

Enantiomeric Resolution and Absolute Stereochemistry of Stable Rotamers of Dimethyl 6,6′-Dimethyl-9,9′-bitriptycyl-2,2′-dicarboxylate as a Stereochemical Analog of (*R**,*R**)- and (*R*,*S*)-Tartaric Acids

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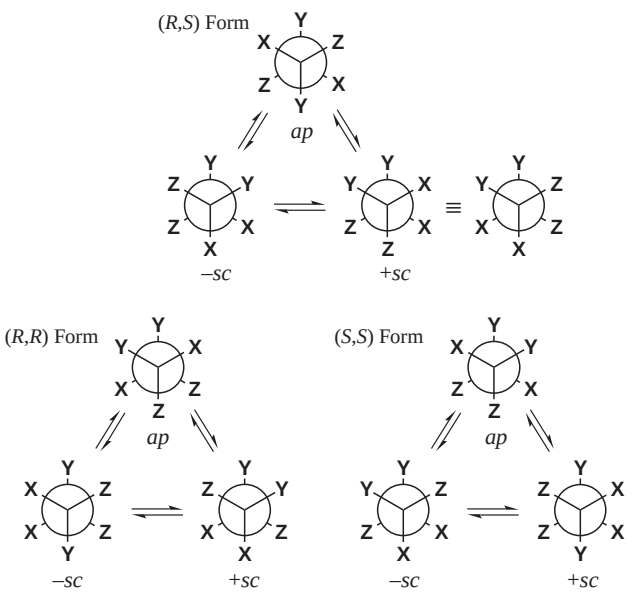
The title 9,9′-bitriptycyl compound, regarded as a stereochemical analogue of tartaric acid, possesses a total of five diastereomers, among which two rotamers belonging to the (*R**,*R**) form were isolated by chromatographic separation. Their relative stereochemistries were determined by X-ray analysis to be *ap*-(*R**,*R**) and *sc**-(*R**,*R**). The enantiomers of these isomers were resolved by chiral HPLC and found to be optically and CD active. To predict the absolute stereochemistry, the CD spectra were calculated by the TDDFT method for the two rotamers as well as the chiral (*R*,*S*) form. The spectral pattern depends on the absolute arrangement of the two COOMe substituted benzeno groups, leading to the assignment of *ap*-(*S*,*S*), *Psc*-(*R*,*R*), and *Msc*-(*R*,*S*) for the (−)-forms. Since the achiral *ap*-(*R*,*S*) form was already known, we established the stereochemical relationship of all of the possible isomers of the tartaric acid-type molecule except for a pair of enantiomers of one missing isomer, the *sc**-(*S**,*S**) form.

We have applied the structure of dimethyl 6,6′-dimethyl-9,9′-bitriptycyl-2,2′-dicarboxylate (**1**) as a stereochemical model of tartaric acid-type compounds, XYZC–CXYZ.[1] The extremely high barrier to rotation about the C9–C9′ bond in the rigid framework[2] allowed us to isolate possible isomers at room temperature. The (*R*,*S*) form, well known as the *meso* form, has three conformational isomers that are exchangeable by the formal C–C bond rotation: One is an achiral isomer of C_i symmetry and the others are a pair of enantiomers of C_1 symmetry (Scheme 1). Such isomers could be separated and identified by using the bitriptycyl structure: Enantiopure samples of the chiral isomer, *sc**-(*R*,*S*) form, were optically active, while the achiral isomer, *ap*-(*R*,*S*) form, was inactive.[1] This experimental result completely eliminates the concept of "internal compensation," which had been proposed more than a century ago to explain the optical inactivity of *meso* compounds.[3]

As for the (*R**,*R**) form, also known as (±) form, there exist three kinds of diastereomeric conformers, each of which has a pair of enantiomers.[4] In contrast to the (*R*,*S*) form, none of the conformers of the (*R**,*R**) form can be converted into its enantiomer by the formal C–C bond rotation because they have different configurations at the two stereogenic centers at the 9,9′ carbons. In the above experiment, we also isolated two isomers from the reaction mixture in addition to the two isomers of the (*R*,*S*) form. Although these isomers may be attributed to any of the three rotamers of the (*R**,*R**) form, the definitive assignment is not established yet. In order to reach the absolute answer to the stereochemistry of the tartaric acid-type molecule, the stereochemistry of these isomers were determined by X-ray analysis. Their enantiomers were resolved by chiral HPLC, and the CD spectra of enantiopure samples were analyzed with the aid of theoretical calculations by the time-dependent density functional theory (TDDFT) to predict the absolute stereochemistry.



Scheme 1. Conformational circuits between possible conformers of (*R*,*S*)- and (*R**,*R**)-tartaric acid-type molecules represented by Newman projections. For the stereochemical symbols, the priority of the CIP rule is assumed to be -CXYZ > X > Y > Z. If X, Y, and Z are regarded as benzeno groups carrying Me, COOMe, and no substituents, respectively, these schemes are applicable to compound **1**.

