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Theoretical CD Spectrum Evaluation of the Indolylfulgide Molecules by Using Semi-Empirical Molecular Orbital Calculations

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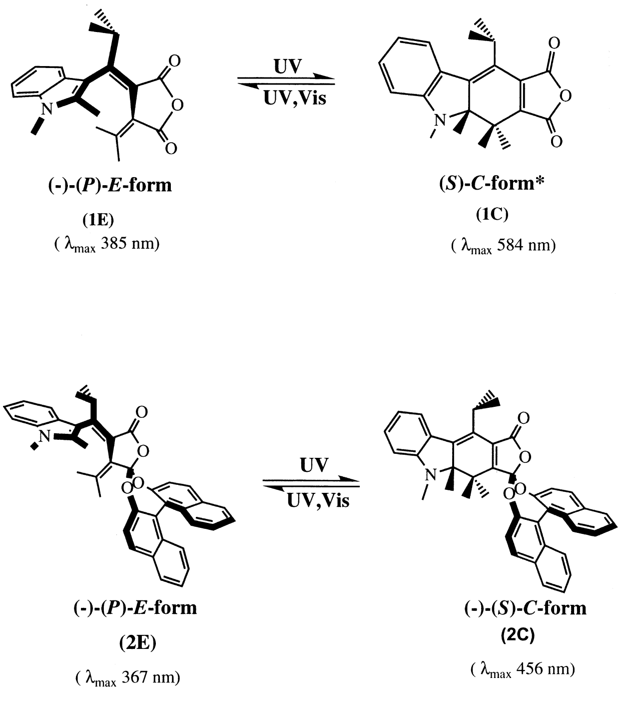
A fulgide is a photochromic molecule which can not be isomerized by a thermal reaction. The CD spectra of the optically resolved helically chiral indolylfulgide (99% enantiomer excess), whose absolute configurations have been determined by an X-ray crystallographic analysis of their binaphthyl derivative, were estimated theoretically within the framework of semi-empirical molecular-orbital calculations. The optical rotatory strength of the indolylfulgide was calculated based on the Rosenfeld equation by using the optimized structures, conformational energies, and molecular orbitals. The estimated CD spectra reproduced characteristic features, such as the peak shape and sign of the Cotton effect, quite well, though the accuracy of the calculated wavelengths for the individual CD peaks' maxima was fair.

The geometrical isomer of the colorless form of an indolylfulgide having an *E*-configuration for a double-bond **1E** is a chiral molecule whose structure is helical due to crowdedness around the triene unit including the indole ring. Because the indolylfulgide is a photochromic molecule, **1E** ($\lambda_{\max} = 385$ nm in toluene) is isomerized by irradiation of UV-visible light to the cyclic form **1C** with blue color ($\lambda_{\max} = 584$ nm in toluene). Conversely, the colored form **1C** is isomerized to **1E** by visible light. Because it has been well-established that this photochromic process obeys the Woodward Hoffmann Rule, the chirality of the fulgide molecules is maintained during photochromic reactions.[1,2] It was shown that **1E** with (+) helicity is isomerized in conrotatory fashion to **1C** having the (*S*) configuration (Scheme1).

It is rather difficult and time-consuming to determine the absolute configuration of each chiral molecule relevant to the above-mentioned photochromic process. We have determined the absolute configurations of the photochromic indolylfulgides based on an X-ray crystallographic experiment on the cyclic form of the binaphthyl derivative of the indolylfulgide **2C**,[2] and could ascertain the enantiomeric purity of **1E** and **1C** by a high-pressure liquid chromatographic analysis (HPLC).

Circular dichroism (CD) spectra give very important structural information by reflecting the absolute configuration and conformational equilibrium. It is very useful and convenient if we can estimate the CD spectrum of the chiral molecule, which organic chemists usually handle in the laboratory, by a theoretical approach in a reasonable computer time. Harada's group has carried out a series of extensive research work on chiral olefins, and have shown that the π-electron self-consistent field/configuration interaction/dipole velocity method can well reproduce the CD spectra obtained by experiments.[3] Because Harada's theoretical approach to estimate CD spectrum deals only with π-electrons, and the chiral molecules studied had a rather strong Cotton effect (large $\Delta\varepsilon$ values), it is interesting to see whether the configuration interaction (CI)/dipole velocity (DV) method, which deals with all valence electrons, can be effective to predict the CD spectra of those chiral molecules which do not seem to have a rather strong chromophore.



(-)-(*P*)-*E*-form
(1E)
($\lambda_{\max}$ 385 nm)

(*S*)-*C*-form*
(1C)
($\lambda_{\max}$ 584 nm)

(-)-(*P*)-*E*-form
(2E)
($\lambda_{\max}$ 367 nm)

(-)-(*S*)-*C*-form
(2C)
($\lambda_{\max}$ 456 nm)

Scheme 1. Photochromism of indolylfulgide and its binaphthyl derivative.
*The sign of the specific rotation of (1C) could not be determined due to the presence of the absorption peak around 589 nm.

