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Absolute Conformation and Chiroptical Properties. VII. 9(1′)-*Msc* and *Psc* Forms of 9-(2-Fluoro-1,1-dimethylethyl)- and 9-(1,1-Dimethylpropyl)-11,12-bis(methoxycarbonyl)-9,10-dihydro-9,10-ethenoanthracenes[1]

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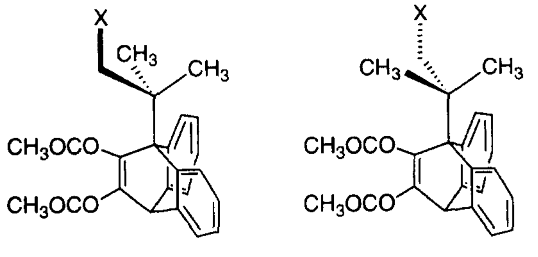
The racemic forms of *sc*-9-(2-fluoro-1,1-dimethylethyl)- and 9-(3-iodo-1,1-dimethylpropyl)-11,12-bis(methoxycarbonyl)-9,10-dihydro-9,10-ethenoanthracene were prepared by treatment of the corresponding carboxylic acid with xenon difluoride and by reduction of 9-(1,1-dimethyl-3-oxopropyl) compound followed by a reaction with iodine in the presence of imidazole, respectively. The fluoro and the iodo compounds were resolved on a chiral column. The absolute conformations of these compounds were determined by deriving them by the same methods from the carboxylic acid and the aldehyde of known absolute conformations. Reduction of the iodo compound with Raney nickel in 1-propanol afforded optically active *sc*-9-(1,1-dimethylpropyl) compound. In the CD spectrum, the *Psc*-(−) fluoro compound showed a broad and large trough at ca. 240 nm, similarly with the other halogen compounds, and a stronger Cotton effect at ca. 220 nm than the other halogen compounds. The *Psc*-(+)-9-(1,1-dimethylpropyl) compound showed a quite different CD spectrum from those of other halogen compounds. Thus the importance of the halogen, though remote from any chromophore, in determining the CD spectra of the title compounds and analogous ones was confirmed.

In a previous paper,[2] we reported that the CD spectra of 9(1′)-*Psc*-9-(2-halo-1,1-dimethylethyl)-11,12-bis(methoxycarbonyl)-9,10-dihydro-9,10-ethenoanthracenes (*Psc*-**1**) showed very similar troughs in their CD spectra at ca. 240 nm, while the amplitude of the Cotton effect observed at ca. 220 nm was dependent on the halogen, the intensity becoming weaker as one goes from a chloro, to a bromo, and then to an iodo substituent (Scheme 1). In this context, it will be interesting to see the results of the two extremes, where the substituent in the 9-substituent is either a fluoro or a methyl. The fluoro substituent can be considered spherically symmetrical and the methyl substituent is of three-fold symmetry in the local environment. Thus these substituents should not affect the chiroptical properties by rotation about the C–C–(X) bond where the X is either a fluoro or a methyl group, as was the case for other halogen compounds.[2] We wish to report the syntheses of those compounds together with their CD spectra in this paper.



