Experimental and theoretical investigations of absolute stereochemistry and chiroptical properties of enantiopure 2,2′-substituted 9,9′-bianthryls

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Abstract—The absolute stereochemistry of axially chiral 2,2′-X_2-9,9′-bianthryls (X=COOH, COOMe, and Cl) was determined by X-ray analysis of the (+)-quinidine salt of the diacid to be (*M*)-(−) or (*P*)-(+). The *M* isomers of these compounds showed specific rotations of −115, −123, and −32, respectively, in acetone. The circular dichroism (CD) as well as UV spectra of the two *M* isomers (X=COOMe and Cl) were investigated with the aid of theoretical calculations by the time-dependent DFT (TDDFT) method. The calculations reasonably reproduced the observed CD bands, and suggested a correlation between the signs of *p* or *β′* bands and the absolute stereochemistry. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

The chiroptical properties of various types of chiral biaryl derivatives, especially substituted biphenyls and 1,1′-binaphthyls, have been investigated for correlation with the absolute stereochemistry about the chiral axis.[1–3] Bianthryls are another class of biaryls that can be chiral when substituents are introduced at appropriate positions. Actually, enantiomers of several 1,1′- and 9,9′-bianthryl derivatives were resolved by standard methods.[4,5] The absolute stereochemistry of the former system, e.g. 2,2′-bis(methoxycarbonyl)-1,1′-bianthryl, was unambiguously established by the exciton coupling theory of the CD spectra.[2,6–8] In contrast, this method was far from practical for the corresponding 9,9′-bianthryl derivatives, which afforded only weak and complicated CD bands because of the mutual orientation of the aromatic chromophores,[2] and their absolute stereochemistry remains unknown to the best of our knowledge. Therefore, we determined the absolute stereochemistry of 2,2′-bis(methoxycarbonyl)-9,9′-bianthryl 1 and related compounds by X-ray analysis (Fig. 1). Their CD as well as UV spectra are discussed with the aid of a modern theoretical method based on the time-dependent density functional theory (TDDFT).[9–11] Because 9,9′-bianthryls are known to form inclusion crystals with various guest molecules,[12–14]

the stereochemical information is essential in applying these enantiopure hosts to the host–guest chemistry.

2. Results and discussion

2.1. Preparation of enantiopure compounds

Enantiopure samples of 9,9′-bianthryl-2,2′-dicarboxylic acid derivatives were obtained by the known method (Scheme 1).[5,15] Racemic acid (±)-**3**, prepared from **2** by a standard method, was resolved by the formation of diastereomeric salts with (+)-quinidine. The treatment of the easily crystallized salt **4** with an acid gave the levorotatory diacid **3** in >99% ee ($[\alpha]_D^{25} = -115$), which was used for the present study. The reaction of (−)-**3** with diazomethane gave the corresponding dimethyl
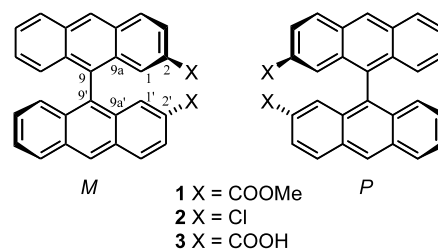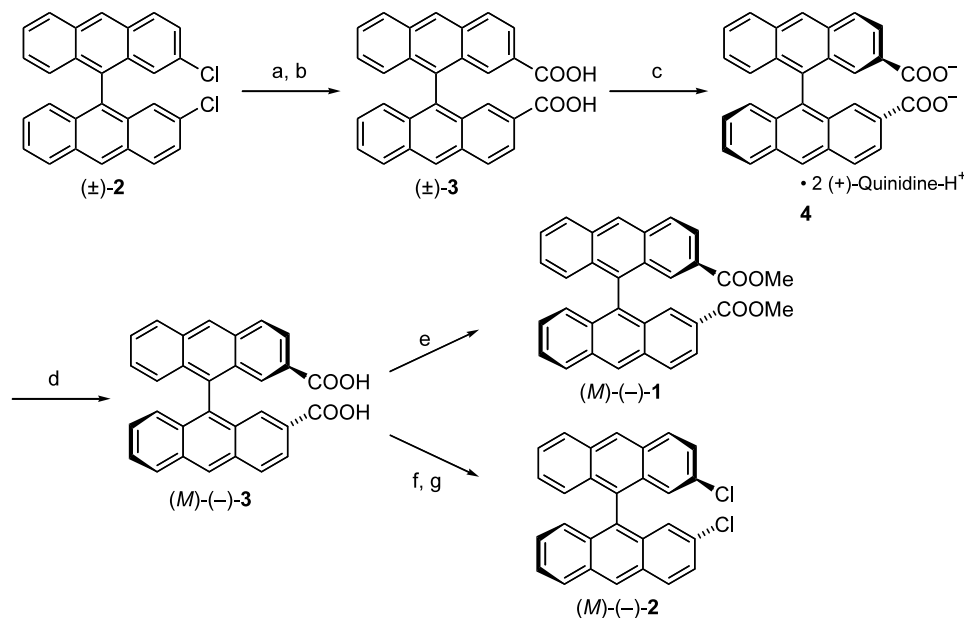