In this paper, we show the applicability and accuracy of the valence electron self-consistent (SCF)/configuration interaction (CI)/dipole velocity (DV) method to evaluate the CD spectra of the indolylfulgide **1E** and **1C** and the colorless form of a binaphthyl-condensed derivative of an indolylfulgide **2E** within the framework of the semi-empirical molecular orbital calculation. Though it has already been reported that the CD spectra of some aromatic hydrocarbons could be accurately reproduced by sophisticated density functional calculations (B3LYP) by Grimme,[4] an easily accessible way to evaluate the CD spectrum by using the semi-empirical molecular orbital calculations may be useful for organic chemists.

Theory

The optical rotatory strength (R) can be calculated based on Rosenfeld's theory.[5] The optical rotatory strength due to electronic excitation from the lower state Ψ_0 to the upper state Ψ_e is described by quantum mechanical theory:

$$R = \mathrm{Im}\,\{\langle \Psi_0|\mu|\Psi_e\rangle\}\cdot\{\langle \Psi_e|\mathbf{m}|\Psi_0\rangle\}, \qquad (1)$$

where, Im is the imaginary part of the calculated numbers, Ψ_0; the wave function of state 0, Ψ_e; the wave function of state e, μ; the electric moment vector, and $\mathbf{m}$; the magnetic moment vector.

It is convenient to work with a dimensionless reduced rotational strength , [R], defined by

$$[R] = 100R/\mathrm{D}\mu_\mathrm{B} = 1.08 \times 10^{40}R, \qquad (2)$$

where D is the Debye unit and μ_B is the Bohr magneton.

The reduced rotational strength, [R], can be transformed to Eq. 3[6–7] by means of the LCAO MO approximation with applying the dipole velocity formalism.[8] In the simplest case, when we assume single-configuration wave functions for the ground and excited states, [R_{ij}] is expressed as shown in Eq. 3. In order to evaluate the electronic transitions more quantitatively, multi-configuration functions for the excited states are necessary:

$$[R_{ij}] = -7313/(E_j - E_i) \times \langle \varphi_i|\nabla|\varphi_j\rangle\cdot\langle \varphi_j|\mathbf{r}\times\nabla|\varphi_i\rangle. \qquad (3)$$

Here, [R_{ij}] is the reduced optical rotatory strength for the $i \rightarrow j$ transition in which an electron in the i-th molecular orbital (φ_i) is excited to the j-th molecular orbital (φ_j); $E_j - E_i$ is the excitation energy for $i \rightarrow j$ electron transition (eV); and ∇ is a gradient operator (Å)

The necessary data for calculating [R_{ij}] in Eq. 3 can be easily obtained by using various types of molecular-orbital calculations available in the laboratory. We have developed the program (RASCAL)[9] to calculate the necessary gradient integrals[10] appearing in Eq. 3 within the framework of the semi-empirical molecular-orbital calculations. Because we want to evaluate the optical rotatory strength of molecules which organic chemists usually handle in the laboratory in an acceptable cpu time with reasonable accuracy, our RASCAL program is coded to calculate the optical rotatory strength by using the molecular orbitals obtained by the PM3 method implemented in the MOPAC program.[11] In order to evaluate the optical rotatory strength expressed in Eq. 3 correctly, accurate excitation energies ($E_j - E_i$) were necessary as well as the relevant molecular orbitals (φ_i, φ_j). However, it is rather difficult to estimate the excitation energy ($E_j - E_i$) accurately by a PM3 molecular orbital calculation, even if CI (Configuration Interaction) is taken into account. Because it is well-known that the ZINDO[12] method is proper for estimating the excitation energy by taking into account the CI, we have adopted the excitation energy ($E_j - E_i$) calculated by the ZINDO molecular orbital calculation for the optimized geometry given by the PM3 method as the appropriate one that should be put in Eq. 3. Conformational analyses were carried out for **1E** with (+) helicity and **1C** having the (S)-configuration. The configuration with regard to the central double bond in the hexatriene unit including the indole ring (orientation of the carbonyl group against the indole ring), the stereochemistry around the single bond connecting the indole ring with the twisted butadiene unit, the orientation of the isopropyl group, and the helicity of the hexatriene unit, are specific geometrical points to be noticed in a conformational analysis. In order to obtain accurate geometries of the stable conformers, a conformational search and a geometry optimization were carried out by the PM3 molecular orbital calculation. Thus, the optical rotatory strength, obtained by putting the appropriate geometry and the relevant information on the molecular orbitals into Eq. 3, must be transformed to molar circular dichroism ($\Delta\varepsilon$), which is a standard physical property in the CD spectrum,

$$\Delta\varepsilon_\mathrm{max} = R \times \lambda_\mathrm{max} / (0.696 \times 10^{-42} \times 3300 \times \Delta\lambda \times \sqrt{\pi}), \qquad (4)$$

where λ_max is the wavelength of the absorption maximum, and $\Delta\lambda$ is the half-width of the absorption peak. The half-width ($\Delta\lambda$) of the each absorption peak was estimated to reproduce the peak shape of the experimentally observed UV-visible spectra, though the calculated wavelengths of the absorption maxima were moved toward a shorter-wavelength region by 50–100 nm.