Results and Discussion

Synthesis and Separation of Isomers. The target compound was prepared by the Diels–Alder reaction of dimethyl

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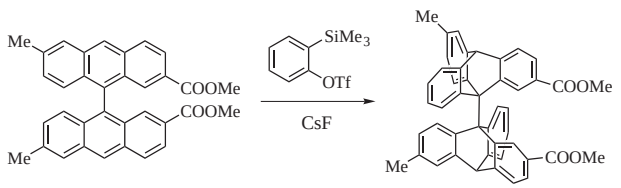
6,6′-dimethyl-9,9′-bianthryl-2,2′-dicarboxylate (**2**) with benzyne (Scheme 2). Although we previously used anthranilic acid and isopentyl nitrite for the generation of benzyne,[1] the use of 2-(trimethylsilyl)phenyl triflate and cesium fluoride was found to afford a better result in terms of purification.[5] The crude products were purified by column chromatography and then by GPC. The isomers were separated by HPLC to obtain four fractions at the retention times of 16, 50, 54, and 62 min in 6% combined yield. Herein after, we designate these isomers as **A**–**D** in the order of elution, and the missing isomer as **E**.

Determination of Stereochemistry. Before attempting the stereochemical assignment, we compiled features in molecular symmetry, stereochemistry, and other properties of all of the possible isomers of **1** in Table 1. The dipole moments were calculated at the HF/3-21G* level for the structures optimized by the AM1 method. The calculated values indicate that the arrangement of the COOMe substituted benzeno groups, *ap* or *sc*, play a dominant role in the overall magnitude. The previous work revealed by X-ray analysis and NMR spectroscopy that **A** and **C** were the *ap*-(*R*,*S*) and *sc**-(*R*,*S*) forms, respectively.[1] The experimental fact that **A** was eluted much more easily than the others in chromatographic separation is consistent with the centrosymmetric structure with no dipole moment. The stereochemistries of three diastereomeric isomers of the (*R**,*R**) form cannot be distinguished by ^{1}H and ^{13}C NMR spectral patterns, because they are all of C_2 symmetry.

Fortunately, we could obtain single crystals suitable for the X-ray analysis of **B** and **D**. The X-ray structures clearly show that these isomers have the (*R**,*R**) configuration at the C9 and C9′ atoms: the ORTEP drawings in Fig. 1 are arbitrarily the (*R*,*R*) forms. The two Me substituted benzeno groups, which are fiducial groups for the conformational nomenclature by the Klyne–Prelog system, are *ap* and +*sc* in the structures of **B** and **D**, respectively, hence their relative stereochemistries are designated as *ap*-(*R**,*R**) and *sc**-(*R**,*R**).[6] In these isomers, the two COOMe substituted benzeno groups are +*sc* or −*sc*, as in the *sc**-(*R*,*S*) form (**C**). Therefore, the retention times of **B**, **C**, and **D** are similar in the HPLC separation, which is consistent with comparable values of the dipole moment. The missing isomer **E** is attributed to the *sc**-(*S**,*S**) form, where the two COOMe substituted benzeno groups are *ap*.



2 **1**
isomeric mixture

Scheme 2. Diels–Alder reaction of **2** with benzyne to form **1**.

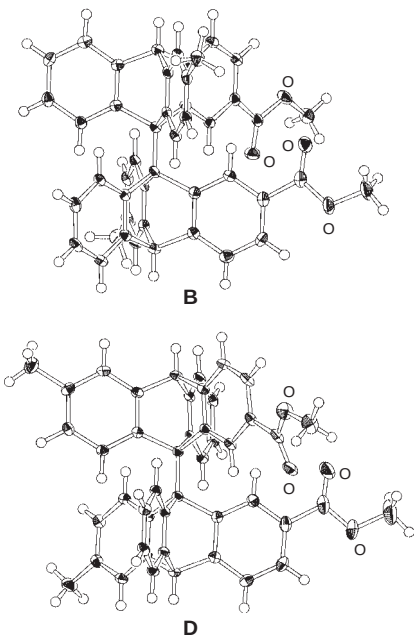


Fig. 1. ORTEP drawings of isomers *ap*-(*R**,*R**)-**1** (**B**) and *sc**-(*R**,*R**)-**1** (**D**). Solvent molecules are omitted for clarity.

