ_{ext} 405 nm ($\Delta\epsilon$ -42.9), 319 (+28.9), and 273 (+103.3).

Compound 1 has a novel molecular structure possessing two identical aromatic groups in the wings of the molecule. Namely, two benzenoid chromophores are situated in chiral positions. So, in such a case, it would be expected that compound 1 might exhibit exciton split Cotton effects due to the exciton coupling between two benzenoid chromophores. However, it was not the case, because the observed CD spectrum of 1 shows no typical exciton split Cotton effects as illustrated in Figure 3. Namely, in the region of the first transition around 378 nm, the CD spectrum shows a single Cotton effect of negative sign, as is distinct from the features of exciton coupling systems which show bisignate Cotton effects. The same is true in the region of the third transition around 285 nm. Therefore, the CD exciton chirality method could not be directly applied to this case.¹⁴ The present results suggest that the π -electron systems of the benzenoid chromophores are strongly conjugated to each other via the diene system of the central cycloheptadiene moiety, losing their nature as an independent benzenoid chromophore.¹⁵ In other words, the present system should be treated as a single conjugated π -electron system which is strongly twisted and spread over the whole area of the molecule.

(14) The fact that the observed Cotton effects are not due to an exciton coupling was also corroborated by the theoretical calculation. Namely, the calculation results revealed that each of the UV bands consists of a single π - π^* transition as shown in Figure 5. It is established that in the case of the exciton coupling of a degenerate system, each of UV bands consists of two π - π^* transitions.

(15) If the conjugation of the π -electron system of compounds 1 and 2 can be interrupted by introducing a saturation in the position of the diene part, the derivatives obtained would exhibit exciton split Cotton effects.

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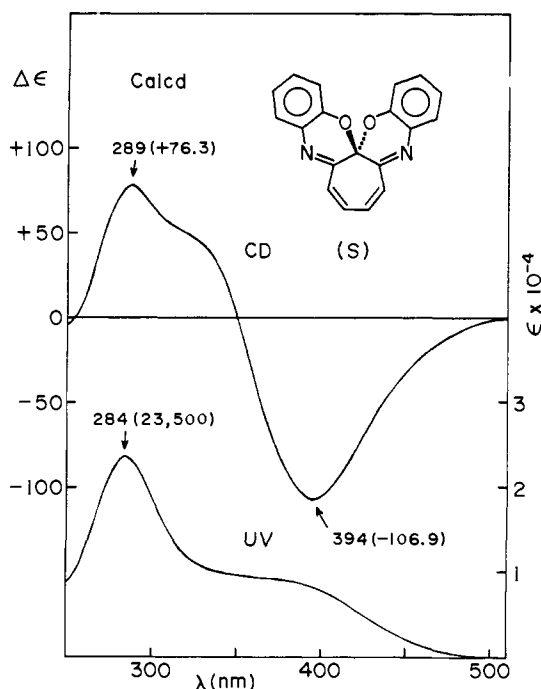


Figure 4. CD and UV curves of (15aS)-cyclohepta[1,2-*b*:1,7-*b'*]bis[1,4]benzoxazine (**1**) calculated by the π -SCF-CI-DV MO method.

When planning to synthesize compound **2**, we expected that compound **2** would exhibit intense exciton split Cotton effects due to the exciton coupling between two naphthalene chromophores, because the long-axis polarized 1B_b transition of naphthalene, in general, gives rise to strong exciton Cotton effects. Namely, we expected that the exciton coupling term might overcome the conjugation effect and might generate bisignate Cotton effects. However, the CD spectrum of compound **2** also shows no exciton split Cotton effects in the region of the 1B_b transition around 250 nm (Figure 6).¹⁵ For these reasons, we next applied the π -electron SCF-CI-DV MO method to the systems (15aS)-**1** and (18aS)-**2** in order to determine the absolute stereostructure by calculation of the CD spectra.

Theoretical Determination of Absolute Stereostructure by Calculation of CD Spectra. The CD and UV curves of (15aS)-**1** obtained by the calculation are illustrated in Figure 4. The UV spectrum curve shows two allowed π - π^* absorption bands, although the first band at longer wavelengths appears as a shoulder: λ_{inf} 394 nm (ϵ 8000) and λ_{max} 284 (23 500). The calculated values are in a good agreement with the observed ones, as listed in Table I. However, analysis of the calculation results clarified that an additional transition is buried around 336 nm and also revealed that each band consists of a single π - π^* transition (Figure 5). The first transition at 394 nm is polarized in the xy plane, while the second and third transitions at 336 and 284 nm, respectively, are polarized along the z axis, i.e., the C_2 -symmetrical axis of the molecule. The dipole strength values of the first, second, and third transitions were calculated to be $D = 13.6 \times 10^{-36}$, 11.7×10^{-36} , and 26.0×10^{-36} cgs unit, respectively.