Psc-**1** *Msc*-**1**

X = Cl, Br, or I

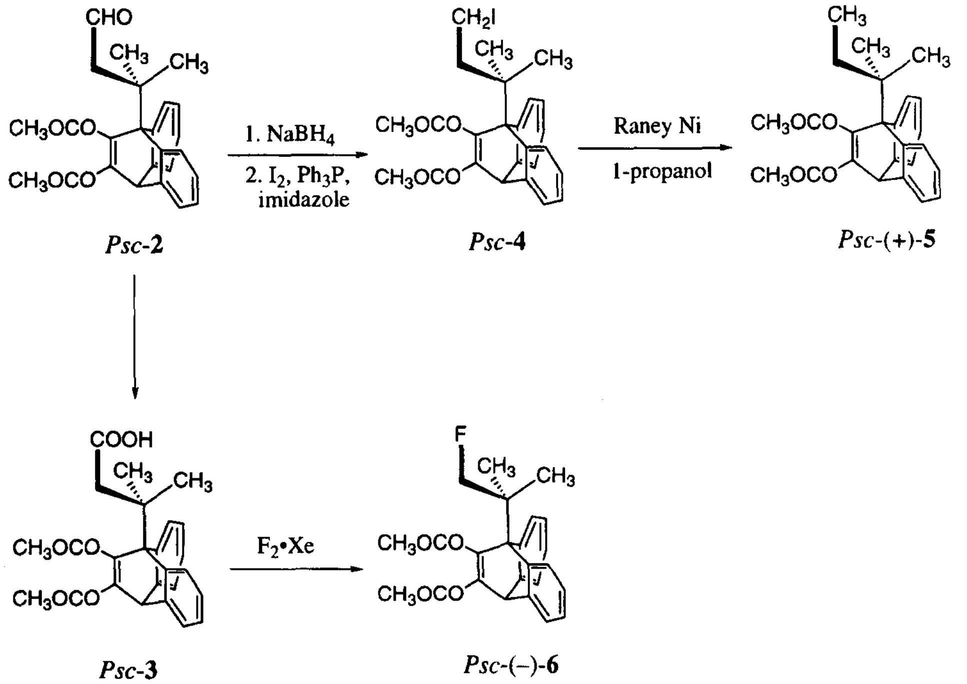
Scheme 1.

Results and Discussion

The synthesis of the fluoro compound (*sc*-**6**) was accomplished by treating the corresponding carboxylic acid (*sc*-**3**) with xenon difluoride (Scheme 2). Although synthesis of a fluoro compound was reported by treating a carboxylic acid with a positive fluorine compound,[3] such was not applicable to this case. Other positive fluoro compounds did not give satisfactory results either. The original method of fluorodecarboxylation of carboxylic acids, using xenon difluoride and hydrogen fluoride,[4] was not successful, whereas the use of xenon difluoride only[5] gave satisfactory results.

The use of 1 mol of xenon difluoride for 1 mol of the carboxylic acid, as reported in the paper,[5] gave *sc*-**6** in a very poor yield, whereas the use of 2 mol of xenon difluoride for 1 mol of *sc*-**3** gave satisfactory yields of *sc*-**6**. The original authors postulate that the mechanisms of the fluorodecarboxylation involve the first formation of xenon fluoride carboxylate, which undergoes intramolecular ionic fluorodecarboxylation in the case of primary carboxylic acids. If this is applicable to the present case, due to the neopentyl-type carboxylic acid, the ionic reaction within the molecule (or ion pair) may be very slow and the second mole of xenon difluoride is required for the formation of **3**. Further study is required for the role of the second mole of xenon difluoride.

The 1,1-dimethylpropyl compound (*sc*-**5**) was synthesized by reduction of the corresponding aldehyde (*sc*-**2**)



Scheme 2. Synthetic routes from *sc*-**2** to *sc*-**5** and *sc*-**6**. Transformations of *Psc* series only are shown.

with sodium tetrahydroborate, replacement of the hydroxy group with iodine by treating the alcohol with the iodine-triphenylphosphine-imidazole system,[6] and then reduction of the resulted iodide (*sc*-**4**) (Scheme 2). The last step posed some difficulties because the compound possessed methoxycarbonyl groups that might be affected by various reducing reagents. We avoided the usage of metal hydrides for this reason and explored radical type reductions. Although tributyltin hydride[7] and samarium(II) iodide[8] failed to give the reduced compound in practical yields, we were finally able to obtain the desired compound (*sc*-**5**) in satisfactory yields by treating the iodide *sc*-**4** with Raney nickel in 1-propanol.

