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Circular Dichroic Power of Chiral Spiro Aromatics. Theoretical Calculation of the CD and UV Spectra of 2,2'-Spirobi[2*H*-benz[*e*]indene] Derivatives

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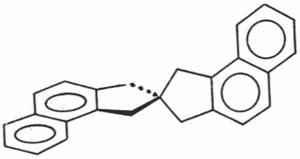
The CD and UV spectra of (2*S*)-2,2'-spirobi[2*H*-benz[*e*]indene]-1,1'(3*H*,3'*H*)-dione (*2*) and (1*R*,1'*S*,2*S*)-1,1',3,3'-tetrahydro-2,2'-spirobi[2*H*-benz[*e*]indene]-1,1'-diyl diacetate (*3*) were theoretically calculated by the application of the π-electron SCF-CI-DV MO method. The shape of component CD and UV bands was approximated by method (A) of the Gaussian distribution, or by method (B) employing the observed band shape of the UV spectra of model compounds. The calculated CD and UV curves were in good agreement with the observed ones. For compound *2*, method (A), calcd CD, $\lambda_{ext} = 318.5$ nm ($\Delta\varepsilon = +5.8$), 250.0 (—63.7), 213.7 (+90.8); obsd. CD, $\lambda_{ext} = 336.2$ nm ($\Delta\varepsilon = +11.9$), 253.2 (—96.1), 214.0 (+112.1). For compound *3*, method (A), calcd CD, $\lambda_{ext} = 279.3$ nm ($\Delta\varepsilon = +6.5$), 224.2 (—590.2), 213.7 (+753.7); obsd. CD, $\lambda_{ext} = 285.0$ nm ($\Delta\varepsilon = +4.4$), 230.2 (—961.5), 221.6 (+567.1). The absolute stereostructures of chiral spiro aromatics *2* and *3* have been thus established by the calculation. The mechanism of the widely spread and weak CD Cotton effects of diketone *2* has been also clarified by the calculation. The calculated CD and UV spectral curves of compound *3* obtained by the application of method (B) were in excellent agreement with the observed ones: calcd CD, $\lambda_{ext} = 282.5$ nm ($\Delta\varepsilon = +10.2$), 231.5 (—1139.5), 221.2 (+474.0); obsd. CD, $\lambda_{ext} = 285.0$ nm ($\Delta\varepsilon = +4.4$), 230.2 (—961.5), 221.6 (+567.1).

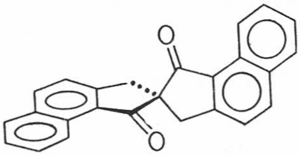
INTRODUCTION

It has been well established that the CD exciton chirality method[1] enables one to determine the absolute stereostructure of organic compounds including various natural products and synthetic chiral compounds in a nonempirical manner. For example, we have recently determined the absolute stereostructures of chiral triptycenes with a nondegenerate chromophore system[2] and those of 2,2'-spirobi[2*H*-benz[*e*]indene] derivatives with a degenerate chromophore system.[3] Namely, in the case of the (2*S*)-1,1',3,3'-tetrahydro-2,2'-spirobi-[2*H*-benz[*e*]indene] system (*1*), the two identical naphthalene chromophores occupy chiral positions to each other. Since the two long axes of the naphthalene moieties constitute a negative exciton chirality, one can easily assign the absolute configuration of the enantiomer, which shows negative first and positive second Cotton effects in the ^1B_b transition region, to be

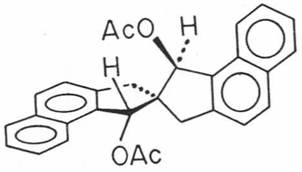
2*S*. In fact, we have determined the (1*R*,1'*S*,2*S*) absolute configuration of $[\mathrm{CD}(-)_{230.2}]$-1,1',3,3'-tetrahydro-2,2'-spirobi[2*H*-benz[e]indene]-1,1'-diyl diacetate (*3*)[4] from the observed CD spectra of negative exciton chirality in the ^1B_b transition region of the naphthalene chromophore.[3] The CD amplitude ($A =$ — 1528.6) of the present exciton split Cotton effects is one of the strongest encountered in common organic compounds.[5] The conclusion on the absolute configuration was consistent with the results of the synthetic works done by Schlögl and his co-worker.[6,7]



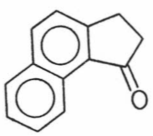
(2S)-**1**



(2S)-
$[\mathrm{CD}(-)_{253.2}]$-**2**



(1R,1'S,2S)-
$[\mathrm{CD}(-)_{230.2}]$-**3**



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The diketo compound, (2*S*)-2,2'-spiro[2*H*-benz[*e*]indene]-1,1'(3*H*,3'*H*)-dione (*2*), also has an exciton coupling system with two degenerate chromophores.[3] In fact, the CD spectrum of *2* shows bisignate Cotton effects. However, the CD Cotton effects are widely spread and their intensities are remarkably diminished in comparison with that of compound *3*. This may be due to the decrease in the symmetry of the naphthalene chromophore by the conjugation with a carbonyl group.

