Absolute Stereochemistry of Dimethyl 9-(1,1-Dimethyl-2-phenylethyl)-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate Rotamers

Shinji TOYOTA, Hideki YAMANE, and Michinori ŌKI*
Department of Chemistry, Faculty of Science, Okayama University of Science, Ridaicho, Okayama 700
(Received July 3, 1992)

Absolute stereochemistry of the title compounds is determined through X-ray analysis of the 11-(−)-menthyl ester of the corresponding 11-carboxylic acid and its CD spectra are reported. Features of the molecular structure are discussed and revival of a term "absolute conformation" is proposed.

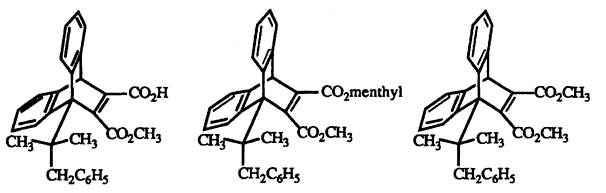
Although a variety of rotational isomers is now isolated at room temperature,[1] examples of optical resolution of those rotational isomers are few.[2—4] Nothing about absolute stereochemistry of rotational isomers has been known (Chart 1).

We had reported resolution of ±*sc*-9-(1,1-dimethyl-2-phenylethyl)-12-methoxycarbonyl-9,10-dihydro-9,10-ethenoanthracene-11-carboxylic acid (**1**) via its (−)-menthyl ester (**2**).[2] We found that crystals of the easily crystallizing menthyl ester (**2**), suitable for X-ray analysis, could be obtained. That finding prompted us to investigate the absolute stereochemistry of the compound.

The syntheses and optical resolution of compound **1** were already reported.[2] However, the reported yield of the menthyl ester (**2**) from **1** was not satisfactory. We used a reaction of lithium (−)-menthyloxide with the acid chloride for the esterification to improve the yield. Hydrolysis of the menthyl ester was carried out as reported and chiroptical properties were determined for the methyl ester (**3**). The enantiomer of compound **1**, to that which was isolated with use of (−)-menthol, was separated in the same way utilizing the (+)-menthyl ester (**2**).

Atomic coordinates, bond lengths, bond angles, and nonbonding interatomic distances of special interests are shown in Tables 1, 2, 3, and 4, respectively. Torsion and dihedral angles of interests are shown in Table 5. An ORTEP drawing together with numberings of atoms is given in Fig. 1, in which the (−)-menthyloxy group is taken to be in conformity with the known stereochemistry of (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexanol.[5,6]

Absolute Stereochemistry and Chiroptical Properties of Dimethyl Ester 3. It is clear, from



1 2 3

Chart 1. Only −*sc* forms are shown.

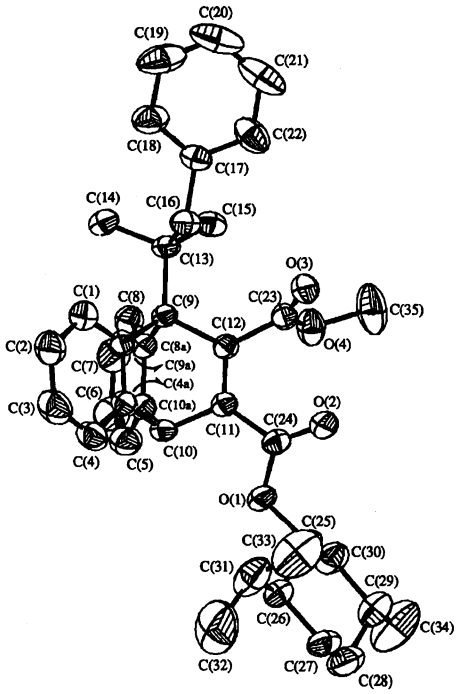


Fig. 1. ORTEP drawing of *Msc*-**2** with thermal ellipsoids at 50% probability (hydrogen atoms are omitted for simplicity).

Fig. 1, that the menthyl ester contains the acid residue (**1**) which has −*sc* or *Msc* conformation about the C(9)–C(13) bond. Its high barrier to rotation about the C(9)-to-C(13) bond assures that we can safely obtain *Msc*-9-(1,1-dimethyl-2-phenylethyl)-12-methoxycarbonyl-9,10-dihydro-9,10-ethenoanthracene-11-carboxylic acid (**1**) by hydrolysis. The series of conversions confirms that the (−)-menthyl ester (**2**), the carboxylic acid (**1**) and the dimethyl ester (**3**) that show $[\alpha]_D^{23}$ of −74.4, −30.2, and −30.4° in chloroform, respectively, belong to the *M* stereochemistry series. Conversely, the (+)-menthyl ester (**2**), the carboxylic acid (**1**), and the dimethyl ester (**3**) that show $[\alpha]_D^{23}$ of +74.4, +30.4, and +30.5° in chloroform, respectively, possess *P* absolute stereochemistry.