The next step is to draw a CD spectrum from the obtained $\Delta\varepsilon_\mathrm{max}$, λ_max, and $\Delta\lambda$ data by assuming that the spectrum shape can be expressed approximately by a Gaussian-type function,

$$\Delta\varepsilon = \Delta\varepsilon_\mathrm{max} \times \exp\{-[(\lambda - \lambda_\mathrm{max})/\Delta\lambda]^2\}. \qquad (5)$$

Not only the circular dichroism ($\Delta\varepsilon$), but also the wavelength (λ_max) for the absorption is an essential physical property to evaluate the CD spectrum correctly. Within the framework of the semi-empirical molecular orbital calculations, it is recognized that evaluating the excitation energy ($E_j - E_i$) is most difficult. Therefore, a rather big wavelength shift (blue-shift) for each CD peak in the calculated CD spectrum, compared to the experimental peak, may be inevitable. In order to obtain a more accurate electronic transition energy, there are two sophisticated theoretical methods: the multi-reference configuration interaction method (MR[SD]-CI),[13] and the complete active space CI with second-order perturbative corrections(CASPT2).[14] However, these two theoretical methods are impractical to carry out for organic chemists regarding the actual computer time.

Results and Discussion

Conformational Analysis. Conformational analyses have been carried out by MOPAC PM3 calculations on **1E** with (+) helicity, **1C** with (*S*) configuration, and **2E**, the colorless open form of the binaphthyl-condensed indolylfulgide. The optimized structures, their relative conformational energies (ΔE), and the populations at 298 K are summarized in Fig. 1. The stereochemistry to be considered to specify each conformation uniquely is as follows (See Scheme 2):

1) The orientation of the nitrogen atom of the indole ring against the carbonyl group with respect to the central double bond ($C^9{=}C^{10}$) of the triene unit including the indole ring. (E: entgegen, Z: zusammen).

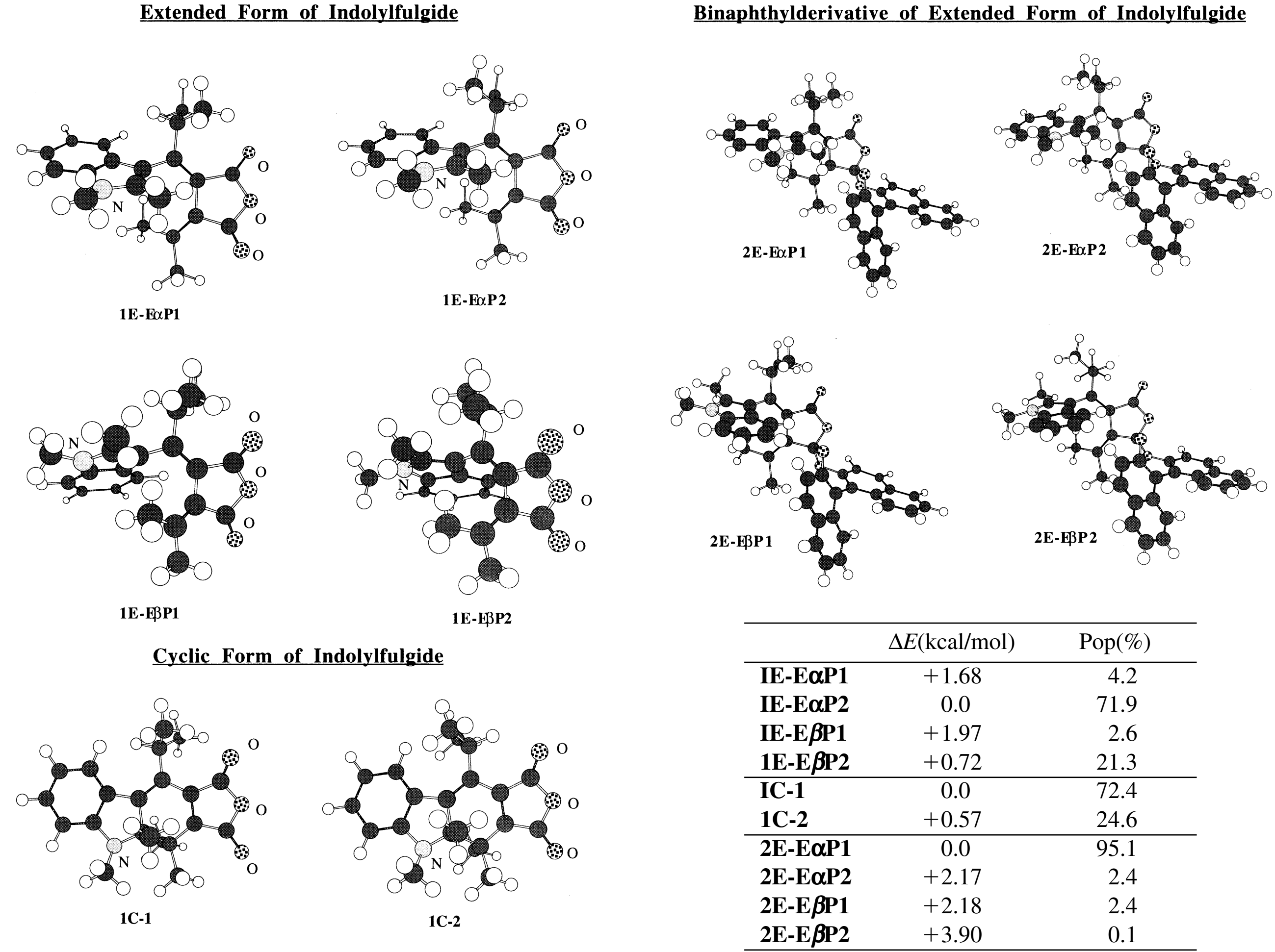
2) The stereochemistry around the single bond (C^3-C^9) connecting the indole ring and the twisted diene unit. (α: *s-cis* conformation, β: *s-trans* conformation).