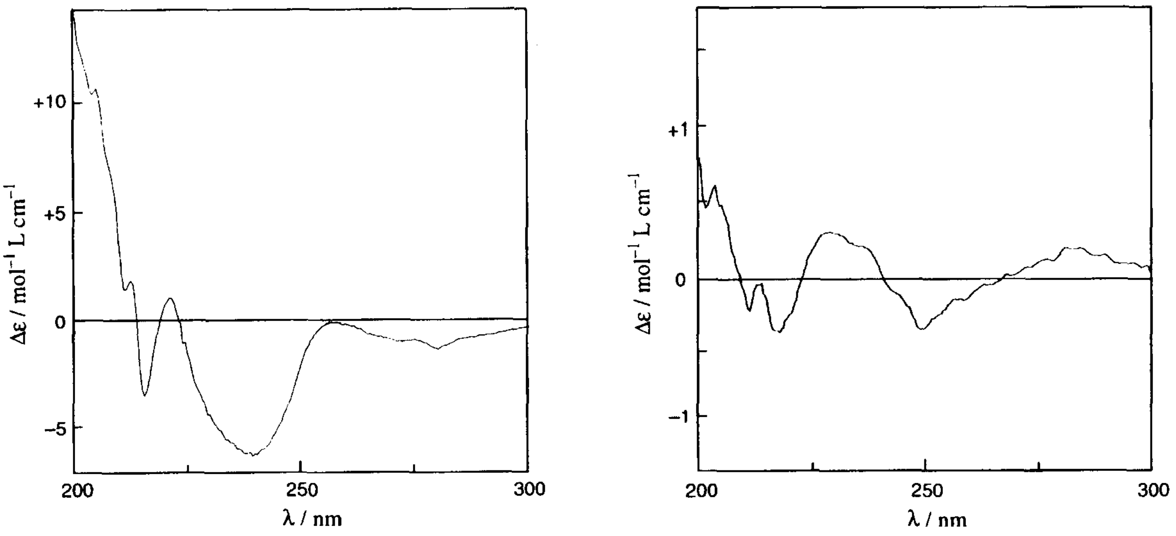
Optical resolution of racemic *sc*-**5** was accomplished at the stage of the iodo compound, *sc*-**4**, through chromatography on a CHIRALPAC AD[9] column. Optical resolution of *sc*-**6** was also possible by chromatography on the same column.

The optically active compounds of known absolute conformations were prepared from the corresponding aldehyde (*sc*-**2**) which was resolved on the CHIRALPACK AD column, as was reported previously.[2] And the title compounds were derived by the method described above. Because it is not very easy to obtain enough quantity of the compounds for characterization and measurements of chiroptical properties, the absolute conformations were determined by comparing the retention time of one of the enantiomers derived from racemic *sc*-**4** with that of *Psc*-**4** on the chiral column. The results were also confirmed by superposition of the chromatographic peak on an analytical column with the same stationary phase, when *Psc*-**4** and one of the enantiomers which exhibited the similar retention time to that of *Psc*-**4** were injected in one batch. In the case of the fluoro compound (*sc*-**6**), its absolute conformation was determined similarly with the case of *Psc*-**4**. *Psc*-**6** of known absolute conformation was derived from the *Psc*-aldehyde **2** via the carboxylic acid (*Psc*-**3**).

The CD spectra of the *Psc* forms of these compounds are shown in Fig. 1. The peaks and troughs in the CD spectra are compiled in Table 1 together with those of *Psc*-9-(2-halo-1,1-dimethylethyl)-11,12-bis(methoxycarbonyl)-9,10-dihydro-9,10-ethenoanthracene (*Psc*-**1**), where the halogen is a chloro, a bromo, or an iodo.

There is one problem to be cleared up for compound *Psc*-**6** before claiming that the conformation is unique or a mixture of two or three components: If the conformation is a mixture, it might affect the CD spectrum. Due to the steric effects of the halogen (Cl, Br, and I), which are much larger than those of hydrogen, it is possible to assume that the halogen takes the position which is upright to the equator of the ethenoanthracene skeleton, as is shown in Scheme 1.[2] However, the van der Waals radius of fluorine is small. It can be argued that the rotation about the $C(CH_2)$–C(*tert*) bond in the 9-substituent takes place, rendering the F-inside conformations possible.

In order to get information on this matter, we examined ^1H NMR spectra of *sc*-**6** at low temperatures. They clearly showed line-broadening at low temperatures, though analyses of these lineshapes were difficult due to their complex natures. We turned then to ^{19}F NMR spectra at low temperatures, which clearly showed the presence of two conformers. The populations of the conformers were ca. 17 : 83 at 150 K. The population of the minor isomer increased as the temperature was raised (Table 3 in Appendix). Applying the van't Hoff's equation, we obtain $\Delta H^\circ = 0.79$ kcal mol^{-1} and $\Delta S^\circ = 2.2$ cal mol^{-1} K^{-1}, as described in the Appendix. From these values, the compound is almost a 1 : 1 mixture of conformers at 300 K, at which temperature the CD spectra were measured. The extrapolation of the results to room temperature may include large errors, but the results still indicate that the population of another isomer is substantial, because



(a) (b)

Fig. 1. CD spectra: (a) *Psc*-(−)-**6**, (b) *Psc*-(+)-**5**.

