

Absolute Stereochemisty and Chiroptical Properties of 3,3′-Bis(methoxycarbonyl)-9,9′-bianthryl

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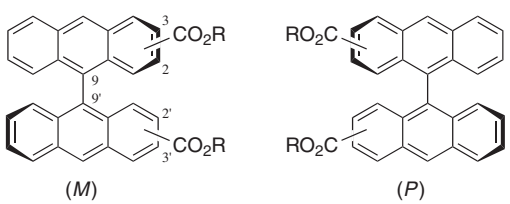
The axially chiral title compound was enantiomerically resolved by the diastereomer method via the camphorsultamamide of the corresponding dicarboxylic acid. The absolute stereochemistry of the (+)- and (−)-forms ($[\alpha]_D$ +32 and −33) was determined by X-ray analysis of one of the diastereomers of the sultamamide to be *P* and *M*, respectively, for the helicity about the C9–C9′ bond. The observed CD and UV spectra were reasonably reproduced by the theoretical calculation based on the time-dependent density functional theory (TDDFT). The CD spectrum of the (*M*)-(−) form features a split curve around 270 nm assignable to the exciton coupling of the β transition and a broad *p* band peak around 380 nm.

9,9′-Bianthryls can be axially chiral when substituents are introduced at appropriate positions. Typical examples of such compounds are 2,2′- and 3,3′-dicarboxylic acids (Chart 1), the enantiomers of which were separated via the diastereomeric quinidine salt several decades ago.[1,2] Although some researchers have investigated the CD spectra or the synthetic applications of these compounds,[3,4] their absolute stereochemistry has remained unknown for a long time. Recently, we reported the absolute stereochemistry of 2,2′-dicarboxylic acid **1** and its dimethyl ester **2** as well as features in their CD spectra with the aid of theoretical calculations by the time-dependent density functional theory (TDDFT).[5,6] We therefore applied this methodology to the 3,3′-substituted derivatives, **3** and **4**, to get further insight into the effect of positions of carboxyl groups on the chiroptical properties. In this paper we present the enantiomeric resolution of **3** via camphorsultamamide, the determination of its absolute stereochemistry, and the elucidation of its CD spectra by the TDDFT approach.

Results and Discussion

Synthesis and Enantiomeric Resolution. The synthetic route is shown in Scheme 1. Reductive dimerization of 3-chloro-9-anthrone **5** with zinc in an acidic solution gave racemic 3,3′-dichloro-9,9′-bianthryl **6** in 64% yield.[7] Compound **6** was transformed into the dicarboxylic acid **3** by the standard method.[4] In the literature, the enantiomers of **3** were resolved by repeated fractional crystallization of the diastereomeric quinidine salt.[1] We chose the chromatographic separation of a covalent derivative, the amide of camphorsultam, which is a useful reagent for the enantiomeric resolution and the determination of absolute stereochemistry.[8,9] The racemic acid (±)-**3** was converted to the corresponding camphorsultamamide via the acid chloride in an ordinary manner. The formed diastereomers were separated by HPLC with almost baseline separation (retention times **7a**: 15.0 min, **7b**: 17.5 min). Each isomer was treated with LiOH to cleave the camphor moieties, and the subsequent methylation gave enantiopure methyl esters **4** in >99% ee. The specific rotations of the methyl esters derived from **7a** and **7b** were $[\alpha]_D^{22}$ +32 and −33, respectively, in acetone. None of the isomers of **4** or **7** underwent isomerization upon heating in nitrobenzene-d_5 at 210 °C for 3 days. This finding indicates that the barrier to isomerization via the rotation about the C9–C9′ bond is higher than 180 kJ mol^{-1}.



1 2,2′ (R = H) **3** 3,3′ (R = H)
2 2,2′ (R = Me) **4** 3,3′ (R = Me)

Chart 1.

Structure and Absolute Stereochemistry. X-ray analysis was carried out for the less easily eluted isomer of the sultamamide **7b**. An ORTEP diagram is shown in Fig. 1, in which the camphor moieties have the known absolute configuration as the internal reference. The torsion angle of C9a–C9–C9′–C9a′ is −104°, this sign meaning that the helicity of the two COOMe groups along the C9–C9′ axis is left-handed or minus *M*. Because **7b** was converted to the (−)-isomer of **4**, the absolute stereochemistry of **4** was now established as (*M*)-(−) or (*P*)-(+).[10] In the X-ray structure of **7b**, the amide nitrogen atoms N1 and N1′ are nearly *anti* relative to the C2 and C2′, respectively (torsion angles 161° and 168°); the camphor moieties lie away from the central chiral axis.