In order to clarify the mechanism of the Cotton effects and establish the absolute stereostructures, we have carried out the theoretical calculation of the CD and UV spectra of 2,2'-spirobi[2*H*-benz[*e*]indene] derivatives by the method of π-electron SCF-CI-dipole velocity MO method.[1,8-10] In this paper we report the calculation results and discuss the mechanism of the Cotton effects. Furthermore, we discuss the shape and intensity of the CD and UV bands of these chiral spiro aromatics.

METHOD OF CALCULATION

Molecular Structure

The molecular geometries of the most stable conformations of (2*S*)-*1* and (2*S*)-*2* were calculated by the method of molecular mechanics (MMPI).[11] Their stereoscopic views are illustrated in Figure 1. The atomic coordinates obtained were used for the following calculation of CD and UV spectra.

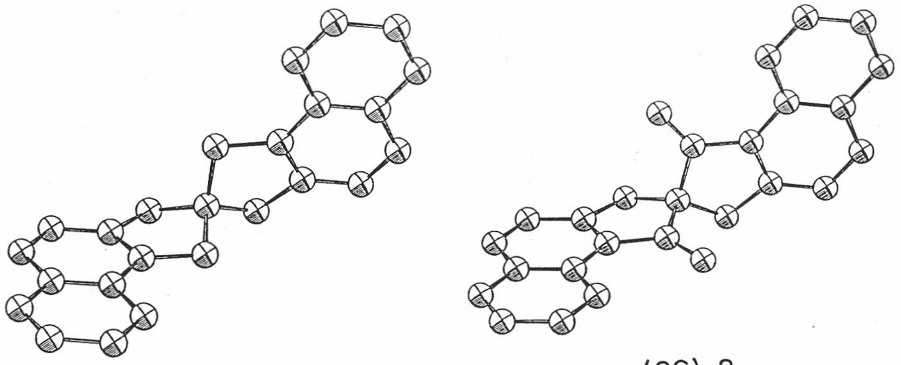
(2S)-1 (2S)-2

Figure 1. Stereoscopic view of the conformations of (2*S*)-1,1',3,3'-tetrahydro-2,2'-spirobi[2*H*-benz[*e*]indene] *1* and (2*S*)-2,2'-spirobi[2*H*-benz[*e*]indene]-1,1'(3*H*,3'*H*)-dione *2* calculated by the molecular mechanics (MMPI).

Numerical Calculation of CD and UV Spectra

The CD and UV spectra of (2*S*)-*2* and (1*R*,1'*S*,2*S*)-*3* were calculated by the π-electron SCF-CI-dipole velocity molecular orbital method.[1,8-10] In the MO calculation, the configuration interactions between all singly excited states were included, and the following standard values of atomic orbital parameters were used: for aromatic carbon, $W(\mathrm{C}) = -11.16$ eV, $(rr \mid rr)(\mathrm{C}) = 11.13$ eV, β (C—C, 1.388 Å) $= -2.32$ eV, $\langle \nabla \rangle$ (C—C, 1.388 Å) $= 4.70 \times 10^{7}$ cm^{-1}; for carbonyl oxygen, $W(\mathrm{O}) = -17.28$ eV, $(rr \mid rr)(\mathrm{O}) = 14.58$ eV, $\beta(\mathrm{C{=}O}) = -2.54$ eV, $\langle \nabla \rangle (\mathrm{C{=}O}) = 5.0 \times 10^{7}$ cm^{-1}. The electric repulsion integral $(rr \mid ss)$ was estimated by the Nishimoto-Mataga equation. The resonance integral and del values were calculated by employing the following equations, respectively;

$$\beta = [S/S\,(\text{C—C, 1.388 Å})]\,\beta\,(\text{C—C, 1.388 Å}) \tag{1}$$

$$\langle \nabla \rangle = [\langle \nabla \rangle (\text{empir, 1.388 Å})/\langle \nabla \rangle (\text{theor, 1.388 Å})]\,\langle \nabla \rangle (\text{theor}) \tag{2}$$

where S is the overlap integral.

In the case of *method (A)*, the component CD and UV bands were approximated by the Gaussian distribution.[12]

$$\Delta\varepsilon(\sigma) = \Sigma\, \Delta\varepsilon_{k} \exp[-((\sigma - \sigma_{k})/\Delta\sigma)^{2}] \tag{3}$$

$$\varepsilon(\sigma) = \Sigma\, \varepsilon_{k} \exp[-((\sigma - \sigma_{k})/\Delta\sigma)^{2}] \tag{4}$$

where $2\,\Delta\sigma$ is the 1/e width of the bands. The $\Delta\sigma$ values were adopted as listed in Table II.