3) Orientation of the methyl groups in the isopropyl group relative to the carbonyl group. (1: two methyl groups are located towards the carbonyl group; 2: two methyl groups extend to the opposite direction against carbonyl group).

4) Helicity of the hexatriene unit (C^2-C^3-C^9-C^{10}-C^{11}-C^{12}). (P: plus sign helicity, M: minus sign helicity).

In order to identify each conformation uniquely, the letters and numbers signifying the above stereochemistry were added to the index letters (**1E**, **1C**) of each compound, such as **1E-E*α*P2**. There are four conformers both for **1E** and **2E**, respectively. Only two stable conformations were found for **1C**. The most stable conformation of **1E** was **1E-E*α*P2**; its population was 72%. In the binaphthyl derivative **2E**, the conformer **2E-E*α*P1** existed dominantly (population: 95.1%) as a most stable one. The cyclization of the hexatriene unit in the E-forms of the indolylfulgides leads to a decrease in the freedom for the C–C bond rotation. Therefore, the cyclic form of the indolylfulgide **1C** showed only two stable conformations with regard to the orientation of the isopropyl group. The most stable conformation of **1C** was **1C-1**, where the two methyl groups on the isopropyl group sandwiched the carbonyl oxygen atom. The population of **1C-1** was 72.4%.

Evaluation of the CD Spectrum. On the basis of the optimized geometry and conformational energies of the conformers given in Fig. 1, the rotational strength (*R*) for each electronic transition was calculated according to Eq. 3. The assignment of each electron configuration, which gives rise to each absorption peak in the UV-visible spectrum, was rather complex. One excited state corresponding to the absorption


Extended Form of Indolylfulgide

Binaphthylderivative of Extended Form of Indolylfulgide

Cyclic Form of Indolylfulgide

	ΔE(kcal/mol)	Pop(%)
IE-EαP1	+1.68	4.2
IE-EαP2	0.0	71.9
IE-E*β*P1	+1.97	2.6
1E-E*β*P2	+0.72	21.3
IC-1	0.0	72.4
1C-2	+0.57	24.6
2E-EαP1	0.0	95.1
2E-EαP2	+2.17	2.4
2E-E*β*P1	+2.18	2.4
2E-E*β*P2	+3.90	0.1

Fig. 1. Structures and populations of the stable conformers of the indolylfulgides and their binaphthyl derivative determined by PM3 calculations.

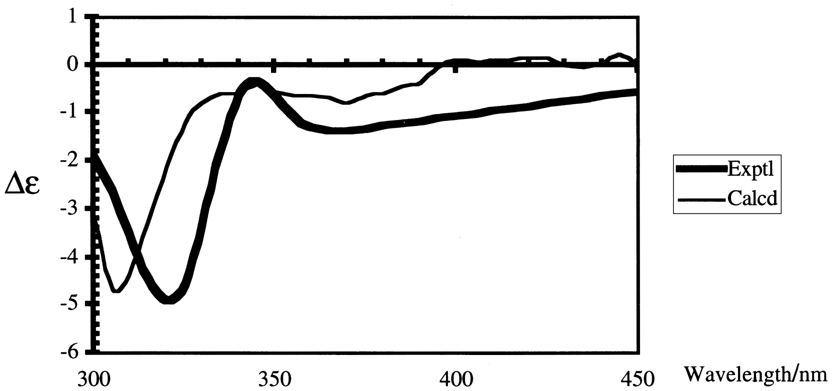
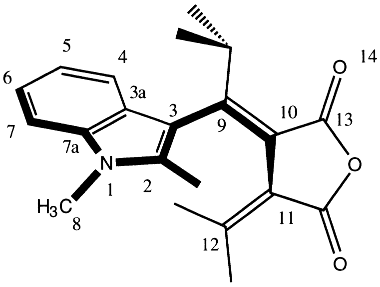
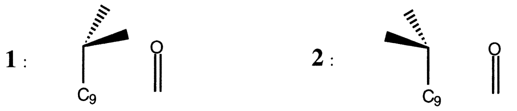