CD Spectrum. The CD spectra of both enantiomers of **4** were measured in THF (Fig. 2). The CD curves of *M* and *P* forms are mirror images of each other, as expected for enantiomers. The *M* isomer afforded relatively intense Cotton effects at 264 ($\Delta\varepsilon$ + 137) and 280 (−155) nm in addition to weak structured peaks and a trough in the range of 340–410 nm. The bands in the short wavelength region look like a typical split curve that would be expected for the exciton coupling.[11] However, careful analyses are required for the substi-

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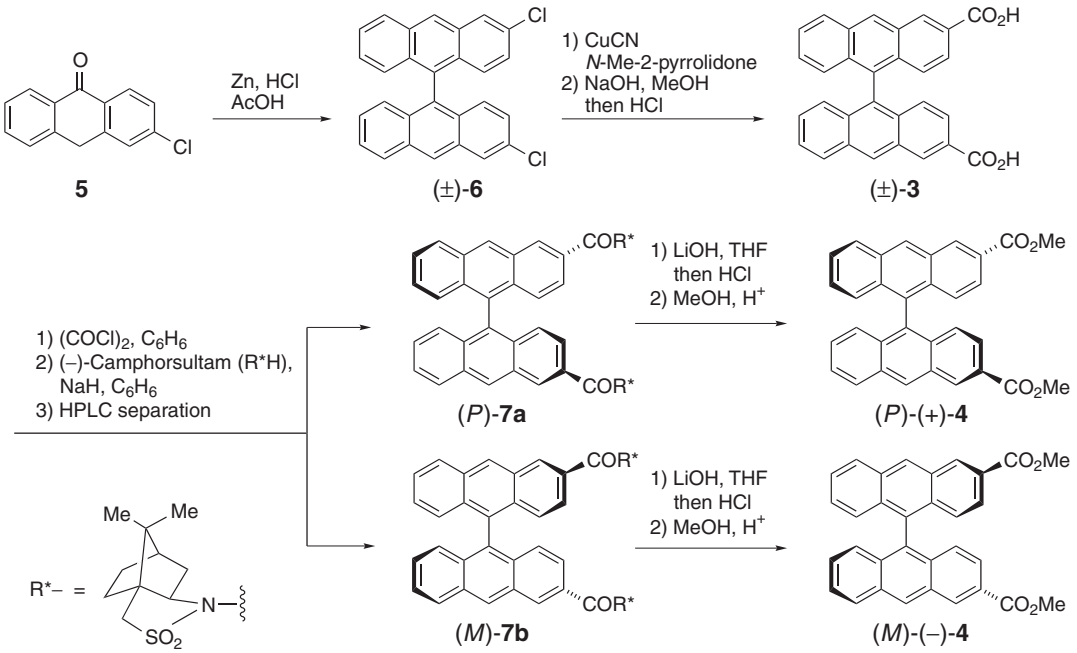

Scheme 1. Synthesis and enantiomeric resolution of **4**.

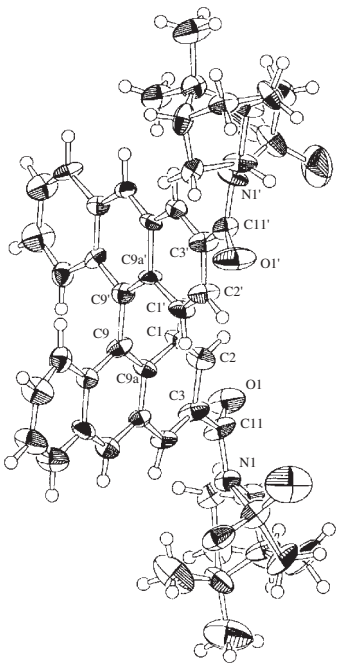

Fig. 1. ORTEP drawing of (*M*)-**7b** with thermal ellipsoids at 50% probability.