Table 1. Peaks and Troughs in CD Spectra of *Psc* Forms of Compounds **1**, **5**, and **6** ($\Delta\varepsilon$'s are shown in parentheses)

Compound	Trough/nm	Peak/nm	Trough/nm	Peak/nm	Trough/nm	Peak/nm
Psc-**6**	215 (−3.48)	221 (1.03)	239 (−6.28)	257 (−0.16)	280 (−1.38)	
Psc-**1** (X = Cl)[a]	216 (−2.63)	219 (1.71)	241 (−8.31)	258 (−0.05)	280 (−0.17)	
Psc-**1** (X = Br)[a]	215 (−2.35)	220 (1.41)	240 (−8.24)	257 (−0.05)	279 (−0.17)	
Psc-**1** (X = I)[a]	216 (−1.04)	220 (−0.26)	241 (−7.55)	258 (0.00)	279 (−0.17)	
Psc-**5**	213 (−0.18)	215 (−0.03)	218 (−0.35)	229 (0.34)	249 (−0.34)	280 (0.22)

a) Taken from Ref. 2.

it definitely increases as the temperature is raised in the temperature range examined. Thus we must postpone drawing any conclusions on the effect of the fluoro substituent until the effects of the second conformer on CD spectra become known.

All the halogen compounds show very similar CD spectra in general: They all show a large trough centered at ca. 240 nm with similar intensities and a Cotton effect at ca. 220 nm with different intensities. However, this may be fortuitous, if one considers the presence of a large amount of another conformer in compound *sc*-**6**. Or else the second conformer may have a similar CD spectrum and/or its effects on the CD spectrum are very small.

By contrast, the 1,1-dimethylpropyl compound (*Psc*-**5**) shows a quite different CD spectrum from those of the halogen derivatives. Incidentally, the methyl compound (*sc*-**5**) showed similar UV absorptions with other halogen compounds. This is again evidence that the halogens remote from the chromophore influence the CD spectra. It also shows that the trough at ca. 240 nm is affected by the substituent. The fading away of the differential absorptions of the polarized light when similar substituents are placed at a stereogenic element is understandable as an analogy of the phenomenon that few or no significant specific rotations for the sodium D line are found with chiral centers that carry very similar substituents.[10]

Table 3. Temperature Dependence of Equilibrium Constants between Two Rotamers in *sc*-**6**

Temp/K	147	150	157	165
K[a]	0.20	0.21	0.23	0.27

a) For the process *ap*→ −*sc*.

Specific rotations of *sc*-**5** and *sc*-**6** are compiled together with other halogen compounds in Table 2. There is a tendency in the halogen compounds, though the tendency may have to be discussed with reservation, because of the presence of another conformer in compound *sc*-**6**: The specific

Table 2. Specific Rotations of Compounds *sc*-**1** (X = Cl, Br, and I), *sc*-**5**, and *sc*-**6**[a]

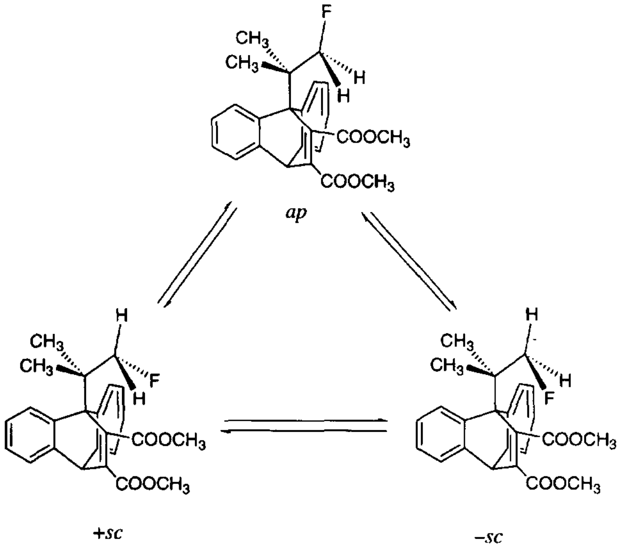
Compound	**6**		**1** (X = Cl)[b]		**1** (X = Br)[b]		**1** (X = I)[b]		**5**	
Form	*Psc*	*Msc*	*Psc*	*Msc*	*Psc*	*Msc*	*Psc*	*Msc*	*Psc*	*Msc*
$[\alpha]_D$	−21.3°	+22.2°	−9.7°	+9.7°	+0.3°	−0.8°	+13.2°	−13.2°	+10.4°	−10.5°

a) For conditions of measurements, see Experimental. b) Taken from Ref. 2.