Fig. 2. Experimental and theoretically evaluated CD spectrum of the open form of the indolylfulgide (**1E**).



Scheme 2. Stereochemistry of Indolylfulgide.

1) Configuration with regard to the C_9–C_{10} double bond.
E: C(13)=O(14) carbonyl group is placed at Entgegen position against N(1) atom of the indole ring.
Z: Zusammen.
2) Streochemistry around the C_3–C_9 single bond.
α: C_2–C_3 bond takes *s-cis* conformation against C_9–C_{10} double bond. β: *s-trans* conformation.
3) Orientation of the isopropyl group connected at C_9 carbon.



4) Helicity of the triene unit (C_2–C_3–C_9–C_{10}–C_{11}–C_{12}).
P: plus sign helicity. **M**: minus sign helicity.

peak is expressed in terms of a linear combination of many excited electronic configuration functions. Therefore, the $\Delta\varepsilon_{\max}$ value at each absorption maximum wavelength ($\lambda_{\max}$) is the sum of the contributions for electron excitations between the ground state and many excited electronic configurations. With regard to the wavelength of the absorption peak, semi-empirical molecular orbital calculations (PM3, INDO, ZINDO) could only estimate an approximate number, even if the configuration interaction (CI) was taken into account. A shorter wavelength shift (at least 50 nm) was observed at these semi-empirical level molecular orbital calculations.

At first, we estimated the CD spectrum of **1E**. The experimental CD spectrum of **1E** is shown in Fig. 2 together with the calculated one. The noticeable CD spectrum peaks are those appearing at $\lambda = 385$ nm ($\Delta\varepsilon = -0.9$) and $\lambda = 325$ nm ($\Delta\varepsilon = -5$). It is important and essential whether the calculation could reproduce these two small and big negative Cotton effect peaks between 380 and 310 nm. ZINDO calculations have predicted that four absorption peaks may arise at 337.5, 328.0, 322.1, and 303.6 nm in the UV-visible spectrum for the most stable conformer, **1E-EαP2**. The relevant electron configurations for each absorption peak are summarized in Table 1. The numbers shown in the column of the configuration indicate the orbital numbers for the electron excitation between the occupied orbital and the unoccupied orbital. For the indolylfulgide, HOMO (Highest Occupied Molecular Orbital) corresponds to orbital No. 65, and LUMO (Lowest Unoccupied Molecular Orbital) corresponds to orbital No. 66. ZINDO calculations showed that the absorption peak at the longest wavelength (337.5 nm) consisted mainly (86%) of the HOMO → LUMO (65 → 66) electronic transition. However, other peaks appeared at shorter wavelengths comprising many electronic transitions, as shown in Table 1. For each electronic transition, the corresponding rotational strength (*R*) was calculated by using the RASCAL program according to Eq. 3. Next, the calculated rotatiory strength was weighted by a percentage of the contribution for this electronic transition; then, the weighted rotational strengths were summed up to give a calculated rotational strength at the absorption maximum. The same process as that stated above was repeated for all possible stable conformers to obtain a number of the rotational strength at the absorption maximum. The calculated rotatory strengths at the absorption maxima of the stable conformers of **1E** were compiled in Table 2. Finally, the population-weighted rotational strength ($R_{\max}$) at the absorption maximum was converted to $\Delta\varepsilon_{\max}$ by using Eq. 4, and the CD spectrum was drawn by assuming the Gaussian-type shape expressed by Eq. 5. Though the numbers of estimated wavelengths for the CD spectrum peaks were smaller by about 20 nm than the experimental ones, the two characteristic negative Cotton effect peaks (small one at 360 nm and large one at 305 nm) could be reproduced by theoretical calculations.