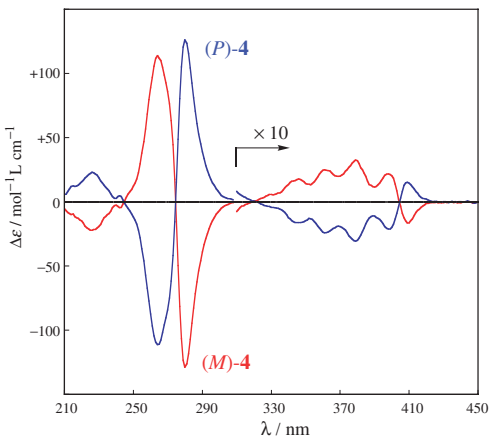

Fig. 2. CD spectra of enantiomers of **4** in THF.

tuted anthracene chromophores because several excitations with various transition moments are involved in this region. We tackled this problem by the theoretical CD calculation using the TDDFT method, which had successfully reproduced the CD spectra of 2,2′-disubstituted 9,9′-bianthry derivatives, as reported in a previous paper.[5]

The calculations were carried out for the *M* isomer of **4**. The structures used for the CD calculation were optimized by the DFT method at the B3LYP/3-21G* level to give three structures with different conformations of the ester moieties (Fig. 3). Their structural and thermodynamic data are listed in Table 1. In any structure, the two 9-anthryl groups nearly bisected each other, with the ester groups coplanar to the attaching anthracene rings either in *syn* or in *anti* form. In the global minimum structure **4b**, one of the carbonyl oxygen atoms is *syn* to the C2 and the other is *anti*. Because the energy differences are very small, the other two conformers also exist in comparable ratios. The calculations of excited states were carried out by the TDDFT method at the B3LYP/3-21G* level for each structure. The calculated UV and CD spectra of the global minimum structure (*M*)-**4b** is shown in Fig. 4(a) with bars indicating the oscillator strengths *f* and the reduced rotational strengths [*R*]; some selected data are compiled in Table 2. The spectral patterns of the other two structures, **4a** and **4c**, are similar to that of **4b**. The average spectrum weighted on the population is compared with the observed one in Fig. 4(b).

The total shape of CD and UV curves was reasonably repro-

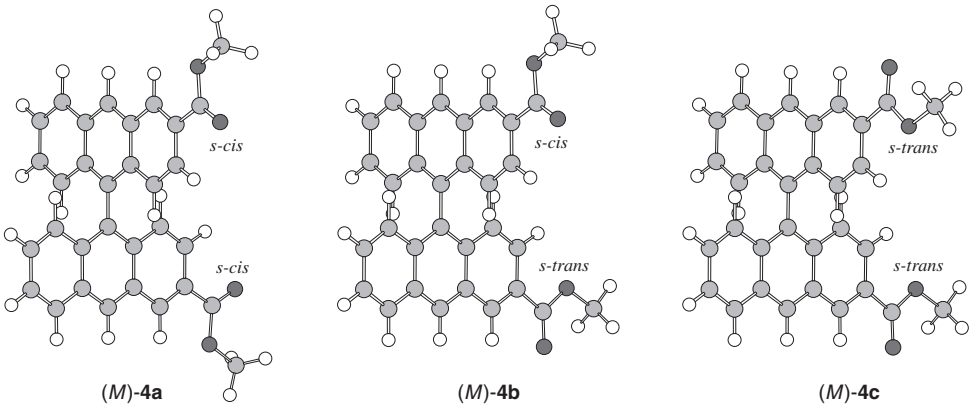

Fig. 3. Optimized structures of (*M*)-**4** at B3LYP/3-21G*.

Table 1. Structural and Thermodynamic Data of the Optimized Structures of (*M*)-**4** by DFT Calculations at B3LYP/3-21G* Level

Conformer	Torsion angle/°a)	Dihedral angle/°b)	Free energy difference/kJ mol^{-1}	Population at 25 °C/%c)
(*M*)-**4a**	−0.3, −0.3	−91.2	1.06	18.7
(*M*)-**4b**	0.0, 180.0	−91.1	0	57.2
(*M*)-**4c**	180.0, 180.0	−87.9	0.42	24.1

a) Torsion angles along C2–C3–C11=O1 and C2′–C3′–C11′=O1′ chains. b) Dihedral angles between the two anthracene rings. c) Calculated by the Boltzmann equation with a statistical contribution.