Table 1. Compilation of Stereochemistry, Symmetry, and Dipole Moments of All Possible Stereoisomers of Dimethyl 6,6′-Dimethyl-9,9′-bitriptycyl-2,2′-dicarboxylate (**1**)

Stereochemistry (absolute)	Conformation[a)] X	Y	Z	Stereochemistry (relative)[b)]	Symmetry	No. of signals[c)]	Dipole moment /D[d)]	Isomer
ap-(*R*,*S*)	*ap*	*ap*	*ap*	*ap*-(*R*,*S*)	C_i (achiral)	1, 18	0.00	**A**
Psc-(*R*,*S*) *Msc*-(*R*,*S*)	+*sc* −*sc*	+*sc* −*sc*	+*sc* −*sc*	*sc**-(*R*,*S*)	C_1 (chiral)	2, 36	1.97	**C**
ap-(*R*,*R*) *ap*-(*S*,*S*)	*ap* *ap*	+*sc* −*sc*	−*sc* +*sc*	*ap*-(*R**,*R**)	C_2 (chiral)	1, 18	1.52	**B**
Psc-(*R*,*R*) *Msc*-(*S*,*S*)	+*sc* −*sc*	−*sc* +*sc*	*ap* *ap*	*sc**-(*R**,*R**)	C_2 (chiral)	1, 18	2.19	**D**
Msc-(*R*,*R*) *Psc*-(*S*,*S*)	−*sc* +*sc*	*ap* *ap*	+*sc* −*sc*	*sc**-(*S**,*S**)	C_2 (chiral)	1, 18	0.52	**E**

a) The conformational relationship between two X's (Y's, or Z's). X: Me substituted benzeno group. Y: COOMe substituted benzeno group. Z: substituent free benzeno group. As for the Klyne–Prelog system, see Ref. 6. b) For the representation with * symbols, see Ref. 6. c) Numbers of NMR signals: Me (or COOMe) proton signals and aromatic carbon signals. d) Calculated at the HF/3-21G* level.

Table 2. Data of Chromatographic Resolution and Specific Rotations of Enantiomers of **B**, **C**, and **D** of Compound **1**

	Retention time/min[a]		α[b]	R_s[c]	Specific rotation $[\alpha]_D^{25}$[d]	
Isomer	1st elution	2nd elution			1st elution	2nd elution
B	19.8	22.9	1.22	0.72	−25	+27
C	19.7	23.3	1.26	0.85	−31	+31
D	20.2	27.3	1.49	1.71	−20	+22

a) Column: Daicel CHIRALCEL OD. Eluent: hexane–2-propanol 50:1. Flow rate: 2.4 mL min^{-1}. b) Separation coefficient. c) Resolution. d) Measured in $CHCl_3$ at *c* 0.05–0.10. Errors are estimated to be ±10%.

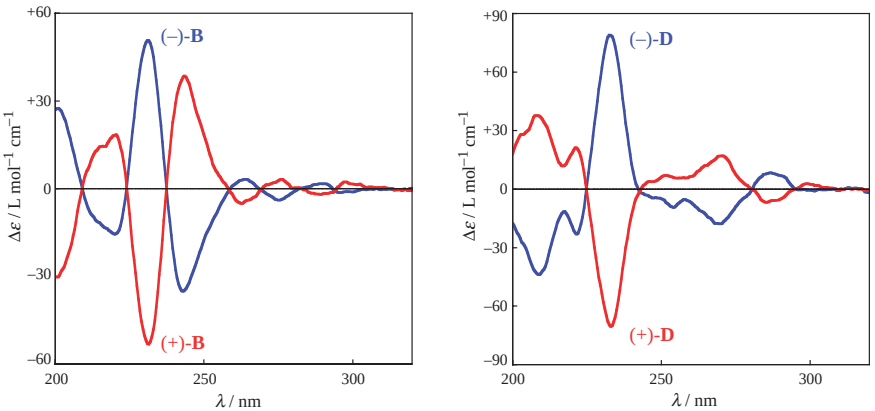


Fig. 2. CD spectra of the both enantiomers of isomers **B** and **D** in MeOH.