Next, the cyclic form of the indolylfulgide **1C** was tested for a theoretical evaluation of the CD spectrum. The specific structural feature unique to the two stable conformers of **1C** is the orientation of the isopropyl group against the carbonyl group. Though the experimental UV-visible spectrum of **1C** showed a rather strong absorption maximum at the visible region around 550 nm, no strong CD spectrum peak was ob-

Table 1. The Corresponding Configurations to Give Rise the Rotatory Strengths for the Most Stable Conformer (**1E-Eαp2**) of the Extended Form of the Indolylfulgide

Wavelength	Configuration	Contribution of the configuration	Calculated rotatory strength	Summed up rotatitory strength
nm		%	esu × 10^{-40}	esu × 10^{-40}
337.5	65 → 66	86.3	−29.37	−25.42
	65 → 68	3.0	−2.22	
328.0	59 → 66	12.3	7.62	0.15
	59 → 70	6.0	3.28	
	59 → 71	4.4	−12.73	
	60 → 66	3.6	22.27	
	60 → 67	3.7	−4.8	
	60 → 70	2.6	−4.79	
	61 → 66	2.6	−58.86	
	61 → 67	31.3	−5.49	
	61 → 68	10.7	−5.39	
322.1	59 → 67	28.3	1.69	−13.30
	59 → 68	5.7	−3.61	
	59 → 71	3.7	−12.74	
	59 → 72	2.5	23.28	
	61 → 66	21.3	−58.86	
	61 → 67	6.1	−5.49	
	61 → 70	6.7	1.11	
	61 → 71	8.5	0.63	
303.6	62 → 69	3.7	−5.99	−3.28
	63 → 68	2.6	19.52	
	64 → 66	3.8	−2.34	
	64 → 67	9.5	−15.02	
	64 → 68	32.8	−3.68	
	65 → 69	37.9	−2.22	

Table 2. The Calculated Rotatory Strengths of the Stable Conformers of the Extended Form of the Indolylfulgide (**1E**)

1E-EαP1	Pop: 4.2%	**1E-EαP2**	Pop: 71.9%	**1E-EβP1**	Pop: 2.6%	**1E-EβP1**	Pop: 21.3%
Wave length	Rotatory strength	Wave length	Rotatory strength	Wave length	Rotatory strength	Wave length	Rotatory strength
nm	esu × 10^{-40}	nm	esu × 10^{-40}	nm	esu × 10^{-40}	nm	esu × 10^{-40}
341.3	−27.76	337.5	−25.42	341.7	1.89	337.6	1.89
326.0	0.75	328.0	0.21	324.7	−2.55	324.7	−2.55
320.5	−11.84	322.1	−13.30	318.8	15.22	318.8	15.22
303.1	−5.37	303.6	−3.28	304.6	−1.98	304.6	−1.98

served in this visible region. Smaller magnitude Cotton effect peaks than those of **1E** were observed at 380, 300 (negative Cotton effect), and 330 (positive Cotton effect) nm in the experimental CD spectrum. The decrease of the $\Delta\varepsilon$ values in the CD spectrum of **1C** seems to be due to a structural change from the twisted hexatriene unit structure **1E** to the planar cyclohexadiene of **1C** by cyclization. We can check the usefulness of this theoretical approach to evaluate the CD spectrum by investigating the following two aspects. One is whether the smaller magnitude of $\Delta\varepsilon$ in **1C** than that of **1E** can be reproduced; the other is whether unique shape changes (negative → positive → negative Cotton effect peaks observed downward from the longer wavelength region) of the CD spectrum can also be reproduced.

ZINDO calculations predicted that the absorption maximum for the longest wavelength peak (corresponding mainly to the HOMO → LUMO electronic transition) may appear at around 440 nm for two stable conformers, **1C-1** and **1C-2**. The estimated wavelength numbers were smaller by about 100 nm than that of the experimental one ($\lambda_{\max}$ = 550 nm). However, this electronic transition did not contribute much to the CD spectrum shape around this wavelength region because the half-width of the absorption peak was rather big, and therefore, the magnitude of the CD spectrum peak ($\Delta\varepsilon_{\max}$) became smaller, according to Eq. 4. The important absorption peaks giving substantial CD spectrum peaks were those predicted to appear

Table 3. The Corresponding Configurations to Give Rise the Rotatory Strengths for the Most Stable Conformer (**1C-1**) of the Cyclic Form of the Indolylfulgide

Wavelength	Configuration	Contribution of the configuration	Rotatory strength for each transition	Summed up rotatory strength
nm		%	esu × 10^{-40}	esu × 10^{-40}
439.3	65 → 66	93.5	−5.02	−5.02
367.7	59 → 69	11.9	−0.44	2.33
	60 → 66	14.8	0.19	
	62 → 66	48.0	2.36	
	62 → 67	5.0	0.23	
343.0	59 → 66	36.7	−5.71	−5.73
	59 → 67	7.1	0.01	
	60 → 66	6.5	0.30	
	61 → 66	8.7	0.08	
	62 → 69	17.1	0.27	
312.4	63 → 68	5.0	0.19	2.70
	64 → 66	2.22	−2.83	
	64 → 67	11.4	0.04	
	65 → 67	35.6	4.56	
	65 → 68	15.4	0.74	
284.6	64 → 66	15.0	−1.92	5.92
	64 → 67	8.7	0.03	
	65 → 67	55.2	7.07	
	65 → 68	15.2	0.73	
270.6	63 → 66	5.7	0.86	−3.40
	64 → 66	46.2	−5.89	
	65 → 68	27.2	1.32	
	65 → 70	5.9	0.31	