Figure 1.

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Scheme 1. *Reagents and conditions*: (a) CuCN, *N*-methyl-2-pyrrolidone; (b) NaOH, MeOH, H_2O, then HCl_{aq}; (c) (+)-quinidine, acetone, crystallization; (d) HCl_{aq}; (e) CH_2N_2, Et_2O; (f) 2-mercaptopyridine-1-oxide, $EtN=C=N(CH_2)_3NMe_2 \cdot HCl$, CH_2Cl_2; (g) CCl_4, *hv*.

ester (−)-**1**, of which specific rotation was $[\alpha]_D^{25} = -123$. Even though a sample of (−)-**1** was heated at 210°C for 3 days, no racemization was observed.[5] Therefore, the barrier to racemization is higher than 170 kJ/mol, and it is unlikely that the racemization takes place under ordinary reaction conditions.

It has been reported that the racemic dichloride (±)-**2** tended to form inclusion crystals with various small organic molecules.[12–14] We also prepared an enantiopure version of this host compound from (−)-**3** by Barton's method.[16,17] Condensation of (−)-**3** and 2-mercaptopyridine-1-oxide gave the corresponding ester, which was then photolytically decomposed in tetrachloromethane to yield the dichloride in moderate yield. The specific rotation of this product was $[\alpha]_D^{25} = -32$, and no evidence of racemization was found by chiral HPLC.

2.2. X-Ray structure and absolute stereochemistry

X-Ray analysis was carried out for the easily crystallized quinidine salt of (−)-**3**. An ORTEP diagram is shown in Figure 2. The structure was solved so that the quinidine moieties had the known absolute configuration, which was used as the internal reference. The dihedral angle between the two anthryl groups is −68.9(8)°, showing that the absolute stereochemistry about the C(9)–C(9′) axis is *M*. Therefore, the absolute stereochemistry of **3** is (*M*)-(−) or (*P*)-(+), and **1** and **2** have the same stereochemical relationship.

The dihedral angle between two anthracene planes in **4** is smaller than those reported in the parent 9,9′-bianthryl (74.7 and 81.8° for two independent molecules in an asymmetric unit).[18] According to

molecular mechanics calculations on 9,9′-bianthryl, the steric interaction energy increases only by 5 kJ/mol by the change in the dihedral angle from 90° (the most stable conformation) to 68°, but further rotation requires much larger energies. This means that the
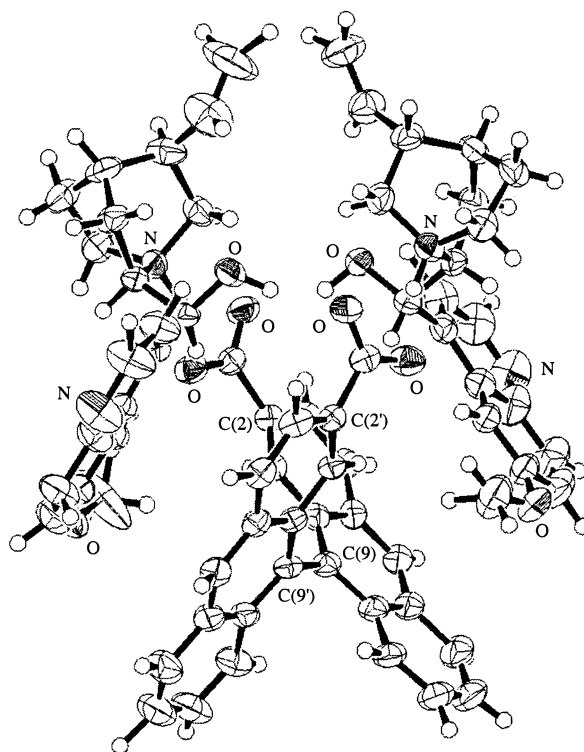