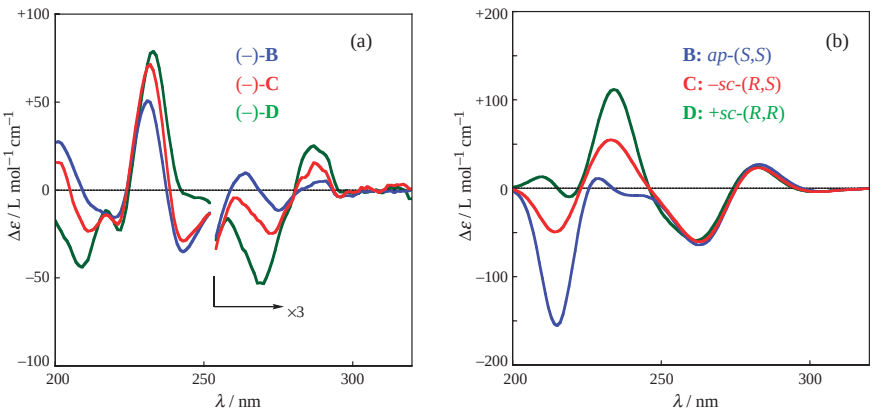
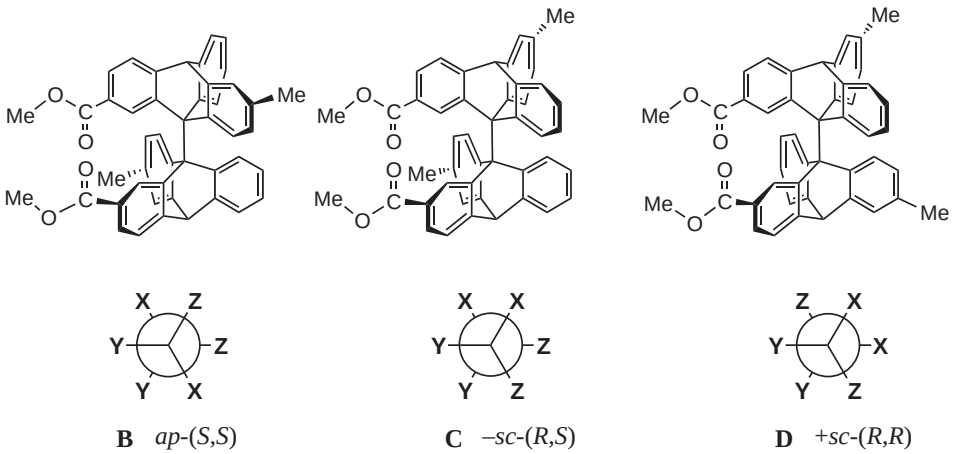


Fig. 3. Observed CD spectra of (−)-**B**–**D** (a) and the calculated spectra at the TDB3LYP/3-21G* level (b).

Enantiomeric Resolution. The enantiomers of **B** and **D** were resolved by chiral HPLC with a Daicel CHIRALCEL OD column. The retention times and specific rotations of these enantiomers are compiled in Table 2 together with the data of **C**. The enantiomers of **D** were resolved with the base-line separation at the retention times of 20.2 and 27.3 min. Because two peaks were partly overlapped in the case of **B**, the resolution was repeated for the complete separation. Thus, the obtained enantiopure samples are optically active, and the specific rotations are of the same magnitude with different signs within experimental errors for each pair of enantiomers. Incidentally, the easily and less easily eluted isomers are levo- and dextro-rotatory for **B** and **D** as well as **C**.

The CD spectra of both enantiomers of **B** and **D** were measured in methanol (Fig. 2). The (−)-form of **B** gives a peak at 231 nm and a trough at 242 nm in addition to small bands in the other regions. The spectrum of the (+)-form is practically the mirror image of that of the (−)-form. The (−)- and (+)-forms of **D** show a relatively strong peak and trough at 233 nm, respectively. The CD spectra of the easily eluted enantiomers or the (−)-forms of isomers **B**, **C**, and **D** are compiled in Fig. 3a. The band shapes are quite similar to each other: a peak at 233 nm and coupled type weak bands at long wavelength.

Theoretical CD Calculations by TDDFT Method. A remaining problem is the absolute stereochemistry of the enantiomers. We attempted to transform the chiral isomers into various derivatives appropriate for the determination of the absolute stereochemistry by X-ray analysis or other methods in vain. Therefore, we tackled this problem with the aid of a the-



B *ap*-(*S*,*S*) **C** –*sc*-(*R*,*S*) **D** +*sc*-(*R*,*R*)

Fig. 4. Configuration and conformation of the molecules used for the calculation of CD spectra.

oretical approach. Recently, a method based on TDDFT has been found to be a useful technique for theoretical CD calculations within a reasonable computational time.[7–9] Although we encountered problems in computing such a large molecule, we managed to calculate the spectra of these isomers at the B3LYP/3-21G* level. The calculations were carried out for one of the enantiomers of **B**–**D** shown in Fig. 4, where the two COOMe substituted benzeno groups are arranged in the *M* (counterclockwise) fashion along the central C–C bond. The calculated spectra are compiled in Fig. 3b. The curves are almost superimposable in the long wavelength region (260–300 nm) with the first positive and the second negative Cotton effects: These bands are approximately attributed to the π(benzene)–π^*(C=O) transition.[10] The spectra have positive and negative Cotton effects at ca. 240 and 225 nm, respectively, although their magnitudes depend on the isomers. This similarity unequivocally indicates that the signal pattern is strongly related to the absolute arrangement of the two COOMe substituted benzeno groups with perturbations by those of other combinations of benzeno groups.