Table 4. The Calculated Rotatory Strengths of the Stable Conformers of the Cyclic Form of the Indolylfulgide (**1C**)

1C-1	Pop: 72.4%	**1C-2**	Pop: 24.6%
Wave length	Rotatory strength	Wave length	Rotatory strength
nm	esu × 10^{-40}	nm	esu × 10^{-40}
439.3	−5.02	446.2	0.35
367.7	2.33	369.1	3.44
343.0	−5.74	345.2	−7.81
312.4	2.70	314.4	4.96
284.6	5.92	288.4	10.19
270.6	−3.40	270.9	−4.67

at 343.0, 312.4, 284.6, and 270.6 nm by calculations. The relevant electron configurations for each absorption peak of the most stable conformer **1C-1** are summerized in Table 3. The calculated rotatory strengths at the absorption maxima of the conformers of **1C** are given in Table 4. The calculated CD spectrum of **1C** was obtained by summing up the contributions of these rotatory strengths due to the electronic transitions. The calculated spectrum shown in Fig. 3 could almost reproduce the essential CD spectrum shape (alternate CD peaks change), though the numbers of the wavelength for the CD peaks were predicted to be shorter by about 40 nm. From this calculation result, we can say that this theoretical approach at the semi-empirical level can evaluate a subtle chiroptical property (CD spectrum) well for the chiral molecules in which there are no strong CD active chromophores, such as asymmetrically oriented aromatic rings and twisted π-units. In molecule **1C**, there are no twisted π-electrons chromophores, and the structural unit which can give rise to CD peaks is only one chiral sp^3 carbon atom. Therefore, σ-electrons are responsible for giving rise to CD peaks.

It is interesting to check whether our theoretical approach can evaluate the CD spectrum of the binaphthyl derivative **2E** more precisely or less precisely than those of the indolylfulgides, **1E** and **1C**. Because **2E** has many large chro-

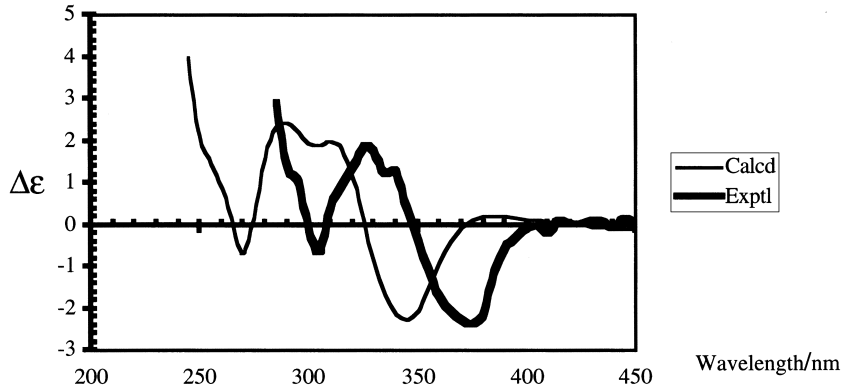


Fig. 3. Experimental and theoretically evaluated CD spectrum of the cyclic form of the indolylfulgide (**1C**).

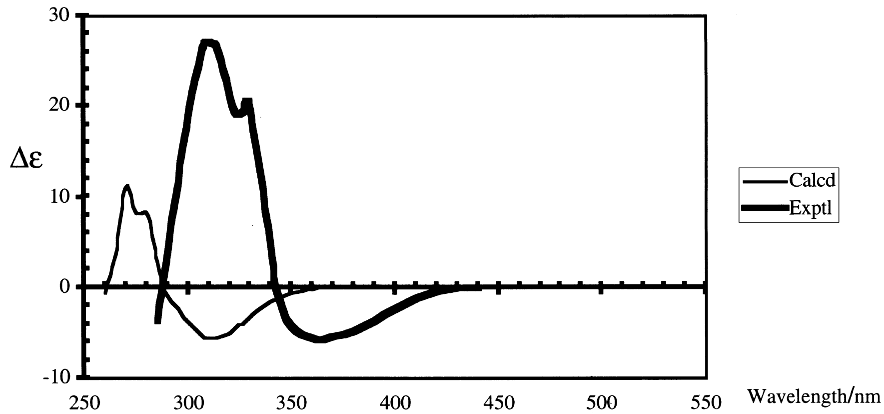


Fig. 4. Experimental and theoretically evaluated CD spectrum of the binaphthyl derivative of the open form of the indolylfulgide (**2E**).