rotation of the halogen compounds of the *Psc* conformation starts from a negative value at the smallest halogen: The negative value decreases in its amount and becomes positive as we descend the periodic table. Here again, compound *Psc*-**5** is different from other halogen compounds, while the specific rotation of this compound is surprisingly large.

Appendix

When ^{19}F NMR spectra were observed at low temperatures, two signals were observed at $\delta = -228$ and -225. From the intensities of these signals, equilibrium constants were obtained, as shown in Table 3. From the data in Table 3, we obtain $\Delta H^\circ = 0.79$ kcal mol^{-1} and $\Delta S^\circ = 2.2$ cal mol^{-1} K^{-1}. The free energy difference at 300 K, simply calculated from these values, amounts to 0.13 kcal mol^{-1}. That means that the two conformers exist in almost the same populations. We assign the more stable rotamer at low temperatures to the *ap* form, which is the upright conformation of the C–F bond (*ap* in Scheme 3) to the equator of the ethenoanthracene skeleton, because that must be more stable than the F-inside conformation (+*sc* and −*sc*) if one considers the steric effects of the groups concerned.



Scheme 3. Three Rotamers of *Psc*-**6**.

It is interesting to note that we observe only two signals in ^{19}F NMR spectra. Because three conformations are expected, as shown in Scheme 3, discussion of the observation is necessary. One of the possibilities is that the barrier separating the +*sc* and −*sc* rotamers is too low for the NMR observation of them. The other is that one of the two rotamers does not exist because of instability.

In order to obtain help, we carried out MM2 calculations of these conformers and the transition structures. The results are shown in Fig. 2. The calculation supports our assignment that the most stable conformation is the *ap* form. However, the energies of +*sc* and −*sc* conformers are only different by ca. 0.5 kcal mol^{-1}. In addition, the barrier separating the +*sc* and −*sc* forms is very low, amounting to only ca 1.5 kcal mol^{-1}. The calculation suggests that the first possibility is the case, that is, the rotational barrier is too low for observation of the two *sc* isomers.

However, we must also admit that the errors involved in the calculation is large, especially for the barrier heights. This is typified by the barrier height separating the *ap* form from the *sc*. The calculated value is ca. 3.8 kcal mol^{-1} or at the maximum 4.5 kcal mol^{-1}, while the observed value is ca. 8 kcal mol^{-1}. Our conclusion is, therefore, that further study is necessary for drawing a definite conclusion, although it is likely that the low barrier to exchange between the two conformers, +*sc* and −*sc*, is responsible to the observed phenomenon, as the MM2 calculation indicates.

Experimental

^{1}H NMR spectra were measured on a Varian Gemini 300 spectrometer, which operated at 300.1 MHz unless otherwise noted. UV spectra and CD spectra were recorded on a Hitachi U-2000 spectrometer and on a JASCO J-720 spectrometer, which was installed at Okayama University. Optical rotation was measured on a JASCO DIP-370 polarimeter with the use of a 3.5 mmϕ × 100 mm cell. For the chiral column, a Hitachi L-6250 pump was used. Melting points are not corrected.