In the case of *method (B)*, the shape of the component CD and UV bands was approximated by the observed shape of the UV bands of model compounds.[13]

$$\Delta\varepsilon(\sigma) = \Sigma\, \Delta\varepsilon_{k}\, f(\sigma^{+} + \sigma_{o} - \sigma_{k}) \tag{5}$$

$$\varepsilon(\sigma) = \Sigma\, \varepsilon_{k}\, f(\sigma^{+} + \sigma_{o} - \sigma_{k}) \tag{6}$$

where $f(\sigma)$ is the function describing the shape of component CD and UV bands and is taken from the observed UV spectrum of a model compound. In the case of compound *3*, the UV spectrum of naphthalene was adopted.

The numerical calculations were carried out on the NEC ACOS-2020 computer at the Computer Center of Tohoku University.

RESULTS AND DISCUSSION

Theoretical Calculation of the CD and UV Spectra of (1,R1'S,2S)-1,1',3,3'-Tetrahydro-2,2'-spirobi[2H-benz[e]indene]-1,1'-diyl Diacetate (3)

The CD and UV curves of diacetate (1*R*,1'*S*,2*S*)-*3* were numerically calculated by the application of the π-electron SCF-CI-DV MO method using method (A) of Gaussian distribution approximation, as shown in Figure 2, where the solid lines show the observed CD and UV spectra, while the dotted lines are the calculated CD and UV curves. The details of the calculation results are listed in Table I. In the UV spectrum, compound *3* exhibits three absorption bands of ^1L_b transition around 320 nm, of ^1L_a transition around 280 nm, and of ^1B_b transition around 228 nm. Among them, only the latter two bands were reproduced by the calculation, because the ^1L_b transition is essentially forbiden. Although the calculated ^1B_b bands is located at a slightly shorter wavelength

TABLE I

Calculated and observed UV and CD spectra of chiral spiro aromatics and a related compound

Compd.	calcd (π-SCF-CI-DV MO)		obsd (EtOH)	
	UV, λ_{max}, nm (ε)	CD, λ_{ext}, nm ($\Delta\varepsilon$)	UV, λ_{max}, nm (ε)	CD, λ_{ext}, nm ($\Delta\varepsilon$)
(2*S*)-*2*	326.8 (16 400)	318.5 (+5.8)	311.7 (20 900)[a]	336.2 (+11.9)
				306.5 (—6.3)
		250.0 (—63.7)		253.2 (—96.1)
	237.0 (52 500)	233.6 (+18.4)	236.0 (46 800)	
	218.3 (59 400)	213.7 (+90.8)	212.8 (80 300)	214.0(+112.1)
4	322.6 (6 800)		329.3 (5 000)	
			304.8 (9 000)	
	234.7 (27 000)		232.5 (23 800)	
	219.3 (30 100)		213.2 (35 300)	
(1*R*,1'*S*,2*S*)-*3*[b]			321.3 (2 700)	322.0 (+1.8)
			313.5 (1 700)	314.0 (+0.8)
			307.0 (2 200)	308.0 (+1.0)
	282.5 (6 300)	279.3 (+6.5)	283.3 (12 500)	285.0 (+4.4)
			279.4 (12 800)	
			274.2 (12 400)	
	218.3(196 800)	224.2 (—590.2)	228.4(172 700)	230.2(—961.5)
		213.7 (+753.7)		221.6(+567.1)
(1*R*,1'*S*,2*S*)-*3*[c]			321.3 (2 700)	322.0 (+1.8)
			313.5 (1 700)	314.0 (+0.8)
			307.0 (2 200)	308.0 (+1.0)
	282.5 (5 000)	282.5 (+10.2)	283.3 (12 500)	285.0 (+4.4)
			279.4 (12 800)	
			274.2 (12 400)	
	226.2(184 500)	231.5(—1139.5)	228.4(172 700)	230.2(—961.5)
		221.2 (+474.0)		221.6(+567.1)

[a] Measured in methanol. [b] Calculated by method (A). [c] Calculated by method (B).