Figure 2. An ORTEP diagram of **4**, (+)-quinidine salt of (*M*)-(−)-**3**, with thermal ellipsoids at 50% probabilities. Solvent molecules are omitted for brevity.

dihedral angles in the 9,9′-bianthryl system are variable within the range of ca. (90±20)° depending on the various factors. A main reason for the small angle in **4** is the interactions between the carboxylate and counter cations in crystal lattices.

2.3. CD and UV spectra

To get further insight into the chiroptical properties of the 9,9′-bianthryls, CD spectra of the *M* isomers were measured in THF. The spectra are given in Figure 3

together with their UV spectra. For (*M*)-**1**, relatively intense troughs were observed at 242 nm (Δε −137) and 268 nm (Δε −31) together with a broad negative band around 400 nm. The CD spectrum of (*M*)-**3** is very similar to (*M*)-**1**. In contrast to the carboxylic derivatives, (*M*)-**2** showed only weak CD bands: complicated bands in the short wavelength range (230–270 nm) and a very broad trough around 380 nm. It is notable that all the compounds give broad negative and structured bands at the longest wavelength due to the π→π* excitation (*p* band) of the anthracene chromophores.
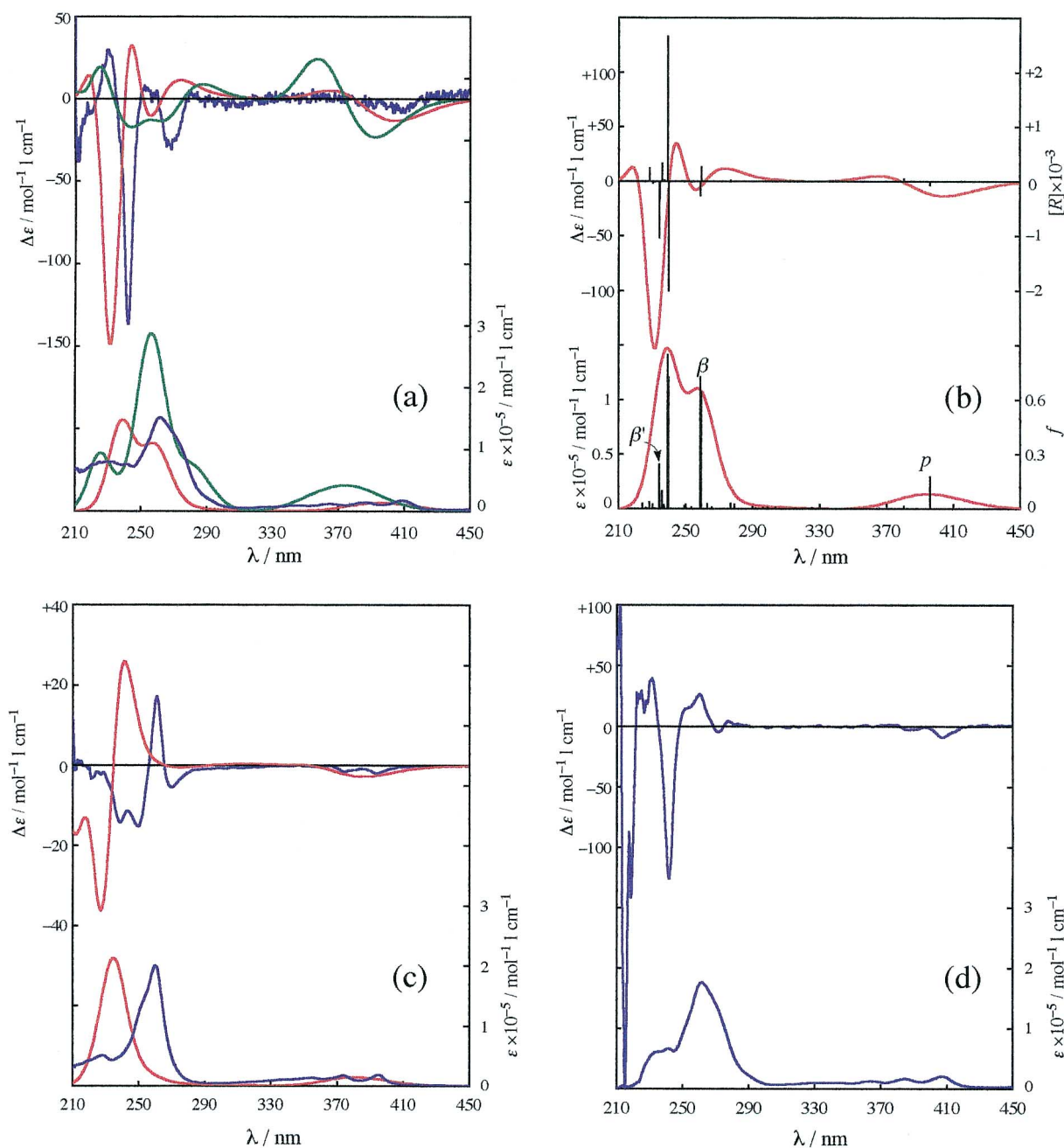