CD spectra of *Psc*- and *Msc*-**3** together with their UV absorption spectra are shown in Fig. 2. Complex CD curves as well as UV absorptions are observed, although it is noticed that the CD peaks well correspond

Table 1. Atomic Coordinates and Equivalent Isotropic Thermal Parameters in Compound **2** [a]

Atom	x	y	z	B_{eq} [b]
O(1)	0.7803(2)	0.1325(1)	0.7145(2)	4.07(4)
O(2)	0.6010(2)	0.0873(1)	0.5813(2)	4.39(5)
O(3)	0.4243(2)	0.1466(1)	0.2870(2)	4.05(4)
O(4)	0.4100(2)	0.2018(1)	0.5106(2)	4.43(5)
C(1)	0.7862(2)	0.3043(2)	0.1273(3)	3.78(6)
C(2)	0.9089(2)	0.2882(2)	0.1017(3)	4.72(7)
C(3)	0.9966(2)	0.2587(2)	0.2148(3)	5.02(8)
C(4)	0.9640(2)	0.2467(2)	0.3578(3)	4.04(6)
C(4a)	0.8422(2)	0.2643(2)	0.3846(2)	3.03(5)
C(5)	0.7869(3)	0.3745(2)	0.7020(3)	4.15(6)
C(6)	0.7261(3)	0.4415(2)	0.7271(3)	4.88(8)
C(7)	0.6280(3)	0.4665(2)	0.6210(3)	4.45(7)
C(8)	0.5889(2)	0.4266(2)	0.4880(3)	4.58(6)
C(8a)	0.6481(2)	0.3589(2)	0.4610(2)	2.88(5)
C(9)	0.6171(2)	0.3036(2)	0.3226(2)	2.62(4)
C(9a)	0.7495(2)	0.2913(2)	0.2685(2)	2.86(5)
C(10)	0.7983(2)	0.2571(2)	0.5366(2)	2.94(4)
C(10a)	0.7461(2)	0.3334(2)	0.5724(2)	3.07(5)
C(11)	0.6849(2)	0.2050(2)	0.5127(2)	2.86(5)
C(12)	0.5903(2)	0.2284(1)	0.4061(2)	2.69(4)
C(13)	0.5086(2)	0.3298(2)	0.1926(2)	2.96(5)
C(14)	0.5416(3)	0.4078(2)	0.1298(3)	3.75(6)
C(15)	0.3811(2)	0.3369(2)	0.2548(3)	3.57(6)
C(16)	0.4919(2)	0.2706(2)	0.0597(2)	3.42(6)
C(17)	0.3785(2)	0.2840(2)	−0.0620(2)	3.47(5)
C(18)	0.3878(3)	0.3296(2)	−0.1873(3)	4.68(7)
C(19)	0.2791(5)	0.3438(2)	−0.2950(4)	6.5(1)
C(20)	0.1655(4)	0.3115(3)	−0.2796(5)	7.0(1)
C(21)	0.1574(3)	0.2634(3)	−0.1614(5)	6.8(1)
C(22)	0.2628(2)	0.2490(2)	−0.0540(3)	5.06(8)
C(23)	0.4665(2)	0.1870(2)	0.3894(3)	3.07(5)
C(24)	0.6799(2)	0.1351(2)	0.6041(2)	3.08(5)
C(25)	0.7941(2)	0.0676(2)	0.8184(3)	3.54(6)
C(26)	0.9341(2)	0.0478(2)	0.8485(3)	4.02(6)
C(27)	0.9531(3)	−0.0142(2)	0.9680(3)	4.52(7)
C(28)	0.9071(3)	0.0100(2)	1.1133(3)	5.04(8)
C(29)	0.7666(3)	0.0298(2)	1.0852(3)	4.72(8)
C(30)	0.7429(3)	0.0899(2)	0.9613(3)	4.60(7)
C(31)	0.9873(4)	0.0281(2)	0.6971(4)	6.4(1)
C(32)	1.1316(5)	0.0190(4)	0.7290(9)	10.8(2)
C(33)	0.9255(6)	−0.0401(3)	0.6133(5)	8.6(2)
C(34)	0.7205(6)	0.0567(3)	1.2310(5)	8.9(2)
C(35)	0.2988(4)	0.1584(3)	0.5237(7)	7.1(1)

a) Values in parentheses are estimated standard deviations. b) $B_{eq}/Å^2=(8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Table 2. Selected Bond Distances in Compound **2**