***sc*-9-(3-Iodo-1,1-dimethylpropyl)-11,12-bis(methoxycarbonyl)-9,10-dihydro-9,10-ethenoanthracene (*sc*-4).** To a solution of 202 mg (0.500 mmol) of the formyl compound (*sc*-**2**)^2 in 3 mL of methanol was added 19 mg (0.50 mmol) of sodium borohydride in portions at 0 °C and the mixture was stirred at that temperature for additional 1 h. Then, the mixture was poured into saturated aqueous

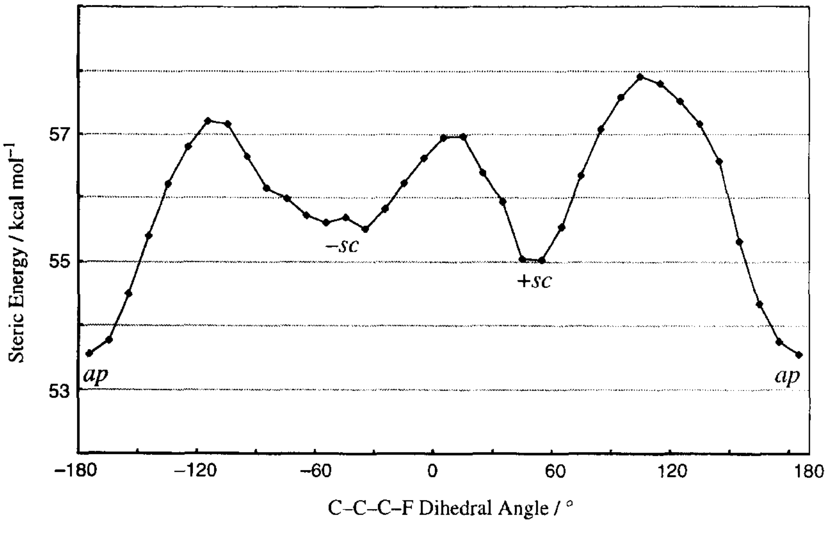


Fig. 2. Steric energies and conformation of *Psc*-**6** (MM2 force-field).

sodium chloride and extracted with ether. The ether layer was dried over anhydrous magnesium sulfate and evaporated to afford a white solid, the crude yield being 95%. This compound was directly used for the next reaction. The following ^{1}H NMR ($CDCl_3$) data were collected: δ = 1.31 (1H, t, J = 5.4 Hz), 1.82 (3H, s), 1.95 (3H, s), 2.40 and 2.77 (2H, AB of ABX_2, J_{AB} = 13.9, J_{AX} = 6.4, and J_{BX} = 7.3 Hz), 3.71 (3H, s), 3.77 (3H, s), 3.95—4.10 (2H, br s), 5.52 (1H, s), 6.95—7.07 (4H, m), 7.33—7.43 (2H, m), 7.70—7.82 (2H, m).

A solution of 804 mg (1.98 mmol) of the hydroxy compound, 1.30 g (4.95 mmol) of triphenylphosphine, 337 mg (4.95 mmol) of imidazole, and 1.01 g (3.96 mmol) of iodine in 20 mL of toluene was heated under reflux for 20 min and cooled. To the mixture was added 5 mL of saturated aqueous sodium hydrogencarbonate, and the mixture was stirred for 5 min. A solution of 500 mg of sodium thiosulfate in 2 mL of water was added and the mixture was extracted with toluene. The extract was dried and the solvent removed in vacuo to yield a white solid in 85% yield.

Racemic *sc*-4: Recrystallized from ethanol, mp 185.0—185.5 °C. Found: C, 57.88; H, 4.77%. Calcd for $C_{25}H_{25}IO_4$: C, 58.15; H, 4.88%. ^{1}H NMR ($CDCl_3$): δ = 1.81 (3H, s), 1.89 (3H, s), 2.72 and 3.09 (2H, AB of ABX_2, J_{AB} = 12.9, J_{AX} = 4.7, J_{BX} = 3.1 Hz), 3.39—3.45 (2H, m), 3.75 (3H, s), 3.77 (3H, s), 5.52 (1H, s), 6.96—7.07 (4H, m), 7.33—7.42 (2H, m), 7.60—7.72 (2H, m).

Preparative HPLC for resolution of the racemic iodo compound was carried out under the following conditions: CHIRALPAC AD (1.0 cm$\phi \times$25 cm), ethanol eluent, 1.4 mL min^{-1} flow rate, 4 mg sample in 1.8 mL 2-propanol for one batch. The retention times were 21.3 and 32.5 min for *Msc* and *Psc* forms, respectively. For determination of absolute conformations, these compounds were submitted to analytical HPLC with the same chiral stationary phase under the following conditions: CHIRALPAC AD (0.45 mm$\phi \times$25 cm), ethanol eluent, 0.4 mL min^{-1} flow rate, 19 kg cm^{-2} pressure. Under these conditions, retention times of *Msc* and *Psc* forms were 14.9 and 23.6 min, respectively, whereas the same compound with the known absolute conformation derived from the aldehyde[2] exhibited the retention time of 14.8 min. The HPLC of a mixture of *Psc*-**4** with the resolved isomer of *sc*-**4**, which exhibited the retention time of 14.9 min, exhibited a single sharp peak on the chiral column at retention time 14.9 min.