Figure 3. Experimental and calculated CD (top) and UV (bottom) spectra of *M* isomers of **1**–**3**. Experimental (THF): blue. Calculated (TDDFT): red. Calculated (ZINDO): green. (a) (*M*)-**1**: Calculated spectra are weighted averages of the three conformers **1a**–**c**. (b) (*M*)-**1b**: Bars indicate *f* and [*R*] of each excitation. Assignments are given for selected excitations. (c) (*M*)-**2**. (d) (*M*)-**3**.

None of the observed bands appear to be characteristically split CD curves for the exciton coupling (the first negative and the second positive or vice versa). This point was previously discussed by Mason et al. on the basis of the approximated exciton theory: the CD bands around 260 nm due to ^1B_b excitation (β band) become nearly zero in 9,9′-bianthryl when the dihedral angle between the two 9-anthryl groups is close to 90°.[2] However, the amplitude and sign are sensitive to the dihedral angle and the substituents on the anthracene rings. Therefore, we decided to perform the theoretical calculation of the CD spectra for the accurate correlation with the absolute stereochemistry.

The calculations were carried out for (*M*)-**1** and (*M*)-**2**, where the inter- or intramolecular interactions are much less significant than **3**. At the beginning, we used the ZINDO method for the calculation of **1**, because it is known to give the CD or UV spectra with reasonable accuracy and computation time.[19–21] However, this semiempirical MO method did not reproduce the experimental spectra well (Fig. 3(a)). Therefore, we applied the TDDFT method, which was one of the modern theoretical methods based on the DFT theory and recently developed as a useful tool for the calculation of excited state energies.[9–11]

The input structures were optimized by the hybrid DFT method at the B3LYP/3-21G* level of theory. (*M*)-**1** afforded three energy minimum structures with different conformations about the C(2)–C(carbonyl) bonds (Fig. 4). The structural and thermodynamic data are compiled in Table 1. In each structure, the dihedral angles between the anthryl groups are nearly −90°, and the methyl groups are always *cis* to the carbonyl oxygen atoms. The conformer **1b**, where one of the C–C bonds is *s-cis* and the other *s-trans*, is the most stable, and the others are less stable by 2–3 kJ/mol than the global minimum.
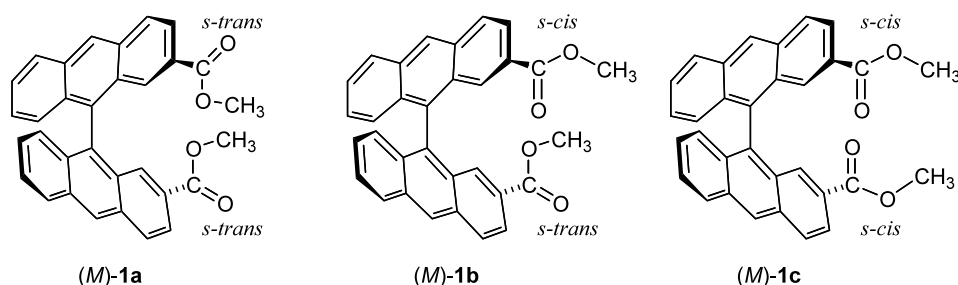
The CD and UV spectra were calculated by the TDDFT method at the same level according to the procedures described in the Experimental section. The spectral patterns of the three conformers **1a**–**c** are quite similar, and the averaged spectrum weighted on the populations is shown in Figure 3(a) together with the experimental and calculated (ZINDO) spectra. The calculated CD and UV spectra agree with the experimental ones, although there is a small blue-shift by ca. 10–20 nm. This discrepancy in wavelength arises mainly from the systematic shift, namely the underestimation or overestimation of excitation energies, inherent in each theory and basis set, and partly from the solvent effects.[11,22] In particular, the total shape and amplitude of the CD curves are excellently reproduced by the TDDFT method, where the systematic shift is only 10 nm even in the short wavelength region. The calculated spectra of the most stable conformer (*M*)-**1b** are shown in Figure 3(b) with oscillator strengths *f* and rotatory strength [*R*] indicated as bars at each excitation energy. This data reveal that negative CD bands at 232 and 405 nm (calcd) are approximately assignable to the β' and *p* bands, respectively. The complicated bands at 240–280 nm are a superposition of several kinds of excitation including the β bands.