In the case of the calculated CD curve, the three transitions afforded negative, positive, and positive Cotton effects, respectively, from the longer wavelength side (Figure 4): λ_{ext} 394 nm ($\Delta\epsilon$ -106.9), λ_{inf} 334 nm ($\Delta\epsilon$ +40.0), and λ_{ext} 289 nm ($\Delta\epsilon$ +76.3). The rotational strengths calculated were $R = -553 \times 10^{-40}$, $+212 \times 10^{-40}$, and $+304 \times 10^{-40}$ cgs unit for the first, second, and third Cotton effects, respectively. The calculated values of wavelength and intensity of Cotton effects are in a good agreement with the observed values except that the $\Delta\epsilon$ value of the first Cotton effect is twice that of the observed spectrum. Namely, the first Cotton effect is opposite in sign to the second and third Cotton effects, and the second Cotton effect appears as a shoulder. It is thus evident that the basic pattern of the CD spectrum curve was well reproduced by the calculation.

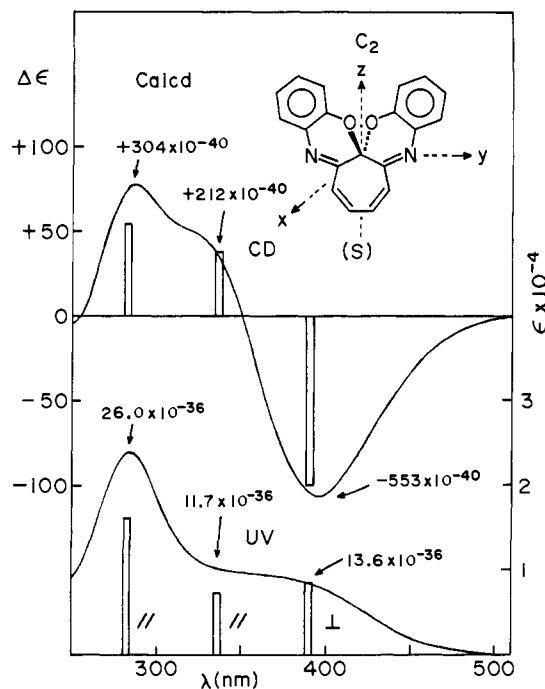


Figure 5. Rotational and dipole strengths and polarization of transition of (15aS)-**1** calculated by the π -SCF-CI-DV MO method. Symbols \perp and \parallel mean perpendicular and parallel, respectively, to the C_2 axis.

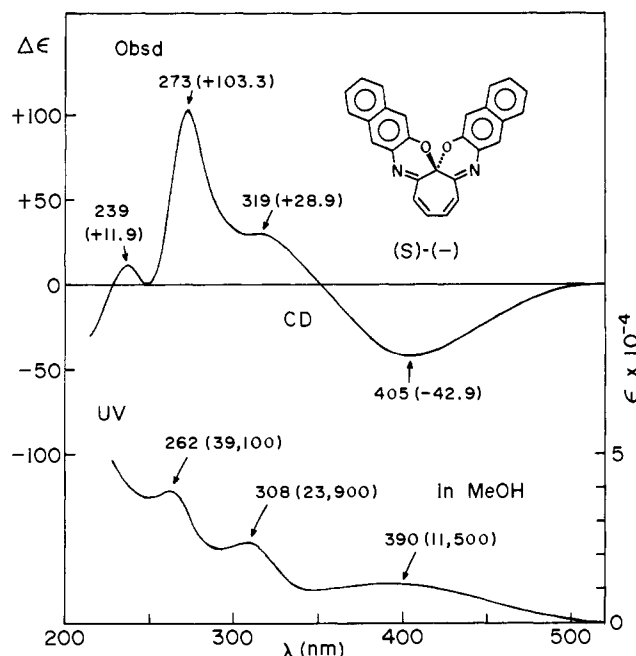


Figure 6. CD and UV spectra of (18aS)-(-)-cyclohepta[1,2-*b*:1,7-*b'*]bis[naphth[2,3-*e*][1,4]oxazine (**2**) in methanol.