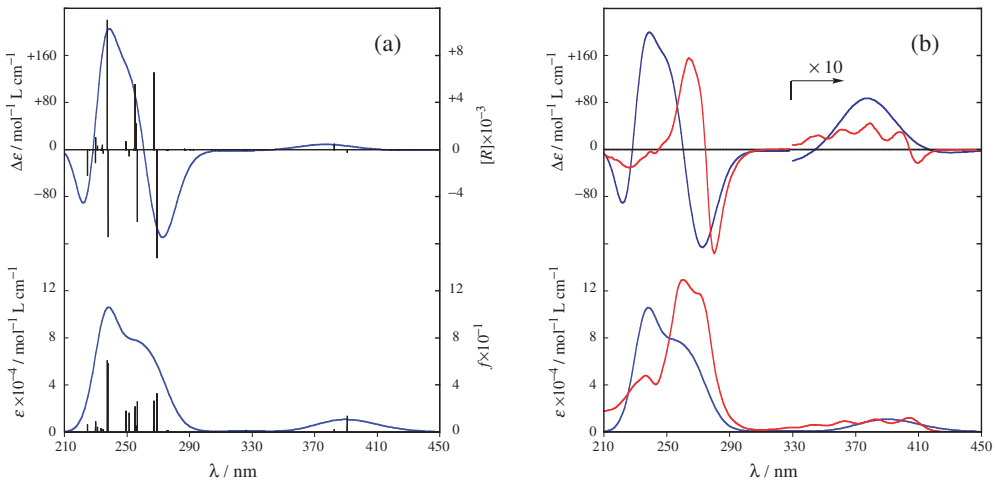

Fig. 4. Calculated CD and UV spectra of (*M*)-**4** at TDDFT/3-21G* level. (a) Spectra of (*M*)-**4b** (blue) with the oscillator strength *f* and the reduced rotatory strength [*R*]. (b) Spectra of weighted averages of the three conformers (blue) with experimental one (red).

duced by the theoretical method, although there are small blue shifts up to 10 nm especially in the short wavelength region. This systematic shift is mainly attributed to the overestimation of excitation energies inherent in the theory and partly to a solvent effect.[6b] The output data in Table 2 indicate that the trough at 273 nm (calcd) is assignable to the β band (^1B_b),[12] and the peak at 239 nm (calcd) is an overlap of some excitations, including other $\pi \rightarrow \pi^*$ and $n_{CO} \rightarrow \pi^*$ transitions. The weak peak around 380 nm is assignable to the *p* band (^1L_a).

These spectral features are in contrast to those of (*M*)-2,2′-bis(methoxycarbonyl)-9,9′-bianthryl (**2**).[5] While the negative Cotton effect at 242 nm ($\Delta\varepsilon$ − 187) due to the β' band is characteristic in (*M*)-**2**, the contribution of this excitation is negligible in (*M*)-**4** (Fig. 5). As for the β transitions around 260 nm, the CD bands are weak for (*M*)-**2** when the dihedral angle between the two anthracene rings is nearly 90°, as pointed out by Mason et al.[3] Furthermore, their intensities and signs are sensitive to the dihedral angle; the input structure should thus be optimized with great care. For (*M*)-**4**, the β transitions have large rotational strengths with an appropriate split width, giving the negative first (at longer wavelength) and the positive second (at shorter wavelength) Cotton effects at 280–260 nm attributed to excited states 15 and 16 in Table 2. Additional calculations suggest that this spectral pattern is not affected so much by a small change in the dihedral angle around

Table 2. Selected Data of UV and CD Calculations by TDDFT Method at the B3LYP/3-21G* Level for (*M*)-**4b**[a)]

Excited state	Energy/eV	λ/nm	Oscillator strength f	Reduced rotatory strength [R]	Assignment[b)]
3	3.1725	390.80	0.1639	−19.66	p
4	3.2408	382.57	0.0217	39.58	p
15	4.6071	269.12	0.4035	−802.54	β
16	4.6393	267.24	0.3239	569.04	β
17	4.8315	256.62	0.3181	−533.18	
18	4.8480	255.74	0.0621	190.61	$n_{CO} \rightarrow \pi^*$
19	4.8593	255.15	0.2640	481.41	
21	4.9307	251.45	0.1984	−44.60	
22	4.9728	249.32	0.2214	55.88	
23	5.2121	237.88	0.7277	−645.36	
24	5.2225	237.40	0.7571	959.09	
25	5.2808	234.78	0.0240	−24.20	$\pi_{CO} \rightarrow \pi^*$
26	5.2933	234.23	0.0172	30.65	$\pi_{CO} \rightarrow \pi^*$
29	5.3158	233.23	0.0320	−0.77	
30	5.3669	231.02	0.0468	23.53	
31	5.3928	229.91	0.1061	84.36	β'
32	5.3978	229.69	0.0460	−95.54	β'
35	5.5188	224.66	0.0766	−189.39	

a) Calculations were carried out for the lowest 35 excited states. Excited states of $f < 0.02$ and $|[R]| < 10$ are not listed. b) The assignment was not given for other aromatic $\pi \rightarrow \pi^*$ excitations.