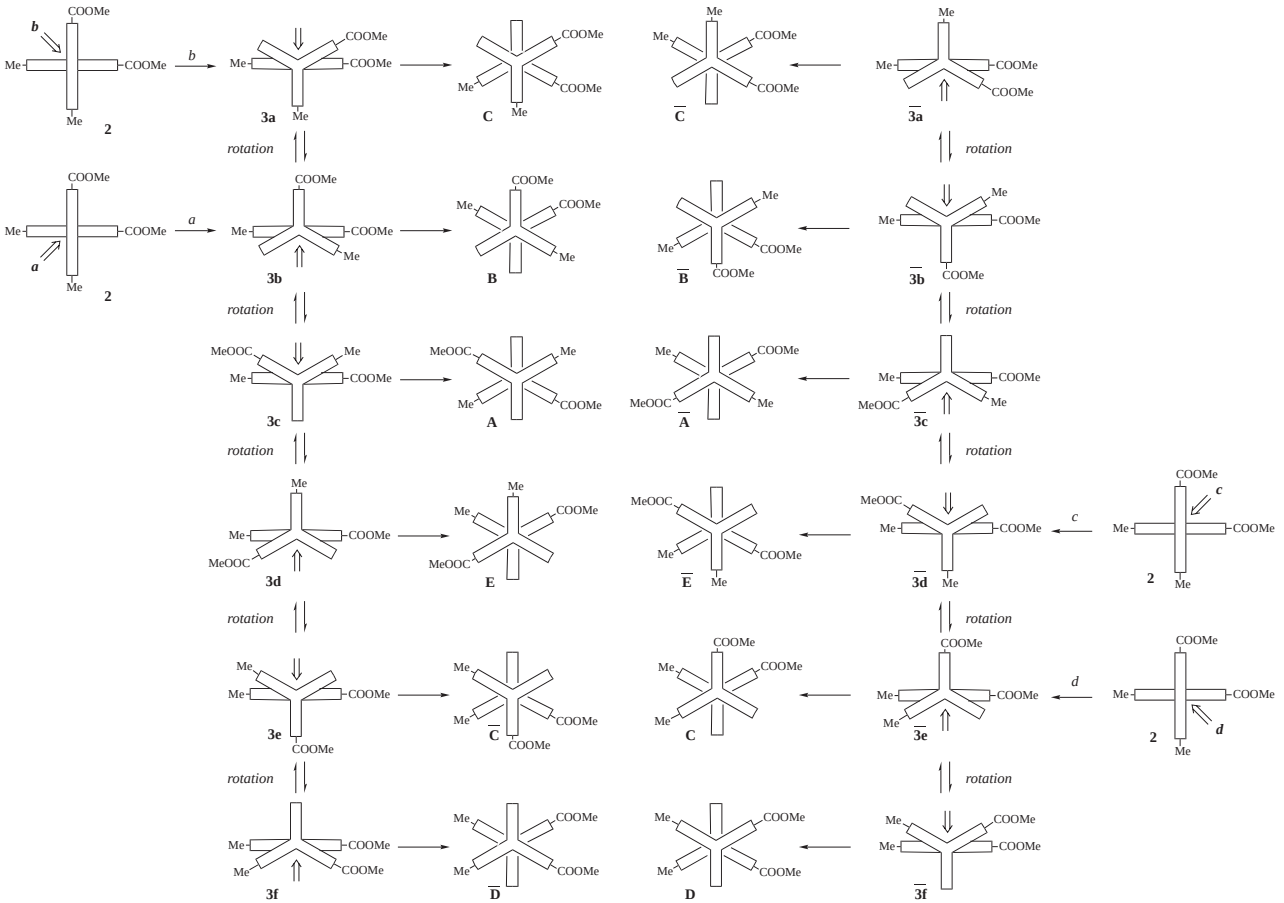
The calculated spectra were compared with the observed spectra of (−)-**B**, **C**, and **D** (Fig. 3). The signal pattern in the long wavelength region, the first positive and the second negative bands, is reasonably reproduced by the calculation, although the calculated amplitudes are larger than the experimental ones. The peak at ca. 235 nm is well reproduced by the calculation for **C** and **D**. As for **B**, there are excitations with positive signs in this region, but a large negative one at 237 nm almost cancels the positive components. Despite a few discrepancies, the calculated spectra are in agreement with the experimental ones. Therefore, we can assign the absolute stereochemistries as follows: *ap*-(*S*,*S*)-(−)/*ap*-(*R*,*R*)-(+) for **B**, *Msc*-(*R*,*S*)-(−)/*Psc*-(*R*,*S*)-(+) for **C**, and *Psc*-(*R*,*R*)-(−)/*Msc*-(*S*,*S*)-(+) for **D**.[11]

The Missing Isomer. The calculated dipole moment suggests that the missing isomer **E** should be less polar than isomers **B**–**D**. Although we carefully checked all fractions during chromatographic separations, especially less polar parts, we could not find an additional isomer of **1**. The heat of formation of **E** is comparable to those of the other isomers (within 4 kJ mol^{-1}). Once the bitriptycyl structure is formed, the isomerization never occurs under ordinary conditions. These facts indicate that the absence of **E** results from kinetic factors.