The signs of the CD Cotton effects calculated for (15aS)-**1** are in accord with those of the observed Cotton effects of the (-)-**1** (Table I). Accordingly, the absolute stereostructure of the troponoid spiro compound (-)-**1** was theoretically determined to be 15aS, as shown in structure **1**. This conclusion is consistent with the results of X-ray crystallographic studies of (-)-3,12-dichlorocyclohepta[1,2-*b*:1,7-*b'*]bis[1,4]benzoxazine (**6**).⁹

The CD and UV curves calculated for the naphthalene homologue (18aS)-**2** are shown in Figure 7. Three UV bands and three CD Cotton effects were calculated as in the case of compound **1**. However, the composition of the bands is much more complex than in the case of **1**; there are six component transitions, the dipole and rotational strengths of which are shown together with the polarization of transition (Figure 7). The polarization

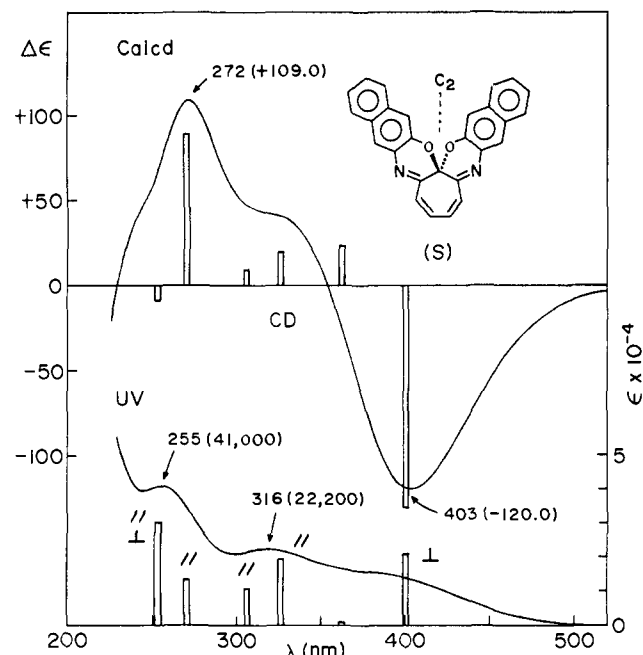


Figure 7. CD and UV curves of (18aS)-cyclohepta[1,2-*b*:1,7-*b'*]bis[naphth[2,3-*e*][1,4]oxazine] (**2**) calculated by the π -SCF-CI-DV MO method. The bar graph indicates the rotational and dipole strengths.

of the first transition at longer wavelengths is perpendicular to the C_2 -symmetrical axis of the molecule. The calculated values of three apparent UV bands agree well with the observed values (Table I).

The CD curve calculated for (18aS)-**2** exhibits three apparent Cotton effects of negative, positive, and positive signs from the longer wavelength side. Although the intensity of the negative Cotton effect of the first transition is much larger than that of the observed one, as in the case of compound **1**, the basic pattern of the calculated CD curve agrees well with that of observed CD spectrum of (-)-**2**. Furthermore, the calculated and observed CD Cotton effects agree in sign with each other. Consequently, the absolute configuration of compound (-)-**2** was determined to be 18aS on the basis of the theoretical calculation of CD spectra.

Concluding Remarks

The present studies clarified that the CD spectra of twisted π -electron systems could be reproduced well by the theoretical calculation based on the π -SCF-CI-DV MO method, and revealed that the absolute stereostructures of cyclohepta[1,2-*b*:1,7-*b'*]bis[1,4]benzoxazine (**1**) and cyclohepta[1,2-*b*:1,7-*b'*]bis[naphth[2,3-*e*][1,4]oxazine] (**2**), chiral spiro compounds synthesized starting from 3-bromo-2-methoxytropone, could be theoretically determined in a reliable manner. The strategy employed here would provide promising routes for the determination of absolute configuration of other twisted π -electron systems including natural and synthetic chiral organic compounds.¹⁶

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Experimental Section

General Procedures. Melting points are uncorrected. IR and UV spectra were obtained using Shimadzu IR-450 and Shimadzu UV-202 spectrophotometers, respectively. ¹H NMR spectra were recorded on a JEOL JNM-PS/PFT100 or a JEOL JNM-GX270 FT spectrometer, employing tetramethylsilane as an internal standard. Mass spectra were obtained on a JEOL JMS-DX300 or a Shimadzu LKB9000 GC-mass spectrometer at 75 eV. Optical rotations $[\alpha]_D$ were determined on a JASCO DIP-181 polarimeter at 25 °C. CD spectra were recorded on a JASCO J-40 spectropolarimeter.