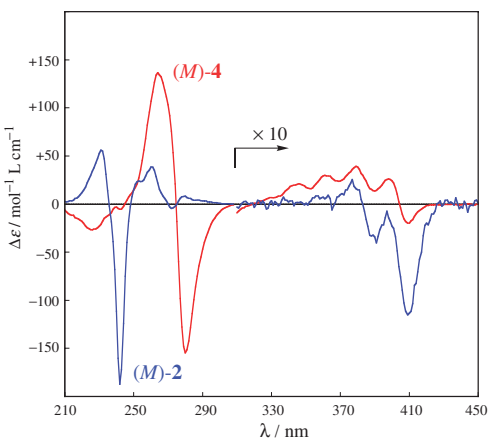

Fig. 5. Comparison of CD spectra of (*M*)-**4** (red) and (*M*)-**2** (blue) in THF.

−90° (or +90°). Therefore, the bisignate shape around 270 nm is a result of an exciton coupling of the β transitions, although there is an overlap with other bands in the short wavelength region. In the p band region, the signs of the CD curves are seemingly different for (*M*)-**2** and (*M*)-**4**, even though these compounds have the same absolute stereochemistry. The calculations suggest that both the compounds have the negative first and the positive second transitions at ca. 390 and 380 nm, respectively. The positive component is more intense than the negative one (excited states 3 and 4 in Table 2) for (*M*)-**4** to give a broad positive band around 380 nm, and the relationship is reversed for (*M*)-**2** to give a negative band at ca. 400 nm.[5] The expanded spectra in Fig. 5 show a delicate balance of the CD curves of structured bands in the p band region. These differences are attributed to the direction and intensity of transition moments, which are perturbed by the position of methoxycarbonyl groups on the anthracene rings. The theoretical calculation by the TDDFT method thus greatly facilitates the analysis of the CD spectra in relation to the absolute stereochemistry.

Experimental

General. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were measured on a Varian Gemini-300 spectrometer at 300 MHz and 75 MHz, respectively. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. UV spectra were measured on a Hitachi U-3000 spectrometer with a 10 mm cell. IR spectra were measured on a JASCO FT/IR-460 spectrometer with a DuraScope attachment by ATR method. CD spectra were measured on a JASCO J-810 polarimeter with a 1 mm cell with THF solutions of ca. 1.0×10^{-4} mol L^{-1} concentration.

(±)-3,3′-Dichloro-9,9′-bianthryl (6). To a refluxing suspension of 1.57 g (6.87 mmol) of 3-chloro-9-anthrone[13] and 1.30 g (19.9 mmol) of zinc powder in 16 mL of acetic acid was slowly added 14 mL of concd HCl from a dropping funnel. After the reaction mixture was further refluxed for 2 h, the whole was poured into 50 mL of water. The insoluble materials were collected by filtration, and washed with water. The organic materials were extracted with dichloromethane. The organic solution was dried over $MgSO_4$ and evaporated. The crude material was purified by chromatography on silica gel with hexane–dichloromethane (50:1) as eluent. Recrystallization from hexane–dichloromethane gave 0.94 g (64%) of the product as yellow crystals; mp 251–253 °C; ^{1}H NMR ($CDCl_3$) δ 6.97–7.20 (6H, m), 7.17 (2H, ddd, J = 1.2, 7.7, 7.9 Hz), 7.47 (2H, ddd, J = 1.2, 7.5, 7.7 Hz), 8.11–8.15 (4H, m), 8.58 (2H, s); ^{13}C NMR ($CDCl_3$) δ 126.0, 126.4, 126.5, 126.6, 126.7, 127.2, 128.4, 128.5, 129.6, 131.3, 131.6, 131.7, 132.1, 133.0; UV ($CHCl_3$) λ_{max} (ε) 262 (245000), 337 (7300), 354 (12500), 374 (20900), 395 nm (26700); Anal. Found: C, 79.64; H, 3.72%. Calcd for $C_{28}H_{16}Cl_2$: C, 79.44; H, 3.81%.