mophores (aromatic rings), the experimental CD spectrum showed a stronger Cotton effect by about tenfold ($\Delta\varepsilon$ varies from -10 to 30) than those of **1E** and **1C**. We first thought that it is rather easier to reproduce these larger Cotton-effect changes of **2E** in the CD spectrum than to reproduce the subtle changes of the $\Delta\varepsilon$ values found in **1E** and **1C**. However, the result was completely opposite (Fig 4). It was very difficult to reproduce the big positive Cotton-effect peaks appeared at 310 and 330 nm in the experimental CD spectrum. The position of the absorption maximum peak at the longest wavelength ($\lambda_{\max}$ = 365 nm) could be estimated fairy well by ZINDO calculations ($\lambda_{\max}$ = 319 nm). This absorption peak, which arose mainly from electronic transitions due to the HOMO(114) → LUMO(115) and next HOMO → next LUMO, contributed to the negative Cotton-effect peak around the 365 nm in the experimental CD spectrum. The calculated CD spectrum could predict this negative Cotton-effect peak fairly well with regard to the shape and magnitude, though the position of the absorption peak shifted toward a shorter wavelength by about 50 nm. However, the positive-Cotton effect peak which appeared around 310–330 nm in the experimental spectrum could not be reproduced well by this theoretical method. Not only the location of the CD spectrum peak, but also the magnitude of the CD peak, was not evaluated well by theory. This poor performance may come from a difficulty to evaluate the electronic state of the **2E** molecule comprising the several distorted π-electron chromophores by semi-empirical molecular orbital calculations. The electronic transitions, which were predicted to appear at the region around 270–280 nm in the ZINDO calculations, did not give the large positive sign rotatory strength shown in the experimental CD spectrum from the calculation.

In conclusion, the valence electron self-consistent (SCF)/configuration interaction (CI)/dipole velocity (DV) method (**SCF/CI/DV**) based on Rosenfeld's theory could be used to evaluate the theoretical CD spectra of the indolylfulgide derivatives fairly well within the framework of the semi-empirical molecular orbital calculations, though the positions of the absorption maxima of the CD peaks were predicted to occur at a shorter wavelength by about 50 nm. The CD spectrum shape could be approximately reproduced with actual computer time. In order to evaluate the CD spectrum well, it is essential to have not only accurate structures and conformational energies of stable conformers, but also to evaluate well the electronic states and electronic transitions relevant to the CD spectra.

Calculations

The optical rotatory strength (R) was calculated with the RASCAL program developed by our group on the SUN SPARC station IPC. Conformational analyses on the fulgide molecules with PM3 semi-empirical molecular orbital calculations were carried out by using the MOPAC program (UNIX version, WinMOPAC version, SONY Cache version). Electronic transitions were evaluated by the ZINDO program implemented in the Cache program.

Experimental

CD spectra were measured on a JASCO J-725 circular dichroic spectrophotometer. UV-vis spectra were recorded by a JASCO V-550 UV-vis spectrophotometer. An analysis of the enantiomer ratio was carried out using a Shimadzu LC-6A high-pressure liquid chromatograph equipped with a Daicel OD-H column. The eluting solvent system was hexane/2-propanol = 90/10 (v/v).

Synthesis and photoreaction of **1E**, **1C**, **2E**, and **2C**, and X-ray crystallographic analysis to determine the absolute configuration of the major diastereomer of **2C** have been described elsewhere.[2] A determination of the absolute configuration of **1C** was done as follows.

To a 7 mL THF solution of **2C** (11.3 mg, 0.0187 mmol) at room temperature was added 0.11 mL of conc. aq HCl (12 mol dm^{-3}); the resulting solution was refluxed for 1.5 h in the dark. To the reaction mixture was added at room temperature sat. aq $NaHCO_3$ and ether, and the organic layer was separated. The aqueous layer was extracted with ether twice, and all of the organic portions were combined and washed with satd. aq NaCl. After drying the organic layer with anhydrous Na_2SO_4, the solvent was evaporated in vacuo. The thus-obtained resulting organic material was purified by silica-gel flash column chromatography to give **1C** (4.0 mg, 0.0119 mmol) in 64% yield, together with (*R*)-1,1′-binaphthyl-2,2′-diol (3.1 mg, 0.0108 mmol, 58%).

A portion of the thus obtained **1C** was dissolved in a small amount of hexane containig 5% (v/v) ethyl acetate, and the solution was irradiated with visible light (> 660 nm) to change **1C** to **1E**. The enantiomer ratio of **1E** was determined by HPLC. The faster moving enantiomer and slower moving enantiomer of **1E** on Daicel OD-H column was 79.7/20.3. Since the starting **2C** had the *S* configuration at the quaternary stereogenic carbon atom, the major enantiomer of **1C** also had the *S* configuration for the carbon atom. Therefore, the faster- moving enantiomer of **1E**, apparently generated from major **1C**, possesses (+) helicity with regard to the hexatriene moiety.

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