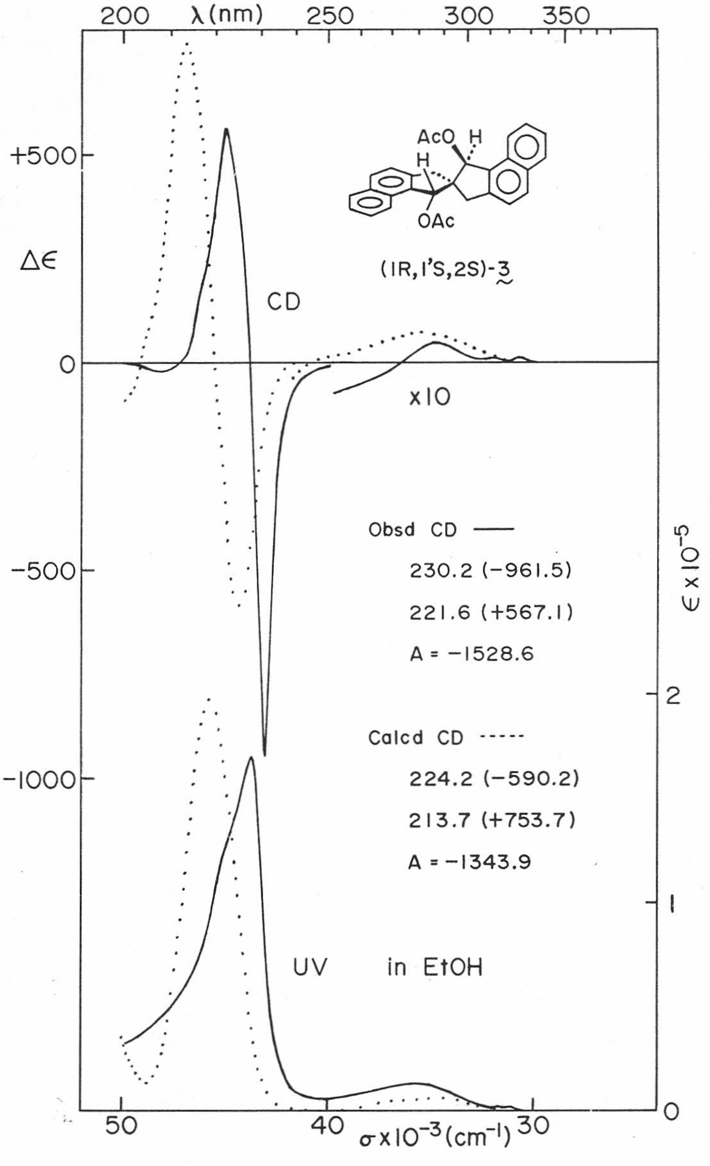

Figure 2. Calculated and observed CD and UV spectra of (1*R*,1'*S*,2*S*)-1,1',3,3'-tetrahydro-2,2'-spirobi[2*H*-benz[*e*]indene]-1,1'-diyl diacetate *3*: dotted lines, calculated; solid lines, observed in ethanol. The CD spectra in the region of the ^1L_a transition (350—250 nm) are expanded ten times in intensity. The calculated CD and UV curves were obtained by method (A) of the Gaussian distribution approximation.

region than the observed one, the pattern and intensity of the principal absorption bands were well reproduced by the calculation: obsd, ^1L_a, $\lambda_{max} =$ 283.3 nm ($\varepsilon = 12500$), ^1B_b, $\lambda_{max} = 228.4$ nm ($\varepsilon = 172700$); calcd, ^1L_a, $\lambda_{max} =$ 282.5 nm ($\varepsilon = 6300$), ^1B_b, $\lambda_{max} = 218.3$ nm ($\varepsilon = 196800$).

In the case of CD spectrum, compound *3* shows a positive Cotton effect at the ^1L_a transition region: $\lambda_{ext} = 285.0$ nm ($\Delta\varepsilon = +4.4$). This positive Cotton effect is well reproduced by the calculation: $\lambda_{ext} = 279.3$ nm ($\Delta\varepsilon = +6.5$). In the case of the ^1L_b transition, the calculation gave no Cotton effects like in the case of UV spectra, although the observed spectrum shows weak positive Cotton effects.

In the ^1B_b transition region, the calculation afforded typical exciton split Cotton effects of negative first and positive second signs, as expected from the exciton coupling mechanism: calcd, $\lambda_{ext} = 224.2$ nm ($\Delta\varepsilon = -590.2$) and $\lambda_{ext} = 213.7$ nm ($\Delta\varepsilon = +753.7$). The calculated sign, intensity, and position of the Cotton effects were in good agreement with those of the observed ones: obsd, $\lambda_{ext} = 230.2$ nm ($\Delta\varepsilon = -961.5$) and $\lambda_{ext} = 221.6$ nm ($\Delta\varepsilon = +567.1$). The present calculation results indicate that the greatest part of the Cotton effects arises from the exciton coupling mechanism.