(±)-3,3′-Dicyano-9,9′-bianthryl. A mixture of 1.00 g (2.36

mmol) of **6** and 2.40 g (26.8 mmol) of CuCN in 20 mL of 1-methyl-2-pyrrolidone was refluxed under Ar atmosphere for 72 h. After cooling, the reaction mixture was treated with 12.5 g (46.2 mmol) of $FeCl_3 \cdot 6H_2O$ in 5 mL of concd HCl for 2 h at 80 °C. The mixture was poured into 50 mL of water. The formed solid was collected by filtration and washed with water several times. The crude material was purified by chromatography on silica gel with hexane–dichloromethane (2:1) as eluent. Recrystallization from hexane–dichloromethane gave 0.89 g (93%) of the product as yellow crystals; mp 296–297 °C; ^{1}H NMR ($CDCl_3$) δ 7.02–7.09 (4H, m), 7.22 (2H, dd, $J = 1.7$, 8.6 Hz), 7.29 (2H, m), 7.57 (2H, ddd, $J = 1.2$, 7.5, 7.8 Hz), 8.23 (2H, d, $J = 8.6$ Hz), 8.62 (2H, s), 8.80 (2H, s); ^{13}C NMR ($CDCl_3$) δ 109.1 (C≡N), 119.1, 125.3, 126.4, 126.7, 127.8, 129.1, 129.3, 129.7, 131.3, 131.6, 132.2, 132.6, 133.3, 136.1; IR (ZnSe) 2226 (C≡N) cm^{-1}; UV ($CHCl_3$) λ_{max} (ε) 265 (319000), 272 (319000), 347 (11800), 365 (17500), 385 (24400), 407 nm (30000); Anal. Found: C, 88.72; H, 3.81; N, 6.79%. Calcd for $C_{30}H_{16}N_2$: C, 89.09; H, 3.99; N, 6.93%.

(±)-9,9′-Bianthryl-3,3′-dicarboxylic Acid (3). To a solution of 27 g (0.47 mol) of KOH in 30 mL of H_2O and 100 mL of MeOH was added 1.00 g (2.47 mmol) of 3,3′-dicyano-9,9′-bianthryl. The suspension was refluxed for 24 h to give a yellow solution, which was then acidified by addition of concd HCl. The formed solid was collected by filtration and washed with water. This material was pure enough to use for the next reaction. The yield was almost quantitative. An analytical sample was obtained by recrystallization from acetone as yellow crystals; mp 388–389 °C; ^{1}H NMR (DMSO-d_6) δ 6.91 (2H, d, $J = 8.8$ Hz), 6.97 (2H, d, $J = 9.1$ Hz), 7.30 (2H, ddd, $J = 1.2$, 6.6, 7.8 Hz), 7.57 (2H, t, $J = 7.8$ Hz), 7.66 (2H, dd, $J = 1.6$, 9.1 Hz), 8.33 (2H, d, $J = 8.4$ Hz), 8.99 (2H, d, $J = 1.8$ Hz), 9.16 (2H, s); ^{13}C NMR (DMSO-d_6) δ 125.0, 125.7, 126.0, 126.2, 127.5, 127.6, 129.1, 130.0, 130.1, 131.4, 131.6, 131.7, 132.1, 132.3, 167.2; IR (ZnSe) 1682.5 (C=O) cm^{-1}; Anal. Found: C, 81.22; H, 4.01%. Calcd for $C_{30}H_{18}O_4$: C, 81.44; H, 4.10%.