To consider the experimental finding, we had drawn the stereochemical courses during the stepwise formation of the bitriptycyl framework, following the analysis proposed by Schwartz et al. (Scheme 3).[2] The first benzyne molecule prefers to attack an anthracene moiety from either of four directions *a*–*d*. The formed monoadduct **3** takes a conformation where one of the benzeno groups in the triptycyl group is bisected to the remaining anthracene group to avoid steric interactions. The second benzyne tends to attack the anthracene moiety from a less hindered side, leading to the final products. It was known that the monoadduct **3** underwent partial rotation about the C9–C9′ bond under the reaction conditions. Therefore, this model might explain the formation of all of the isomers, even though the initial attack may occur from any direction. The effects of Me and COOMe groups on the course of reaction are difficult to predict because both steric and electronic factors influence the reactivity of the diene moiety in the anthracene group. The above discussion suggests that the absence of isomer **E** is attributable to either or both of the two factors: the population of the intermediate leading to **E** (**3d**) is negligibly small, or the cycloaddition toward this intermediate requires a large energy.

Conclusion

We have established the relative stereochemistries of the two rotamers of (R^*,R^*)-**1** as a stereochemical model of tartaric acid. These isomers were resolved into a pair of enantiomers by chiral HPLC, and their absolute stereochemistries were determined by a theoretical method. These results as well as those reported previously for (*R*,*S*)-**1**[1] show that we have separated seven of the nine possible isomers of (*R*,*S*)- and (R^*,R^*)-**1** in Scheme 1 including enantiomers: One is optically inactive and the others, three pairs of enantiomers, are optically active. Although one rotamer is still missing for (R^*,R^*)-**1**, the above results clearly instruct us that molecules of an (R^*,R^*)-tartaric acid compound consist of three diastereomeric conformers. In general cases where the C–C bond rotation occurs rapidly on the laboratory and NMR time scales, the physical and spectroscopic properties of such compounds are averages of those of three conformers weighted on their populations. Similarly, the chiroptical properties of an enantiopure



Scheme 3. Stereochemical courses during the stepwise formation of 9,9′-bitriptycyl structure. Double shafted arrows indicate the preferred directions of the attack of benzynes. Bars indicate the enantiomeric relationship. The reactions from (*M*)-9,9′-bianthryl **2** are similarly depicted.

compound, namely (*R*,*R*) or (*S*,*S*) form, are weighted averages of those of three enantiopure conformers.

Experimental

General. ^{1}H NMR spectra were measured on a Varian Gemini-300 spectrometer at 300 MHz. Melting points are not corrected. High-resolution mass spectra were measured on a JEOL JMS-700 MStation spectrometer. GPC was carried out with a Japan Analytical Industry Co. LC-908 Recycling HPLC system using JAIGEL-1H and -2H columns (eluent: chloroform). Preparative HPLC was carried out with a HITACHI L-6250 pump using a Develosil 60-7 column (20 mmϕ × 250 mm). Optical rotation was measured on a JASCO DIP-370 polarimeter with the use of a 10 mmϕ × 100 mm cell. CD spectra were measured on a JASCO J-820 spectropolarimeter with the use of a 1 mm cell. Most of the analytical and spectroscopic data had already been reported in the previous paper.[1] Only important or additional data are described here for each isomer. The samples of each isomer were obtained in such small quantities that the compounds were characterized by HRMS, and their purities were confirmed by ^{1}H NMR spectra.

Synthesis and Separation of 1. To a refluxing solution of 2.00 g (4.01 mmol) of dimethyl 6,6′-dimethyl-9,9′-bianthryl-2,2′-dicarboxylate[1] and 12.2 g (80.3 mmol) of cesium fluoride in 1 L of acetonitrile was added a solution of 4.88 mL (20.1 mmol) of 2-(trimethylsilyl)phenyl triflate in 80 mL of acetonitrile with a syringe in 1.5 h. The reaction mixture was further refluxed for 2 h, and the solvent was removed by evaporation. The residue was passed through a plug column on silica gel with dichloromethane, and then separated by GPC with chloroform into three fractions, where the desired compound was rich in the second fraction (1.37 g). This crude material was separated by HPLC with hexane–dichloromethane 1:4, and the four isomers **A**–**D** were eluted at the retention times of 16, 50, 54, and 62 min, respectively, together with several unidentified products. Each isomer was further purified by HPLC under the same conditions. The yields of these isomers were 43 mg (**A**), 27 mg (**B**), 56 mg (**C**), and 28 mg (**D**), and the combined yield was 5.9%. If necessary, each isomer was purified by recrystallization from benzene or toluene.