*Calculation of the CD and UV Spectra of (2*S*)-2,2'-Spirobi[2*H*-benz[*e*]indene]-1,1'(3*H*,3'*H*)-dione* (2)

The CD and UV spectra of diketone (2*S*)-*2* were calculated in a similar manner using the Gaussian approximation method (A). In the present case, the atomic orbital parameters for heteroatoms were adopted as listed in the section of Method of Calculation. Since the two carbonyl carbons are in the position of 1,3-relation, they can make a homoconjugation like in the case of spiroconjugation. So, at first we incorporated the homoconjugation term in the calculation. However, in addition to the fact that the CD intensity obtained with the nil-homoconjugation is smaller than the observed one, as illustrated in Figure 3, the calculated CD intensity further decreases with increasing homoconjugation term. Therefore, in the present calculation, the homoconjugation term was neglected.

The UV spectrum of diketone (2*S*)-*2* exhibits, in the region of the ^1L_a transition, a broad band of medium intensity at 312 nm and a weak band which appears as a shoulder around 335 nm (Figure 3). From the viewpoint of the UV intensity, these two bands are considered to be $\pi \rightarrow \pi^*$ transitions. So, the $n \rightarrow \pi^*$ transition of the naphthalene-ketone chromophore, if any, may be buried in the relatively intense ^1L_a bands.

In the ^1B_b transition region, two intense UV bands are observed: $\lambda_{max} = 236.0$ nm ($\varepsilon = 46800$) and $\lambda_{max} = 212.8$ nm ($\varepsilon = 80300$). For the appearance of the two absorption bands in the ^1B_b transition region, one may assume that the exciton coupling between two chromophores causes the split of the ^1B_b transition into the two bands. However, this is not the case, because the monomeric ketone *4* also shows two absorption bands in the ^1B_b transition (Figure 4). The calculation reproduced these two absorption bands together with the ^1L_a band.

The CD spectrum of (2*S*)-*2* shows weak positive and negative Cotton effects, $\lambda_{ext} = 336.2$ nm ($\Delta\varepsilon = +11.9$) and $\lambda_{ext} = 306.5$ nm ($\Delta\varepsilon = -6.3$), in the ^1L_a transition region, although the calculation produced a single positive Cotton effect (Figure 3). Since the location of the first positive Cotton effect (336.2 nm) corresponds to that of the UV shoulder around 335 nm, the positive Cotton effect may be assigned to the $\pi \rightarrow \pi^*$ transition. If so, the positive sign

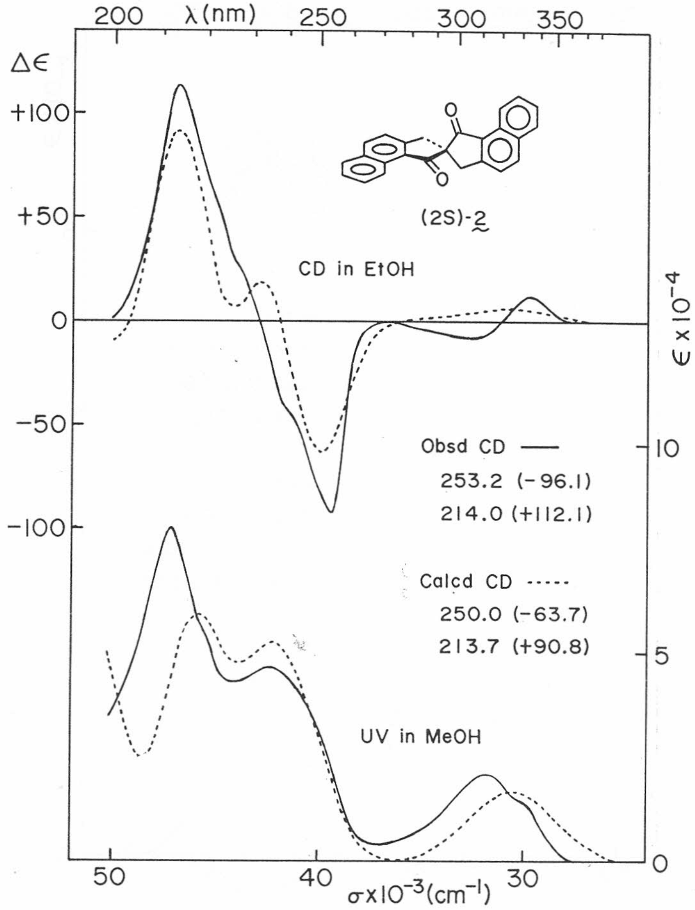

Figure 3. Calculated and observed CD and UV spectra of (2*S*)-2,2'-spirobi[2*H*-benz[*e*]indene]-1,1'(3*H*,3'*H*)-dione *2*: dotted lines, calculated; solid lines, observed. The calculated CD and UV curves were obtained by method (A).

of the calculated Cotton effect agrees with that of the observed one. Furthermore, the location of the negative second Cotton effect (306.5 nm) is also close to that of the UV absorption maximum (311.7 nm). Therefore, the second Cotton effect may be also assigned to the π→π* transition. Another possibility is that the second negative Cotton effect may be caused by the n→π* transition, which is buried in the ^1L_a transition in the case of the UV spectrum. However, it is difficult to reach a definite assignment.