7-(*N*-3-(2-Hydroxy)naphthalenylamino)cyclohepta[*b*]naphth[2,3-*e*]-[1,4]oxazine Hydrobromide (5**).** A solution of 3-bromo-2-methoxytropone (**3**) (0.500 g, 2.33 mmol) and 3-amino-2-naphthol (**4**) (0.463 g, 2.91 mmol) in 5 mL of *n*-butyl alcohol was heated at 120 °C in a sealed tube for 5 days. After cooling to room temperature, the unreacted **4** which deposited as crystals was removed by filtration, recovering **4** (0.200 g, 40%). The filtrate was concentrated and the residue was chromatographed on silica gel (benzene/methanol 20:1). Elution with methanol gave compound **5** as the most polar fraction (0.250 g, 22%). The product was further purified by recrystallization from methanol giving red brown prisms: mp 150–151 °C dec; UV (MeOH) λ_{\max} 432, 362, 343, 313, 286, 272, 263, and 223 nm; UV (MeOH/3 M NaOH) λ_{\max} 465, 376, 354, 324, 280, 268, and 239 nm; high-resolution mass spectrum, m/z 403.1365, (calcd for $C_{27}H_{19}N_2O_2$; m/z 403.1445).

Cyclohepta[1,2-*b*:1,7-*b'*]bis[naphth[2,3-*e*][1,4]oxazine] (2**).** To a solution of compound **5** (0.100 g, 0.207 mmol) in methanol (5 mL) was added 3 M aqueous NaOH solution (0.1 mL, 0.30 mmol). The mixture was allowed to stand at room temperature for 4 h, poured into water, and extracted with chloroform. The organic layer was washed with water and evaporated to dryness, giving a crude product of compound **2** (0.060 g, 73%). The product was purified by chromatography on silica gel (benzene) and by recrystallization from benzene to afford **2** as yellow needles: mp 253–255 °C; ¹H NMR (270 MHz, CDCl₃) δ 6.61 (2 H, m, 8,9-H), 7.01 (2 H, m, 7,10-H), 7.02 (2 H, s, 17,20-H), 7.41 (4 H, m, 2,3,14,15-H), 7.55 (2 H, m, 1,16-H), 7.93 (2 H, m, 4,13-H), 8.17 (2 H, s, 5,12-H); IR (KBr) ν_{\max} 1635 cm⁻¹; UV (MeOH) λ_{\max} 386 nm (log ϵ 4.16), 307 (4.43), 262 (4.63); high-resolution mass spectrum, m/z 400.1256, (calcd for $C_{27}H_{16}N_2O_2$; m/z 400.1211).

General Procedure for Chromatographic Optical Resolution. The column with a chiral stationary phase of (+)-poly(triphenylmethyl methacrylate)¹³ was mounted in a HPLC apparatus, cooled at 15 °C, and equilibrated with methanol as eluent. The samples were injected as methanol solutions. Separation of enantiomers was monitored by a UV detector. Since a small amount of the polymer of the chiral stationary phase was present as a contaminant, the fraction of each enantiomer resolved was purified by preparative TLC on silica gel, or by recrystallization.

(15aS)-(-)-Cyclohepta[1,2-*b*:1,7-*b'*]bis[1,4]benzoxazine (1**).** The levorotatory enantiomer was obtained as the first-eluted fraction on the HPLC: yellow crystals with mp 184–185 °C; $[\alpha]_D$ -4700° (*c* 0.0018, MeOH); UV (MeOH) λ_{\max} 378 nm (ϵ 7900), 285 (23 500); CD (MeOH) λ_{ext} 398 nm ($\Delta\epsilon$ -45.3), 340 (0.0), 287 (+80.4). The second-eluted fraction gave the (+) enantiomer, the CD spectrum of which was antipodal to that of the (-) enantiomer.

(18aS)-(-)-Cyclohepta[1,2-*b*:1,7-*b'*]bis[naphth[2,3-*e*][1,4]oxazine] (2**).** The (-) enantiomer was obtained as the first-eluted fraction on the HPLC: $[\alpha]_D$ -4360° (*c* 0.003 255, MeOH); UV (MeOH) λ_{\max} 390 nm (ϵ 11 500), 308 (23 900), 262 (39 100); CD (MeOH) λ_{ext} 405 nm ($\Delta\epsilon$ -42.9), 352 (0.0), 319 (+28.9), 273 (+103.3). The second-eluted fraction gave the (+) enantiomer.

Acknowledgment. This work was supported in part by grants from the Ministry of Education, Science and Culture, Japan (No. 59430005 to N.H.), and the Suntory Institute for Bioorganic Research.