Atom–Atom	Distance/Å
C(8a)–C(9)	1.568(3)
C(9)–C(9a)	1.572(3)
C(9)–C(12)	1.574(3)
C(9)–C(13)	1.577(3)
C(4a)–C(10)	1.496(3)
C(10)–C(10a)	1.518(4)
C(10)–C(11)	1.514(3)
C(11)–C(12)	1.342(3)
C(12)–C(23)	1.500(3)
C(11)–C(24)	1.487(4)
C(13)–C(14)	1.554(4)
C(13)–C(15)	1.546(3)
C(13)–C(16)	1.570(3)

Table 3. Selected Bond Angles in Compound **2**

Atom–Atom–Atom	Angle/°
C(8a)–C(9)–C(9a)	103.4(2)
C(8a)–C(9)–C(12)	101.2(2)
C(8a)–C(9)–C(13)	115.7(2)
C(9a)–C(9)–C(12)	105.0(2)
C(9a)–C(9)–C(13)	114.4(2)
C(12)–C(9)–C(13)	115.4(2)
C(4a)–C(10)–C(10a)	106.6(2)
C(4a)–C(10)–C(11)	106.0(2)
C(10a)–C(10)–C(11)	105.4(2)
C(10)–C(11)–C(12)	114.2(2)
C(10)–C(11)–C(24)	121.8(2)
C(12)–C(11)–C(24)	124.0(2)
C(9)–C(12)–C(11)	115.2(2)
C(9)–C(12)–C(23)	126.0(2)
C(11)–C(12)–C(23)	118.4(2)

Table 4. Selected Nonbonding Distances in Compound **2**

Atom–Atom	Distance/Å
O(2)–O(3)	3.164(3)
O(2)–O(4)	2.881(3)
O(3)–C(15)	3.417(3)
O(3)–C(16)	3.140(3)
C(1)–C(14)	3.194(4)
C(1)–C(16)	3.165(3)
C(8)–C(14)	3.159(3)
C(8)–C(15)	3.220(3)

to the UV absorptions. Apparently, π–π^* transitions of the benzene rings with possible participation of the α,β-unsaturated carbonyl moieties contribute to the CD spectra. Their theoretical analysis is awaited.

Structure of the Menthyl Ester 2. Bond lengths and bond angles are normal except those discussed below and benzene rings and the olefinic part, C(11) and C(12), are planar.

Table 2 shows that abnormal bond lengths are found in the C(9) region. Bonds connecting C(9) to the benzene rings and the olefinic moiety are all longer than a normal C_{sp^2}–C_{sp^3} bond and the C(9)–C(13) bond as well as the C(13)–C(16) is long with respect to normal C_{sp^3}–C_{sp^3} bonds, although the lengthening of the latter bonds is less important. This type of lengthening is observed in 9-substitued triptycenes[7] and is interpreted as that it is necessary to avoid severe steric congestion. It is interesting that the similar structure is observed in this compound which lacks one of the benzene rings of triptycenes. The methoxycarbonyl group at the 12-position seems to play important roles in this feature. The long bond of C(13)–C(16) is not well understood at the present time but it may well be to avoid steric effects

Table 5. Selected Torsion Angles in Compound **2**

Atom–Atom–Atom–Atom	Angle/°
C(12)–C(9)–C(13)–C(16)	−64.3
C(9)–C(13)–C(16)–O(17)	172.1
C(11)–C(12)–C(23)–O(3)	−108.6
C(11)–C(12)–C(23)–C(4)	−70.7
C(12)–C(23)–O(1)–C(25)	−171.6
C(12)–C(11)–C(24)–O(2)	10.2
C(12)–C(11)–C(24)–O(1)	−171.5
C(11)–C(24)–O(1)–C(25)	−179.9
C(13)–C(16)–C(17)–C(22)	−93.5
C(13)–C(16)–C(17)–C(18)	88.5