***Msc*-4:** Recrystallized from hexane, mp 84—115 °C (decompn.). Found: C, 58.05; H, 4.89%. Calcd for $C_{25}H_{25}IO_4$: C, 58.15; H, 4.88%. $[\alpha]_D^{25}$ − 15.3° (c 0.99, $CHCl_3$). The ^{1}H NMR spectrum was identical with that of the racemic mixture.

***Psc*-4:** Recrystallized from hexane, mp 83—115 °C (decompn.). Found: C, 58.59; H, 5.18%. Calcd for $C_{25}H_{25}IO_4$: C, 58.15; H, 4.88%. $[\alpha]_D^{25}$ + 16.1° (c 0.99, $CHCl_3$). The ^{1}H NMR spectrum was identical with that of the racemic mixture.

***sc*-9-(1,1-Dimethylpropyl)-11,12-bis(methoxycarbonyl)-9,10-dihydro-9,10-ethenoanthracene (*sc*-5).** The foregoing iodo compound (50.0 mg or 96.8 μmol) in 10 mL of 1-propanol was mixed with ca. 700 mg of Raney nickel W2[11] and the mixture was refluxed for 1 h. After cooling, the Raney nickel was removed by filtration and the filtrate evaporated in vacuo. The residue was submitted to preparative TLC with 4 : 1 hexane-ethyl acetate eluent to afford the desired compound in a pure form. The yield was 59%. Both *Msc* and *Psc* forms were prepared in the same way and the yields were ca. 70%.

***sc*-5 (Racemic Form):** Recrystallized from hexane, mp 131.5—133.0 °C. Found: C, 76.59; H, 6.54%. Calcd for $C_{25}H_{26}O_4$: C, 76.90; H, 6.71%. ^{1}H NMR ($CDCl_3$): δ = 1.14 (3H, t, J = 7.2 Hz), 1.77 (3H, s), 1.84 (3H, s), 2.04 and 2.48 (2H, AB of ABX_3, J_{AB} = 14.0 Hz, J_{AX} = 7.0, J_{BX} = 7.2 Hz), 3.70 (3H, s), 3.76 (3H, s), 5.51 (1H, s), 6.93—7.04 (4H, m), 7.31—7.40 (2H, m), 7.63—7.70 (1H, m), 7.70—7.78 (1H, m).

***Msc*-5:** Recrystallized from hexane, mp 140.5—141.5 °C. Found: C, 76.57; H, 6.60%. Calcd for $C_{25}H_{26}O_4$: C, 76.90; H, 6.71%. $[\alpha]_D^{29}$ − 10.5° (c 1.56, $CHCl_3$). This compound exhibited an identical ^{1}H NMR spectrum with the racemic form.

***Psc*-5:** Recrystallized from hexane, mp 140.0—141.0 °C. Found: C, 76.81; H, 6.60%. Calcd for $C_{25}H_{26}O_4$: C, 76.90; H, 6.71%. $[\alpha]_D^{29}$ + 10.4° (c 1.49, $CHCl_3$). ^{1}H NMR was identical with that of *Msc*.

***sc*-9-(2-Fluoro-1,1-dimethylethyl)-11,12-bis(methoxycarbonyl)-9,10-dihydro-9,10-ethenoanthracene (*sc*-6).** To a solution of 109 mg (0.259 mmol) of *sc*-9-(2-carboxy-1,1-dimethylethyl)-11,12-bis(methoxycarbonyl)-9,10-dihydro-9,10-ethenoanthracene (*sc*-**3**) in 10 mL of dichloromethane, was added 87.7 mg (0.518 mmol) of xenon difluoride and the mixture was stirred at room temperature for 22 h. The solvent was evaporated and the residue was purified by preparative TLC. The pure sample was obtained by recrystallization from hexane-dichloromethane. The yield was 61 mg (60%).