***ap*-(*R**,*R**)-1 (B):** mp 335–338 °C (dec); ^{1}H NMR ($CDCl_3$) δ 2.25 (6H, s), 3.51 (6H, s), 5.61 (2H, s), 6.40 (2H, dd, J = 1.5, 8.4 Hz), 6.62 (2H, dt, J = 1.5, 7.6 Hz), 6.66 (2H, d, J = 8.4 Hz), 6.86 (2H, d, J = 7.7 Hz), 7.01 (2H, dt, J = 1.1, 7.1 Hz), 7.37 (2H, d, J = 1.5 Hz), 7.41 (2H, s), 7.51 (2H, dd, J = 1.3, 7.2 Hz), 7.57 (2H, d, J = 7.7 Hz), 7.71 (2H, dd, J = 1.6, 7.7 Hz); UV (MeOH) λ (ε) 207 (56200), 231 (29000, sh), 263 (7800), 292 nm (2500); HRMS (FAB) Found: m/z 650.2427, Calcd for $C_{46}H_{34}O_4$: $[M]^+$, 650.2457.

***sc**-(*R**,*R**)-1 (D):** mp 350–355 °C (dec. and partly sublimed); ^{1}H NMR ($CDCl_3$) δ 2.26 (6H, s), 3.49 (6H, s), 5.61 (2H, s), 6.43 (2H, d, J = 8.3 Hz), 6.60 (2H, dt, J = 1.2, 7.6 Hz), 6.75 (2H, d, J = 8.0 Hz), 6.80 (2H, d, J = 7.7 Hz), 7.01 (2H, dd, J =

1.2, 7.2 Hz), 7.37 (2H, d, $J = 1.5$ Hz), 7.39 (2H, s), 7.53 (2H, dd, $J = 1.2$, 7.4 Hz), 7.57 (2H, d, $J = 7.7$ Hz), 7.71 (2H, dd, $J = 1.5$, 7.7 Hz); UV (MeOH) λ (ε) 207 (62100), 231 (30200, sh), 264 (8000), 291 nm (2500); HRMS (FAB) Found: m/z 650.2444, Calcd for $C_{46}H_{34}O_4$: $[M]^+$, 650.2457.

Enantiomeric Resolution by HPLC. Chiral HPLC was carried out with the HITACHI pump using a Daicel CHIRALCEL OD semi-preparative column (10 mmϕ × 250 mm). The eluent was hexane–2-propanol 50:1, and the flow rate was 2.4 mL min^{-1}. About 0.2 mg of a sample of **B** or **D** was injected for each separation. The chromatographic data are listed in Table 1. The NMR spectra of the enantiomers are identical with those of the corresponding racemic compound.

The easily eluted isomer of **B** [*ap*-(*S*,*S*)-(−)-**1**]: $[\alpha]_D^{25}$ −25 (*c* 0.05, $CHCl_3$); CD (3.1×10^{-5} mol L^{-1}, CH_3OH) λ ($\Delta\varepsilon$) 220 (−15.6), 231 (+50.7), 243 (−35.2), 264 (+3.3), 275 nm (−3.9); HRMS (FAB) Found: m/z 650.2457, Calcd for $C_{46}H_{34}O_4$: $[M]^+$, 650.2457.

The less easily eluted isomer of **B** [*ap*-(*R*,*R*)-(+)-**1**]: $[\alpha]_D^{25}$ +27 (*c* 0.05, $CHCl_3$); CD (3.1×10^{-5} mol L^{-1}, CH_3OH) λ ($\Delta\varepsilon$) 221 (+18.5), 232 (−53.2), 244 (+38.5), 263 (−5.1), 276 nm (+3.3); HRMS (FAB) Found: m/z 650.2419, Calcd for $C_{46}H_{34}O_4$: $[M]^+$, 650.2457.

The easily eluted isomer of **D** [*Psc*-(*R*,*R*)-(−)-**1**]: $[\alpha]_D^{25}$ −20 (*c* 0.05, $CHCl_3$); CD (3.1×10^{-5} mol L^{-1}, CH_3OH) λ ($\Delta\varepsilon$) 209 (−44.0), 218 (−11.5), 222 (−23.2), 233 (+78.9), 270 (−17.8), 287 nm (+8.4); HRMS (FAB) Found: m/z 650.2502, Calcd for $C_{46}H_{34}O_4$: $[M]^+$, 650.2457.

The less easily eluted isomer of **D** [*Msc*-(*S*,*S*)-(−)-**1**]: $[\alpha]_D^{25}$ +22 (*c* 0.05, $CHCl_3$); CD (3.1×10^{-5} mol L^{-1}, CH_3OH) λ ($\Delta\varepsilon$) 208 (+37.7), 217 (+11.8), 221 (+21.0), 233 (−70.4), 271 (+17.0), 285 nm (−6.8); HRMS (FAB) Found: m/z 650.2463, Calcd for $C_{46}H_{34}O_4$: $[M]^+$, 650.2457.