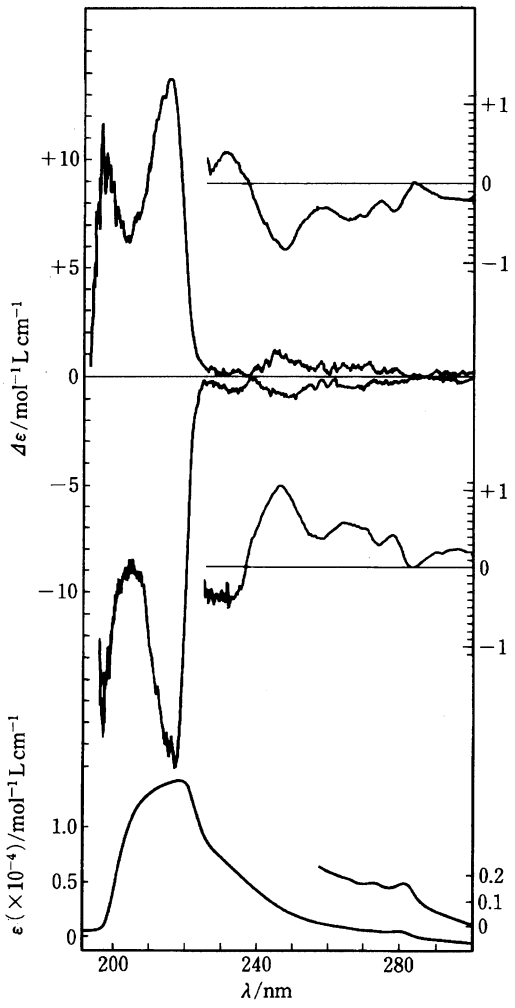


Fig. 2. CD and UV spectra of compound **3**. Top: CD spectrum of *Psc*-**3**. Middle: CD spectrum of *Msc*-**3**. Bottom: UV spectrum of racemic **3**.

again, because as discussed later the carbonyl oxygen of the 12-methoxycarbonyl group is in proximity of C(16).

Table 3 shows that bond angles around C(9) are also abnormal. Apex angles of C(9) which is the top of a pyramid with bases of C(8a), C(9a), and C(12) are all smaller than normal tetrahedral angles and, to compensate these small angles, the angles outside of the ethenodihydroanthracene skeleton involving C(9) are all larger than the normal. These values may be compared with those in dialkyl 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylates.[8—10] The comparison indicates that the internal angles of the skeleton at C-9 in compound **2** are significantly smaller than those in compounds which lack the 9-substituent. This sharpening of the internal angles is again attributed to the steric congestion in this region and is observed in triptycenes as well. Bond angles involving the carbons in the olefinic moiety are also unusual. The angle C(9)–C(12)–C(23) is large as an sp^2-hybridized carbon at the expense of C(9)–C(12)–C(11) and C(11)–C(12)–C(23) angles. This is undoubtedly caused by the steric effects of the 9-substituent. Similarly, the angle C(12)–C(11)–C(24) is large, though to a less extent, at the expense of the angle C(10)–C(11)–C(12). This means that the menthyl ester group is giving a buttressing effect to the methoxycarbonyl group but the former is also bent away from the latter, thus saving the steric strain due to the 9-substituent.

Table 4 shows that the nonbonding distance between C(16) and O(3) is very small. Steric effects of the neighboring (−)-menthyloxycarbonyl group as well as those of the 9-substituent prevent the 12-methoxycarbonyl group from being coplanar with the olefinic moiety. It is possible that the electron-rich O(3) is more favored to be in the vicinity of the C–H group due to weak charge-transfer interactions.[11] The unusually small distance between O(4) and O(2) may be interpreted in the same way because O(2) is electron-deficient and O(4) electron-rich. The methyl groups and the methylene in the 9-substituent are at about 3.2 Å distance from the peri carbon of the ethenodihydroanthracene skeleton. These distances are commonly observed in 9-*tert*-alkyltriptycene compounds.[12]

It is seen in Table 5 that the ester moiety at the position 11 is close to a planar position with the olefinic bond, whereas the 12-ester group is strongly rotated from the plane, though the effect is not observed for C(olefin)–C(carbonyl) bond lengths. The reason for this conformation is not well understood because two similar planar groups tend to take similar rotation angles if they are attached to a planner moiety and yet coplanarity is prohibited by the steric effect,[13] and, indeed, those are the cases in structures of dialkyl 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylates.[8—10] It is possible that rotation of the menthyloxycarbonyl plane causes more steric interference with a benzene ring than that of the methoxycarbonyl because of the bulkiness of the menthyl group. The plane of the phenyl group in the substituent at the 9-position is almost perpendicular to the C–C bond which connects it to the tertiary carbon of the substituent and is almost upright to the ethenodihydroanthracene skeleton. This conformation must be the most stable because the phenyl can avoid interaction with the ethnoanthracene skeleton and the methyl groups, C(14) and C(15), in this conformation.

As is seen in Table 6, the dihederal angles made by two benzene rings and the etheno bridge are rather normal to indicate that the 9-substituent exerts almost the same steric effects to the three groups. This is reasonable because the methyl and the methylene groups are of about the same size. However, close examination discloses that the dihedral angle made by Benzene 2 and the olefin planes is small and that between Benzene 1 and the olefin is large. It seems that the phenyl group in the 9-substituent, though remote, exerts some influence to the structure of the ethenodihydroanthracene.