Racemic *sc*-6: Mp 250.0—252.5 °C. Found: C, 72.88 ; H, 5.95%. Calcd for $C_{24}H_{23}FO_4$: C, 73.08; H, 5.88%. ^{1}H NMR ($CDCl_3$) δ = 1.84 (3H, d, J = 2.6 Hz), 1.99 (3H, d, J = 2.8 Hz), 3.73 (3H, s), 3.77 (3H, s), 5.00 and 5.28 (2H, AB of ABX, J_{AB} = 9.5, J_{AX} = 46.9, J_{BX} = 47.4 Hz), 5.53 (1H, s), 6.99—7.04 (4H, m), 7.26—7.41 (2H, m), 7.65—7.79 (2H, m).

The racemic mixture was separated by HPLC on a CHIRALPAK AD column under the following conditions: eluent 1 : 1 hexane–2-propanol, flow rate 1.5 mL min^{-1}, pressure 17 kg cm^{-2}. The retention times for *Psc*-**6** and *Msc*-**6** were 19.9 and 36.8 min, respectively.

***Psc*-6:** Recrystallized from hexane, mp 149.5—150.0 °C. Found: C, 73.15; H, 5.95%. Calcd for $C_{24}H_{23}FO_4$: C, 73.08; H, 5.88%. $[\alpha]_D^{25}$ − 21.3° (c 1.01, $CHCl_3$). The ^{1}H NMR spectrum of this compound was identical with that of racemic *sc*-**6**.

***Msc*-6:** Recrystallized from hexane, mp 149.0—149.5 °C. Found: C, 72.98; H, 5.92%. Calcd for $C_{24}H_{23}FO_4$: C,73.08 ; H, 5.88%. $[\alpha]_D^{25}$ + 22.2° (c 1.00, $CHCl_3$). The ^{1}H NMR spectrum of this compound was identical with that of racemic *sc*-**6**.

CD Spectra. These were recorded with methanol solutions of 1.00×10^{-5} and 1.00×10^{-3} mol L^{-1} concentrations for *Psc*-**6** and *Psc*-**5**, respectively. A cell of 0.2 mm was used for *Psc*-**6** and that of 1.0 mm for *Psc*-**5** in the wavelength region of 200—300 nm. The spectra were recorded four times; the integrated spectra are shown in Fig. 1. The peaks and troughs are given in Table 1.

UV Absorption Spectra. These were recorded with a methanol solution of 1.0×10^{-5} mol L^{-1} concentrations for both *sc*-**6** and *sc*-**5**. A cell of 1.0 cm in length was used. The spectrum of *sc*-**6** with peaks (log ε in parentheses) at 215 (4.48) and 279 (3.29) nm and a shoulder at ca. 240 nm was very similar to those of other halogen compounds [peaks at 218 (4.65) and 279 (3.18) nm with a shoulder at ca. 240 nm].[2] Compound *sc*-**5** showed absorption peaks at 217 (3.42) and 279 (2.56) nm. However, the spectra were different in details at various wavelengths.

Low-Temperature NMR Spectra. ^{19}F NMR spectra at low temperatures were recorded on a Bruker AMX R-400 spectrometer which operated at 376 MHz. Temperatures were calibrated with the methanol signals. A solution of 12.3 mg of compound *sc*-**6** in 0.60 mL of dichloromethane-d_2 was used for the measurement. Two signals, at δ = −228 and −225 for *ap* and *sc* conformers respectively, were observed at low temperatures. The populations of the rotamers are shown in Table 3.

MM Calculations. The molecular mechanics calculations of *Psc*-**6** were performed by the Chem3D Plus program with a PowerMac computer. The MM2 force field parameters were used without modification, although quantities of some parameters were not high. At first, structural optimizations were carried out for several possible conformations about the methoxycarbonyl groups. The structure at the global minimum was consistent with the X-ray structure of *Msc*-**1** (X = Br) reported in the previous paper,[2] and was used as the initial structure for the calculations, of which results are shown in Fig. 2. The structure was optimized every time as the initial C_9–C–C–F dihedral angle is changed. The dihedral angle was changed from -180 to $+180°$ with $10°$ intervals by the use of the dihedral drive option.

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