Camphorsultamamide of (±)-9,9′-Bianthryl-3,3′-dicarboxylic Acid (7). To a suspension of 99 mg (0.23 mmol) of **3** in 8 mL of dry benzene were added 0.070 mL (0.96 mmol) of oxalyl dichloride and a small drop of DMF. The mixture was stirred for 15 h at room temperature to give a clear yellow solution. The volatile materials were removed by evaporation. The yellow residue was practically pure acid dichloride, which was used for the next reaction without further purification. (±)-9,9′-Bianthryl-3,3′-dicarboxylic dichloride: ^{1}H NMR ($CDCl_3$) δ 7.07 (2H, dd, $J = 0.9$, 8.7 Hz), 7.09 (2H, d, $J = 9.0$ Hz), 7.31 (2H, m), 7.57 (2H, dd, $J = 0.8$, 8.4 Hz), 7.66 (2H, dd, $J = 2.1$, 9.0 Hz), 8.26 (2H, d, $J = 8.7$ Hz), 8.96 (2H, s), 9.16 (2H, d, $J = 2.1$ Hz); IR (ZnSe) 1744 (C=O) cm^{-1}. To a solution of 117 mg (0.55 mmol) of (−)-camphorsultam in 10 mL of dry benzene was added 26 mg (0.65 mmol) of sodium hydride, which was prepared by washing a commercially available oil suspension with hexane. After the solution was stirred for 30 min, a solution of the acid dichloride in 30 mL of benzene was slowly added. The reaction mixture was stirred for 15 h, and the solvent was removed by evaporation. The crude product was purified by chromatography on silica gel with hexane–dichloromethane (1:1) as eluent to afford 166 mg (86%) of a mixture of diastereomeric sultamamides as green oil. The diastereomers were separated by HPLC with a Develosil 60-5 column (20 mmϕ × 500 mm) and ethyl acetate–hexane (3:2) as eluent. Two fractions were eluted at 15.0 and 17.5 min. Each isomer was purified by recrystallization from ethyl acetate. Easily eluted isomer (**7a**): yield 72%, yellow crystal; mp 288–290 °C; $[\alpha]_D^{22}$ −64.1 (*c* 0.20, acetone); ^{1}H NMR ($CDCl_3$) δ 1.07 (6H, s), 1.37–1.53 (4H, m), 1.46 (6H, s), 1.88–2.16 (10H, m), 3.47 and 3.60 (4H, ABq, $J = 13.8$ Hz), 4.26 (2H, d, $J = 6.0$ Hz), 7.05 (2H, d, $J = 9.0$ Hz), 7.12 (2H, d, $J = 9.0$ Hz), 7.22 (2H, m), 7.39 (2H, dd, $J = 1.5$, 9.0 Hz), 7.49 (2H, t, $J = 8.0$ Hz), 8.16 (2H, d, $J = 8.1$ Hz), 8.72 (2H, d, $J = 1.5$ Hz), 8.85 (2H, s); ^{13}C NMR ($CDCl_3$) δ 19.9, 21.4, 26.5, 33.1, 38.4, 45.1, 47.8, 48.1, 53.6, 66.1, 124.5, 125.9, 126.9, 127.0, 127.2, 128.8, 129.6, 130.07, 130.14, 131.9, 132.4, 132.5, 133.0, 133.1, 169.8; Anal. Found: C, 68.56; H, 6.41; N, 2.96%. Calcd for $C_{50}H_{48}N_2O_6S_2 \cdot 2(C_4H_8O_2)$: C, 68.75; H, 6.37; N, 2.76%. Less easily eluted isomer (**7b**): yield 60%, yellow crystal, $[\alpha]_D^{22}$ −116.9 (*c* 0.20, acetone); mp 334–335 °C; ^{1}H NMR ($CDCl_3$) δ 1.06 (6H, s), 1.35–1.54 (4H, m), 1.44 (6H, s), 1.88–2.17 (10H, m), 3.47 and 3.58 (4H, ABq, $J = 13.8$ Hz), 4.26 (2H, t, $J = 6.0$ Hz), 7.02 (2H, d, $J = 9.0$ Hz), 7.15 (2H, d, $J = 9.3$ Hz), 7.28 (2H, t, $J = 9.0$ Hz), 7.44 (2H, dd, $J = 1.8$, 9.0 Hz), 7.47 (2H, t, $J = 7.2$ Hz), 8.17 (2H, d, $J = 8.4$ Hz), 8.71 (2H, d, $J = 0.9$ Hz), 8.84 (2H, s); ^{13}C NMR ($CDCl_3$) δ 20.2, 21.4, 26.6, 33.2, 38.4, 45.1, 47.9, 48.2, 53.6, 66.1, 124.7, 125.8, 126.7, 127.1, 127.2, 128.8, 129.7, 130.1, 130.2, 131.9, 132.4, 132.6, 132.9, 133.0, 170.0; Anal. Found: C, 71.44; H, 5.76; N, 3.33%. Calcd for $C_{50}H_{48}N_2O_6S_2$: C, 71.74; H, 5.78; N, 3.35%.