Stereochemical Terminology and Nomenclature. A term "absolute configuration" was invoked by Bijvoet[14] when he determined absolute stereochemistry of optically active tartaric acid through X-ray excitation of a specific atom and this term is used by Cahn–Ingold–Prelog rules[15] and IUPAC tentative rules of stereochemical nomenclature.[16] The latter two use the same term even for absolute stereochemistry of biphenyls and ansa compounds, though implicit.

Since the chiral structure in rotational isomers is due to rotation about a single bond, it is appropriate to consider the case as an example of axial chirality. Then the IUPAC rule as well as the Cahn–Ingold–Prelog rule recommends the use of *P* and *M* to designate the absolute stereochemistry.

Recent extensive studies of molecular dynamics by NMR spectroscopy[17] demand the rethinking in general concept of configuration and conformation, however. The general tendency implies that configuration refers to the relative position or order of arrangement of atoms in space which characterizes a particular stereoisomer,[18] whereas conformation is a portion of configuration that can be interchanged by rotation of bonds or by inversion about an atom. By this definition, "absolute configuration" of optically active biphenyls, ansa compounds, and the rotational isomers as are reported in this paper will be less informative, although the term is implicitly used in the Cahn–Ingold–Prelog paper and in the IUPAC rule. On this basis, we propose a term "absolute conformation".[19]

Although a term "absolute conformation" was proposed earlier for interpretation of CD spectra,[20,21] it has not received general acceptance, especially because of the newer definition of configuration.[18] However, what we are interested in is the matter of conformation itself and it will be appropriate to revive the term for discussion of absolute stereochemistry of rotational isomers.

It will be more informative to add specific conformation after *P* or *M* in the case of ethane or propene derivatives to designate absolute conformations, like *Psc* or *Msc*. In biphenyls and ansa compounds, the conformation is often unknown, although it is possible, for example, for a biphenyl to take two diastereomeric conformations (**4a** and **4b**) in a given absolute stereochemistry of *P* or *M* (Chart 2). In these cases, *P* or *M* may be used without specifying the conformation. Thus mere presentation of absolute stereochemistry by *P* or *M* should be taken as that the conformation is unknown or it is a mixture of conformation.

We believe that this designation of absolute stereochemistry is useful, when we consider enantiomers of twisted olefins. They are often *Pap* and *Map* pairs (or *PE* and *ME*) as well as *Psp* and *Msp* (or *PZ* and *MZ*) pairs.

When we designate absolute conformation in a molecule, it is necessary to give a locant. We may use the locants used in the nomenclature of olefins if the bond in question is involved in the main chain, e. g. *Msc*-2-butane. If the bond in question is that which connects a mother nucleus and a substituent, as is the present case, we may use the locant of the substituent with a prime. Then the compound in question is named as dimethyl [*Msc*-9(1′)]- or [*Psc*-9(1′)]-9-(1,1-dimethyl-2-phenylethyl)-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate. We can name in a similar way, even though rotation about a single bond is prohibited at more than one bond.

We have extensively used the symbols, for example $\pm sc$, in our works on conformations.[22] We should like to retain these symbols because they are convenient in discussion on stereochemistry, when absolute conformation is unknown yet it is necessary to discuss by distinguishing the two enantiomeric isomers or by distinguishing a $+sc$ or $-sc$ conformation from an *ap* or *sp* conformation in ethane derivatives. It is also true that the usage of $+sc$ or $-sc$ in discussing conformations relatively to those, that are present in a molecule including an *ap* conformation, is convenient. In a traditional way, it may be possible to use P^* and M^* but it is not our choice because P^*sc, for example, should be used when absolute conformation is known yet we are treating a racemic mixture.

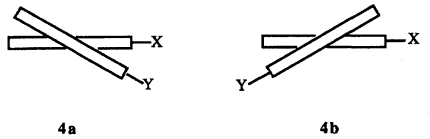
Table 6. Dihedral Angles

Plane-Plane	Angle/°
Benzene 1 - Benzene 2	121.1
Benzene 1 - Olefin	122.6
Benzene 2 - Olefin	116.1

Benzene 1: C(1)–C(2)–C(3)–C(4)–C(4a)–C(9a), Benzene 2: C(5)–C(6)–C(7)–C(8)–C(8a)–C(10a), Olefin: C(11)–C-(12)–C(9)–C(10).