In the ^1B_b transition region, the negative first and positive second Cotton effects were well reproduced by the calculation: obsd, $\lambda_{ext} = 253.2$ nm ($\Delta\varepsilon = -96.1$) and $\lambda_{ext} = 214.0$ nm ($\Delta\varepsilon = +112.1$); calcd, $\lambda_{ext} = 250.0$ nm ($\Delta\varepsilon = -63.7$) and $\lambda_{ext} = 213.7$ nm ($\Delta\varepsilon = +90.8$). The (2*S*) absolute configuration of $[CD(-)_{253.2}]$ -*2* was thus definitely established by the present theoretical calculation.

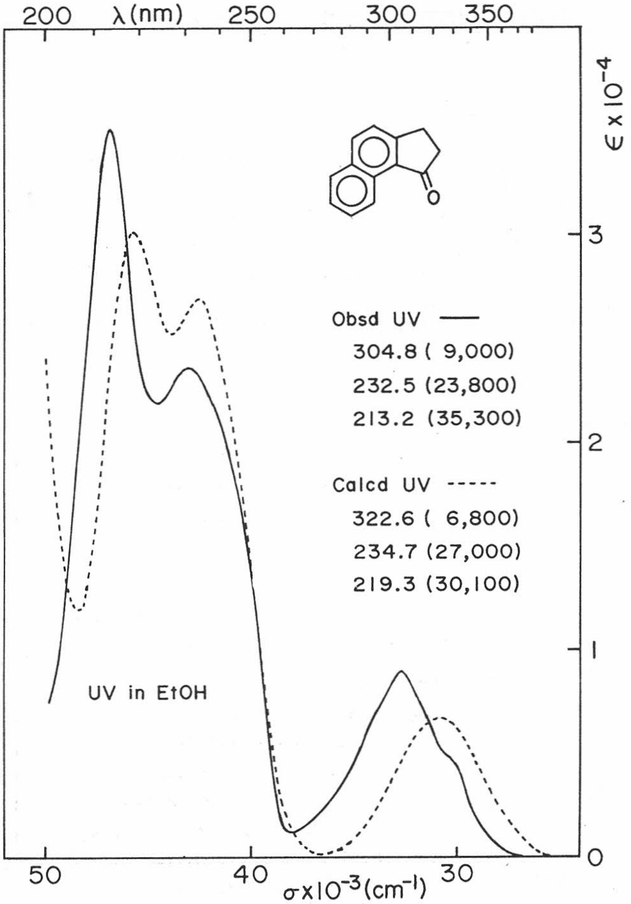

Figure 4. Calculated and observed UV spectra of 2,3-dihydro-1*H*-benz[*e*]inden-1-one *4*: dotted line, calculated; solid line, observed in ethanol.

Unlike the cases of the usual exciton coupling, the splitting of the present bisignate Cotton effects in the ^1B_b transition region is anomalously large. This phenomenon may be due to the splitting of the ^1B_b transition of naphthalene into several transitions by the conjugation of the naphthalene chromophore with a carbonyl group. In order to clarify this point, we calculated the UV spectrum of 2,3-dihydro-1*H*-benz[*e*]inden-1-one *4* by applying method (A). As shown in Figure 4, the calculated UV curve also gives two absorption bands in the ^1B_b transition region, in addition to the band of the ^1L_a transition. Thus, we analyzed the component transitions contained in the apparent three absorption bands. As illustrated in Figure 5, the calculations revealed that the UV absorption bands of compound *4* are composed of six individual transitions. Among them, the first two transitions (Nos. 1 and 2) around 30000 cm^{-1} are attributable to the original ^1L_a transition of naphthalene, because transition No. 1 is polarized almost along the short axis of the chromophore. On the other hand, transition No. 2 is very weak.

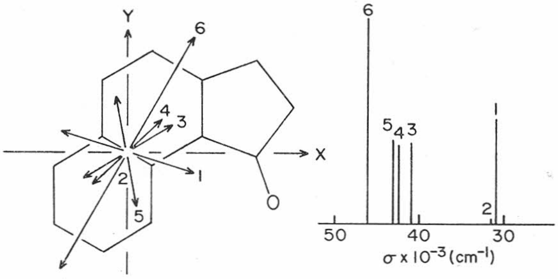

Figure 5. Calculated polarization, relative intensity of dipole strength, and transition energy of 2,3-dihydro-1*H*-benz[*e*]inden-1-one *4*.