Enantiopure 3,3′-Bis(methoxycarbonyl)-9,9′-bianthryl. To a solution of 18.1 mg (0.022 mmol) of **7b** in 2 mL of THF was added 9.4 mg (0.22 mmol) of $LiOH \cdot H_2O$. The reaction mixture was stirred overnight at room temperature. The solvent was evaporated, and the residue was treated with 5 mL of 6 mol L^{-1} HCl. The formed solid was collected by filtration and washed with dichloromethane and then with water. A solution of this yellow solid in 4 mL of methanol was refluxed with a catalytic amount of sulfuric acid for 15 h. The volatile materials were removed by evaporation and the residue was dissolved in dichloromethane. The organic solution was washed with water, dried over $MgSO_4$, and evaporated. The crude product was purified by chromatography on silica gel with dichloromethane as eluent. Recrystallization from hexane–dichloromethane afforded 6.7 mg (65%) of the pure compound as yellow crystals. (*M*)-(−)-**4**: mp 286–287 °C; $[\alpha]_D^{22}$ −33 (*c* 0.10, acetone); ^{1}H NMR ($CDCl_3$) δ 3.97 (6H, s), 7.07 (4H, m), 7.22 (2H, m), 7.50 (2H, m), 7.67 (2H, dd, $J = 1.7$, 9.2 Hz), 8.20 (2H, d, $J = 8.6$ Hz), 8.84 (2H, s), 8.96 (2H, d, $J = 1.7$ Hz); ^{13}C NMR ($CDCl_3$) δ 52.3, 124.6, 125.9, 126.6, 126.9, 127.2, 128.9, 129.9, 130.3, 131.8, 132.5, 132.6, 132.7, 132.9, 167.1 (one signal is missing due to overlapping); IR (ZnSe) 1718 (C=O) cm^{-1}; CD (THF) λ ($\Delta\varepsilon$): 226 (−26.8), 264 (+136.5), 280 (−154.6), 345 (+2.6), 360 (+3.5), 379 (+3.9), 393 (+2.3), 410 nm (−1.8); Anal. Found: C, 81.48; H, 4.27%. Calcd for $C_{32}H_{22}O_4$: C, 81.69; H, 4.71%. The easily eluted isomer of the sultamamide **7a** was similarly converted into the methyl ester. (*P*)-(+)-**4**: mp 286–287 °C; $[\alpha]_D^{22}$ +32 (*c* 0.10, acetone); CD (THF) λ ($\Delta\varepsilon$): 226 (+27.5), 264 (−133.5), 280 (+151.4), 344 (−2.0), 359 (−2.8), 378 (−3.8), 395 (−2.5), 409 nm (+2.5); Anal. Found: C, 81.38; H, 4.99%. Calcd for $C_{32}H_{22}O_4$: C, 81.69; H, 4.71%. The racemic dimethyl ester was prepared from the racemic dicarboxylic acid in an ordinary manner. (±)-**4**: mp 309–310 °C; IR (ZnSe) 1709 (C=O) cm^{-1}; UV (acetone) λ_{max} (ε) 260 (162000), 344 (7600), 363 (11300), 383 (13300), 404 nm (14800); Anal. Found: C, 81.30; H, 4.59%. Calcd for $C_{32}H_{22}O_4$: C, 81.69; H, 4.71%.

X-ray Analysis. A crystal of **7b** (0.40 × 0.20 × 0.10 mm) was grown from a hexane–dichloromethane solution. The diffraction data were collected on a Rigaku RAXIS-IV imaging plate diffrac-

tometer with Mo Kα radiation ($\lambda = 0.71070$ Å) to a maximum θ value of 25.0° at −100 °C. A total of 16 × 5.00° oscillation images were collected, each being exposed for 150.0 min. 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 on a comtec O2 workstation. The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, and the rest were included in fixed positions. Among 5262 observed reflections, 3321 reflections ($I > 1.0\sigma(I)$) were used for the refinement of 542 variables. The function minimized was $\Sigma[w(|F_o| - |F_c|)^2]$, where $w = [\sigma_c{}^2|F_o| + (p^2/4)|F_o|^2]^{-1}$ ($p = 0.200$). Formula $C_{50}H_{48}N_2O_6S_2$, F. W. 837.06, orthorhombic, space group $P2_12_12_1$ (#19), $a = 13.186(2)$, $b = 29.336(3)$, $c = 12.010(1)$ Å, $V = 4646.1(8)$ Å^3, $Z = 4$, $D_{calcd} = 1.197$ g cm^{-3}, μ(Mo Kα) = 1.64 cm^{-1}, $R1 = 0.096$, $wR2 = 0.156$, GOF 1.20.[14] Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC 246132.

Theoretical CD Calculation. The calculations were carried out by the Gaussian 98 program[15] on a Linux computer. The structures were optimized by the hybrid DFT method at the B3LYP/3-21G* level. The calculations of excited states were carried out by the TDDFT method at the B3LYP/3-21G* level to afford the excitation energies, oscillator strengths, transition velocity dipole moments, and transition magnetic dipole moments for the lowest 35 excited states for each conformer. The CD spectra were obtained from these output data by the standard method reported previously.[5,6a,b] Each excitation was treated as a Gaussian type function with a half band width of 1800 cm^{-1}.

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