Experimental

^{1}H NMR spectra were measured on a JEOL GSX-400 or



4a **4b**

Chart 2.

a Varian Gemini-300 spectrometer operating at 400 and 300 MHz, respectively. Optical rotation was measured on a JASCO DIP-370 polarimeter. Elemental analyses were performed by a Perkin-Elmer 240C analyzer.

UV spectra were recorded with a Hitachi U-2000 spectrophotometer on the racemic mixuture of **2**. Spectra were recorded as hexane solutions with concentrations of 5.1×10^{-4} mol L^{-1} for the region of 255—300 nm and 5.0×10^{-5} mol L^{-1} for the whole region between 200—300 nm. The cell length was 1.0 cm. The following absorption maxima were recorded (wavelength/nm with log ε in parentheses are give): 217.8 (4.2), 271.0 (3.2), 279.4 (3.2).

CD spectra were measured with a JASCO J-600 spectropolarimeter. The spectra were measured for methanol solutions with concentration of ca. 2×10^{-4} mol L^{-1} and the cell lengths were 0.2 and 1.0 mm. The following maxima and minima were recorded (wavelengths with $\Delta\varepsilon$ in parentheses are given).

Msc-**3**: 203 (−8.7), 215 (−18.2), 231 (−0.35), 246 (1.03), 256 (0.40), 265 (0.59), 274 (0.29), 278 (0.44), 283 (0.02), 296 (0.25).

Psc-**3**: 203 (6.3), 215 (14.0), 231 (0.42), 246 (−0.84), 256 (−0.29), 265 (−0.46), 274 (−0.22), 278 (0.42), 283 (−0.00), 296 (−0.20).

(−)-Menthyl [*Msc*-9(1′)]-9-(1,1-Dimethyl-2-phenylethyl)-12-methoxycarbonyl-9,10-dilhydro-9,10-ethenoanthracene-11-carboxlate (*Msc*-2). To a solution of 210 mg (1.33 mmol) of (−)-menthol in 6 mL of anhydrous tetrahydrofuran, was added 0.60 mL (0.97 mmol) of a 15% solution of butyllithium in hexane under a nitrogen atmosphere. To this solution, was gradually added 404 mg (0.885 mmol) of the acid chloride in 5 mL of tetrahydrofuran, which was prepared from 419 mg (0.956 mmol) of the acid (**1**)[2] and 0.45 mL (5.2 mmol) of oxalyl dichloride in 27mL of dry benzene. The mixture was stirred for 2.5 h at room temperature and then heated under reflux for 3 h. The mixture was poured into water, neutralized, and then extracted with ether. The ether extracts were dried over magnesium sulfate and the solvent was evaporated. The residue was submitted to silica-gel chromatography (1 : 1 hexane–dichloromethane eluent). A diastereomeric mixture of the menthyl esters was obtained in 72% overall yield from the carboxylic acid. The product was purified by crystallization from hexane, mp 195—196°C (lit, 199—200°C).[2] $[\alpha]_D^{23}$ −74.4° (c=0.853, $CHCl_3$) (lit, −77.0° c=5.7 in $CHCl_3$ at 25°C).[2] ^{1}H NMR ($CDCl_3$) δ=0.74 (3H, d, J=6.9 Hz), 0.89 (3H, d, J=7.2 Hz), 0.91 (3H, d, J=7.2 Hz), 0.80—1.16 (3H, m), 1.40—1.56 (2H, m), 1.64—2.16 (4H, m) 1.83 (3H, s), 1.87 (3H, s), 3.44 and 3.79 (2H, ABq, J=13.7 Hz), 3.75 (3H, s), 4.78 (1H, dt, J=4.3 and 10.9 Hz), 5.57 (1H, s), 6.96—7.13 (4H, m), 7.25—7.48 (7H, m), 7.74 (1H, m), 7.95 (1H, d, J=7.4 Hz).

[*Msc*-9(1′)]-9-(1,1-Dimethyl-2-phenylethyl)-12-methoxycarbonyl-9,10-dihydro-9,10-ethenoanthracene-11-carboxylic Acid (*Msc*-1). Mp 185.5—187.0°C, $[\alpha]_D^{23}$ −30.2 (c=0.812, $CHCl_3$) was obtained from the (−)-menthyl ester by the published method[2] with the use of ethanolic potassium hydroxide. Reported mp and $[\alpha]_D$ are 188—190°C (decomp) and −24.6 at 32°C ($CHCl_3$, c=2.4), respectively. ^{1}H NMR ($CDCl_3$) δ=1.84 (3H, s), 1.85 (3H, s), 3.74 (3H, s), 3.74 and 3.79 (2H, ABq, J=13.7 Hz), 5.55 (1H, s), 6.96—7.13 (4H, m), 7.26—7.48 (7H, m), 7.73 (1H, m), 7.96 (1H, d, J=8.0 Hz).