TABLE II

The observed Δσ values of the UV absorption bands and the corresponding Δσ values employed for the calculation of CD and UV curves

Compd.	Transition	Obsd. Δσ, cm^{-1}	Employed Δσ, cm^{-1}
4	^1L_a	2982	3000
	^1B_b	2348	2000
(2*S*)-*2*	^1L_a	2958	3000
	^1B_b	2704	2000
naphthalene	^1L_a	2983	
	^1B_b	1552	
(1*R*,1'*S*,2*S*)-*3*	^1L_a	3220	3000
	^1B_b	1949	1500

Among the four transitions beyond 40000 cm^{-1}, transition No. 6 retains the original character of the ^1B_b transition of naphthalene, because the transition is the strongest in intensity and is polarized strictly along the long axis of the naphthalene moiety. On the other hand, the polarizations of the remaining three transitions (Nos. 3, 4, and 5) of medium intensity deviate a little from the long axis. The original ^1B_b transition is thus broadened by the conjugation with a carbonyl group. This is the main reason why diketone *2* shows broader and weaker exciton split Cotton effect than those of diacetate *3*.

*Calculation of the CD and UV Spectra of (1*R*,1'*S*,2*S*)-1,1',3,3'-Tetrahydro-2,2'-spirobi[2*H*-benz[e]indene]-1,1'-diyl Diacetate* (3) *by Method (B) Employing the Observed UV Band Shape*

By the calculation using method (A), the absolute stereostructure of compound *3* has been unambiguously determined, as discussed above. However, the imbalance between intensities of the first and second Cotton effects was not reproduced by the calculation. Namely, although the first Cotton effect is larger than the second in the observed spectrum, the calculation gave a weaker first Cotton effect than the second Cotton effect (Figure 2). The main reason for this gap is the vibronic structure of the absorption band; the observed ^1B_b absorption band is steeper on the longer wavelength side and broader on the shorter wavelength side, different from the symmetrical shape of the Gaussian distribution. In order to overcome this point, we adopted the shape of the observed UV band as the shape of the component CD bands.

As illustrated in Figure 6, the calculated CD and UV curves are in an excellent agreement with the observed ones. The imbalance between the first

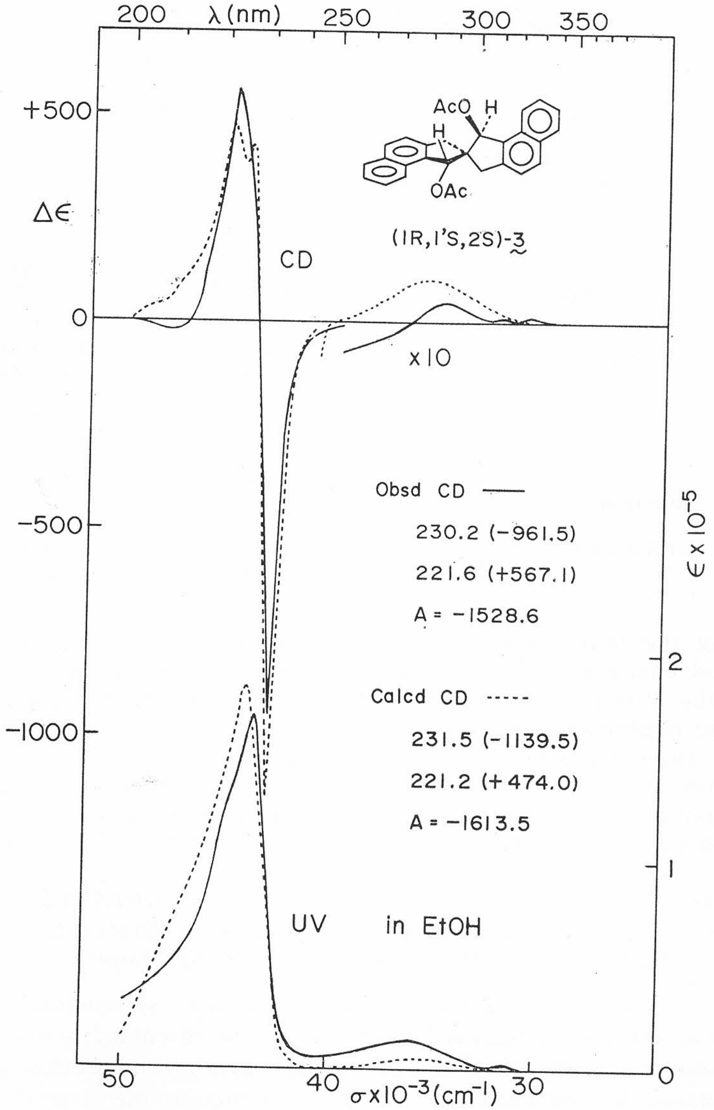

Figure 6. Calculated and observed CD and UV spectra of (1*R*,1'*S*,2*S*)-1,1',3,3'-tetrahydro-2,2'-spirobi[2*H*-benz[*e*]indene]-1,1'-diyl diacetate *3*: dotted lines, calculated; solid lines, observed in ethanol. The CD spectra in the region of the ^1L_a transition (350—250 nm) are expanded ten times in intensity. The calculated CD and UV curves were obtained by method (B) where the shape of the component CD and UV bands was adopted from the observed UV band shape of naphthalene.