The specific rotations and CD spectra of the enantiomers of **C** were remeasured with solutions at higher concentrations to obtain reliable data. The easily eluted isomer of **C** [*Msc*-(*R*,*S*)-(−)-**1**]: $[\alpha]_D^{25}$ −31 (*c* 0.10, $CHCl_3$); CD (3.1×10^{-5} mol L^{-1}, CH_3OH) λ ($\Delta\varepsilon$) 211 (−23.4), 217 (−14.1), 221 (−19.5), 232 (+71.3), 243 (−29.0), 260 (−1.5), 272 (−8.2), 287 nm (+5.1); HRMS (FAB) Found: m/z 650.2481, Calcd for $C_{46}H_{34}O_4$: $[M]^+$, 650.2457. The less easily eluted isomer of **C** [*Psc*-(*R*,*S*)-(+)-**1**]: $[\alpha]_D^{25}$ +31 (*c* 0.10, $CHCl_3$); CD (3.1×10^{-5} mol L^{-1}, CH_3OH) λ ($\Delta\varepsilon$) 212 (+19.8), 217 (+12.8), 221 (+18.4), 232 (−72.1), 244 (+27.1), 262 (+0.3), 272 (+7.3), 290 nm (−3.7); HRMS (FAB) Found: m/z 650.2428, Calcd for $C_{46}H_{34}O_4$: $[M]^+$, 650.2457.

X-ray Analysis. Compound *ap*-(*R**,*R**)-**1** (**B**) was crystallized from a hexane–toluene solution to give a crystal ($0.35 \times 0.20 \times 0.15$ mm^3) containing toluene molecules in a 1:1 ratio. Compound *sc**-(*R**,*R**)-**1** (**D**) was crystallized from a hexane–benzene solution to give a crystal ($0.35 \times 0.20 \times 0.20$ mm^3) containing benzene molecules in a 1:2 ratio. The diffraction data were collected on a Rigaku RAXIS-IV imaging plate diffractometer with Mo Kα radiation ($\lambda = 0.71070$ Å) to a maximum 2θ value of 55.0° at −150 °C. The reflection data were corrected for the Lorentz-polarization effects and secondary extinction. The structure was solved by the direct method (SIR 92) and refined by the full-matrix least-squares method by using a teXsan program. The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, and the rest were included in fixed positions. All observed unique reflections were used for the refinement. The function minimized was $\Sigma w(F_o^2 - F_c^2)^2$, where $w = [\sigma^2(F_o)^2]^{-1}$. *ap*-(*R**,*R**)-**1**: Formula $C_{46}H_{34}O_4 \cdot C_7H_8$, fw 742.91, monoclinic, space group $P2_1/n$ (#14), $a = 10.5210(6)$, $b = 34.513(3)$, $c = 11.4804(8)$ Å, $\beta = 112.934(4)°$, $V = 3839.2(5)$ Å^3, $Z = 4$, $D_{calcd} = 1.285$ g cm^{-3}, μ(Mo Kα) = 0.80 cm^{-1}, Number of data 7996, $R1 = 0.050$, $wR2 = 0.128$, GOF 1.25. *sc**-(*R**,*R**)-**1**: Formula $C_{46}H_{34}O_4 \cdot 2(C_6H_6)$, fw 807.00, triclinic, space group $P\bar{1}$ (#2), $a = 9.1758(4)$, $b = 11.5182(4)$, $c = 21.964(1)$ Å, $\alpha = 76.869(3)$, $\beta = 80.500(1)$, $\gamma = 69.931(2)°$, $V = 2113.8(2)$ Å^3, $Z = 2$, $D_{calcd} = 1.268$ g cm^{-3}, μ(Mo Kα) = 0.78 cm^{-1}, Number of data 8022, $R1 = 0.056$, $wR2 = 0.162$, GOF 1.30.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-278402 and -278403 for compound *ap*-(*R**,*R**)-**1** and *sc**-(*R**,*R**)-**1**, respectively. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Computational Methods. The calculations were carried out by the Gaussian 98 program[12] on a Linux computer or on a Windows computer. For the calculations of dipole moments, the structure of each isomer was optimized by the AM1 calculation. In the global minimum structure, the carbonyl oxygen atoms in the COOMe moieties were *syn* to the C(1) atoms of the triptycene groups, and the methyl groups were *syn* to the carbonyl oxygen atoms, as found in the X-ray structures. The dipole moments were calculated at the HF/3-21G* level. For the calculations of CD spectra, the structures of isomers **B**–**D** were optimized by the hybrid DFT method at the B3LYP/3-21G* level. The conformation of the COOMe moieties is the same as above (Fig. 4). The calculations of excited states were carried out by the TDDFT method at the B3LYP/3-21G* level to provide the excitation energies, oscillator strengths, transition velocity dipole moment, and transition magnetic dipole moments for the lowest 50 excited states for each conformer. The CD spectra were obtained from these output data by the standard method reported previously.[7–9] Each excitation was treated as a Gaussian type function with a half band width of 1800 cm^{-1}.

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