Dimethyl [*Msc*-9(1′)]-9-(1,1-Dimethyl-2-phenylethyl)-9,10-dihydro-9,10-ethenoanthrancene-11,12-dicarboxylate (*Msc*-3). This compound was prepared by treating an ether solution of the carboxylic acid with an ethereal solution of diazomethane. The product was recrystallized from dichloromethane-methanol, mp 103—105°C, $[\alpha]_D^{23}$ −30.4° (c=0.703, $CHCl_3$). Found: C, 79.45; H, 6.23%. Calcd for $C_{30}H_{28}O_4$: C, 79.62; H, 6.24%. ^{1}H NMR ($CDCl_3$) δ=1.84 (3H, s), 1.85 (3H, s), 3.76 (3H, s), 3.79 (3H, s), 3.47 and 3.80 (2H, ABq, J=13.3 Hz), 5.55 (1H, s), 6.97—7.12 (4H, m), 7.28—7.48 (7H, m), 7.72 (1H, m), 7.95 (1H, d, J=8.0 Hz).

(+)-Menthyl [*Psc*-9(1′)]-9-(1,1-Dimethyl-2-phenylethyl)-12-methoxycarbonyl-9,10-dihydro-9,10-ethenoanthracene-11-carboxylate (*Psc*-2). Mp 195—196°C, $[\alpha]_D^{23}$ +74.4° (c=0.866, $CHCl_3$). The compound was similarly prepared as the *Msc* compound. ^{1}H NMR ($CDCl_3$) δ=0.73 (3H, d, J=7.0 Hz), 0.89 (3H, d, J=7.4 Hz), 0.91 (3H, d, J=7.0 Hz), 0.81—1.15 (3H, m), 1.44—1.55 (2H, m), 1.69—2.03 (4H, m), 1.83 (3H, s), 1.87 (3H, s), 3.43 and 3.79 (2H, ABq, J=13.7 Hz), 3.75 (3H, s), 4.78 (1H, dt, J=4.5 and 10.9 Hz), 5.58 (1H, s), 6.95—7.12 (4H, m), 7.26—7.47 (7H, m), 7.74 (1H, m), 7.94 (1H, d, J=7.4 Hz).

[*Psc*-9(1′)]-9-(1,1-Dimethyl-2-phenylethyl)-12-methoxycarbonyl-9,10-dihydro-9,10-ethenoanthracene-11-carboxylic Acid (*Psc*-1). Mp 185—187°C, $[\alpha]_D^{23}$+30.4° (c=0.838, $CHCl_3$). The compound was similarly prepared as above. ^{1}H NMR ($CDCl_3$) δ=1.84 (3H, s), 1.85 (3H, s), 3.74 (3H, s), 3.47 and 3.79 (2H, ABq, J=13.9 Hz), 5.55 (1H, s), 6.97—7.12 (4H, m), 7.27—7.48 (7H, m), 7.74 (1H, m), 7.96 (1H, d, J=8.1 Hz).

Dimethyl [*Psc*-9(1′)]-9-(1,1-Dimethyl-2-phenylethyl)-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (*Psc*-3). Mp 103.5—104.5°C, $[\alpha]_D^{23}$ 30.5° (c=0.711, $CHCl_3$). The compound was similarly prepared from the carboxylic acid. Found: C, 79.32; H, 6.21. Calcd for $C_{30}H_{28}O_4$: C, 79.62; H, 6.24. ^{1}H NMR ($CDCl_3$) δ=1.84 (3H, s), 1.85 (3H, s), 3.76 (3H, s), 3.80 (3H, s), 3.47 and 3.80 (2H, ABq, J=13.9 Hz), 5.55 (1H, s), 6.97—7.12 (4H, m), 7.28—7.48 (7H, m), 7.73 (1H, m), 7.95 (1H, d, J=8.0 Hz).