and second Cotton effects is well reproduced: obsd CD, $\lambda_{ext} = 230.2$ nm ($\Delta\varepsilon = -961.5$) and $\lambda_{ext} = 221.6$ nm ($\Delta\varepsilon = +567.1$), $A = -1528.6$; calcd CD, $\lambda_{ext} = 231.5$ nm ($\Delta\varepsilon = -1139.5$) and $\lambda_{ext} = 221.2$ nm ($\Delta\varepsilon = +474.0$), $A = -1613.5$. The (1*R*,1'*S*,2*S*) absolute stereochemistry of [CD(—)$_{230.2}$]-*3* has been further established by the calculation.

The present studies clarified that in the typical cases of exciton coupling such as diacetate *3*, method (B) employing the observed UV band shape provides better calculation results than method (A) with the Gaussian distribution approximation. On the other hand, in the cases of complex compounds such as diketone *2*, method (A) is useful.

CONCLUDING REMARKS

By the numerical calculation of CD spectra using the π-electron SCF-CI-DV MO method, we have established the absolute stereostructures of chiral spiro aromatics, 1,1',3,3'-tetrahydro-2,2'-spirobi[2*H*-benz[*e*]indene]-1,1'-diyl diacetate *3* and 2,2'-spirobi[2*H*-benz[*e*]indene]-1,1'(3*H*,3'*H*)-dione *2*, and have also clarified the mechanism of their CD Cotton effects. Furthermore, we have revealed that the calculated CD and UV spectral curves of diacetate *3* obtained by the application of both the π-electron SCF-CI-DV MO method and method (B) emploing the observed UV band shape were in an excellent agreement with the observed CD and UV spectra. This calculation method can be useful for the determination of the absolute configurations of other similar chiral aromatics.[14]

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SAŽETAK

Cirkularno-dikroična snaga kiralnih spiro aromata. Teorijski računi CD i UV spektara 2,2'-spirobi[2*H*-benz[*e*]indenskih] derivata

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CD i UV spektri (2*S*)-2,2'-spirobi[2*H*-benz[*e*]inden]-1,1'-(3*H*,3'*H*)-diona (*2*) i (1*R*,1'*S*,2*S*)-1,1',3,3'-tetrahidro-2,2'-spirobi[2*H*-benz[*e*]inden]-1,1'-diil acetata (*3*) teorijski su proračunati primjenom metode π-electron SCF-DV MO. Oblik sastavnih CD i UV vrpci aproksimiran je ili metodom (A) Gaussove raspodjele ili (B) metodom upotrebe zapaženih vrpci u UV spektrima modelnih spojeva. Proračunane CD i UV krivulje dobro su se slagale s opaženima. Za spoj *2*, prema metodi (A), rač. CD, $\lambda_{ext} = 318.5$ nm ($\Delta\varepsilon + 5.8$), 250.0 (— 63.7), 213.7 (+ 90.8); opaž. CD, $\lambda_{ext} = 336.2$ nm $\Delta\varepsilon = + 11.9$), 253.2 (— 96.1), 214.0 (+ 112.1). Za spoj *3*. prema metodi (A), rač. CD, $\lambda_{ext} = 279.3$ nm ($\Delta\varepsilon = + 6.5$), 224.2 (— 590.2), 213.7 (+ 753.7); opaž. CD, $\lambda_{ext} = 285.0$ nm ($\Delta\varepsilon = + 4.4$), 230.2 (— 961.5), 221.6 (= 567.1).

Tako je računima utvrđena apsolutna stereostruktura kiralnih spiro-aromata *2* i *3*. Računima je također objašnjen mehanizam vrlo raširenog i slabog CD Cottonova efekta za diketon *2*. Proračunane CD i UV spektralne krivulje za spoj *3*, dobivene primjenom metode B, izvanredno su se slagale s opaženima: rač. CD, $\lambda_{ext} =$ $= 282.5$ nm ($\Delta\varepsilon = + 10.2$), 231.5 (— 1139.5), 221.2 (+ 474.0); opaž. CD, $\lambda_{ext} = 285.0$ nm ($\Delta\varepsilon = + 4.4$), 230.2 (— 061.5), 221.6 (+ 567.1).