X-Ray Crystallography of Compound 2.[23] A crystal used for the measurement was grown from hexane and its size was $0.45\times0.40\times0.35$ mm^3. X-Ray data were obtained on a MAC Science MXC18 four circle diffractometer with Mo $K\alpha$ radiation (λ=0.71073 Å). The scan mode was the 2θ method in the range of $2\theta<30°$ and the ω–2θ method in $2\theta>30°$, and the scan rate was 4° min^{-1}. The scan range was calculated by $0.82°+0.35°\tan\theta$. The structure was solved by the direct method (MULTAN78) and refined by the full-matrix least squares method by using a CRYSTAN program. Anisotropic thermal parameters were employed for non-hydrogen atoms and isotropic for hydrogens. All the hydrogen atoms were found in a differential map and no absorption correction was employed. Total number of measured unique reflections was 4985 within the range $2°<2\theta<60°$ and 4155 reflections with $|F_o|>3\sigma|F_o|$ were used for the structure determination and refinement. The function minimized was $\Sigma[w(|F_o|^2-|F_c|^2)^2]$, where $w=[(\sigma_c|F_o|)^2+0.0004|F_o|^2]^{-1}$. Formula $C_{39}H_{44}O_4$, F.W. 576.80, monoclinic, space group $P2_1$, a=10.666(2), b=17.765(3), c=8.866(2) Å, β=98.54-

(2)°, $V=1661.3(5)$ Å^3, $Z=2$, $D_c=1.15$ g cm^{-3}, $\mu=0.40$ cm^{-1}. $R=0.050$, $R_w=0.050$.

We wish to thank Professor K. Takeda and Ms. Y. Moriyama of this University for their assistance in measuring the CD spectra. We also wish to thank Professors E. L. Eliel, K. Mislow, and J. Sandström for their valuable comments.

References

1) M. Ōki, *Top. Stereochem.*, **14**, 1 (1984).
2) G. Yamamoto, M. Nakamura, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **48**, 2952 (1975). In the paper, the numbering of carbons is different from that used in the present paper, carbons 11 and 12 being 12 and 11, respectively. In the present paper, the numbering is in conformity with what is used in Chemical Abstracts.
3) L. H. Schwartz, C. Koukotas, P. Kukkola, and C. S. Yu, *J. Org. Chem.*, **51**, 995 (1986).
4) R. Isaksson, M. Öki, J. Sandström, M. R. Suissa, and S. Toyota, *Acta Chem. Scand., Ser. B.*, in press.
5) V. Prelog, *Helv. Chim. Acta*, **39**, 308 (1953).
6) V. Prelog and H. L. Meier, *Helv. Chim. Acta*, **39**, 320 (1953).
7) M. Ōki, N. Takiguchi, S. Toyota, G. Yamamoto, and S. Murata, *Bull. Chem. Soc. Jpn.*, **61**, 4295 (1988), and papers cited therein.
8) J. Trotter and F. C. Wireko, *Acta Crystallogr., Sect. C*, **47**, 1275 (1991).
9) J. Trotter and F. C. Wireko, *Acta Crystallogr., Sect. C*, **47**, 1277 (1991).
10) J. Trotter and F. C. Wireko, *Acta Crystallogr., Sect. C*, **47**, 1470 (1991).
11) M. Ōki, *Acc. Chem. Res.*, **23**, 351 (1990).
12) M. Mikami, K, Toriumi, M. Konno, and Y. Saito, *Acta Crystallogr., Sect. B*, **31**, 2474 (1975).
13) For example, see: G. M. Brown and H. A. Levy, *Acta Crystallogr., Sect. B*, **35**, 785 (1979).
14) J. M. Bijvoet, A. F Peerdeman, and A. J. van Bommel, *Nature*, **168**, 271 (1951).
15) R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5**, 387 (1966).
16) L. C. Cross and W. Klyne, *Pure Appl. Chem.*, **45**, 11 (1976).
17) M. Ōki, "Applications of Dynamic NMR Spectroscopy to Organic Chemistry," VCH Publishers, Deerfield Beach (1984).
18) K. S. Hayes, M. Nagumo, J. F. Blount, and K.Mislow, *J. Am. Chem. Soc.*, **102**, 2773 (1980)
19) A referee argues that the term "absolute conformation" is inappropriate because conformation includes that which is not chiral. We believe, however, that distinguishing absolute stereochemistry of chiral compounds which originates from restricted rotation or inversion is necessary. We may limit the usage of "absolute conformation" only for those which are chiral and need specification. It will be worthwhile to point out that even in *ap* or *sp* conforamations, there can be chiral isomers as are exemplified by twisted olefins.
20) C. Djerassi, R. Records, E Bunnenberg, K. Mislow, and A. Moscowitz, *J. Am. Chem. Soc.*, **84**, 870 (1962).
21) G. Snatzke, *Angew. Chem.*, **91**, 380 (1979); *Angew. Chem., Int. Ed. Engl.*, **18**, 363 (1979).
22) G. Yamamoto and M. Ōki, *Bull. Chem. Soc. Jpn.*, **63**, 3550 (1990).
23) Tables of coordinate for the hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, and complete thermal F_o-F_c data are deposited as Document No. 9055 at the Office of the Editor of Bull. Chem. Soc. Jpn.