The calculations were similarly carried out for (*M*)-**2**, which gave a single optimized structure with the dihedral angle of −91.0°. Because of lack of suitable parameters for the Cl atom in the ZINDO method, the calculation was done only by the TDDFT method (Fig. 3(c)). The calculation suggests positive and negative Cotton effects at 243 and 228 nm, respectively, corresponding to the UV absorption at 235 nm (β band). This CD pattern looks consistent with that observed at 250–265 nm. However, extreme care is necessary for the correlation with the absolute stereochemistry, because this CD band strongly depends on the dihedral angle

(*M*)-**1a**   (*M*)-**1b**   (*M*)-**1c**

Figure 4.

Table 1. Optimized structures of (*M*)-**1** by DFT calculations at B3LYP/3-21G* level

	Conformation[a]	Dihedral angle (°)[b]	Free energy difference (kJ/mol)[c]	Population (%)[c]
(*M*)-**1a**	*s-cis, s-cis*	−89.0	3.0	11.1
(*M*)-**1b**	*s-cis, s-trans*	−89.8	0	74.8
(*M*)-**1c**	*s-trans, s-trans*	−90.0	2.4	14.1

[a] Conformation about the C(2)–C(carbonyl) single bond. *cis* and *trans* denote the relationship between C(1) and the carbonyl oxygen.
[b] Dihedral angle between the two anthracene rings.
[c] At 298 K.

between the anthracene groups as discussed above. In contrast to (*M*)-**1**, the β' bands around 220 nm are much weaker than the β bands in (*M*)-**2**. A broad trough around 385 nm (*p* band) was also reproduced by the TDDFT method except for the vibrational structures. Because this feature is common to **1**, we consider the sign of the *p* band region a helpful clue for the elucidation of the absolute stereochemistry of 2,2'-substituted 9,9'-bianthryls as (*M*)-CD(−) or (*P*)-CD(+). To confirm the scope of this correlation, the CD spectra of other 9,9'-bianthryls are under investigation.

As described above, the TDDFT method can reasonably reproduce the experimental CD and UV spectra with reasonable computational expense for **1** and **2**. This improvement relative to the ZINDO method is attributed to the accuracy in the estimated excitation energies and transition moments. The absolute stereochemistry can be elucidated by the sign of characteristic bands, the *p* bands for both the compounds and the β' bands for **1**. Although there is still room for improvement, the TDDFT method is a useful tool for the study of chiroptical properties of homochiral compounds, especially when other conventional methods such as the exciton chirality method are difficult to apply or other theoretical methods only give ambiguous results.

3. Experimental

3.1. General

Melting points are uncorrected. NMR spectra were measured on either Varian Gemini-300 spectrometer ([1]H: 300 MHz, [13]C: 75 MHz) or JEOL Lambda-500 spectrometer ([1]H: 500 MHz). UV spectra were measured with a Hitachi U-3000 spectrometer with a 10 mm cell. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter with a $3.5\phi \times 100$ mm cell. CD spectra were measured on a JASCO J-810 polarimeter with a 1 mm cell. High-resolution mass spectra were measured on a JEOL MStation-700 spectrometer by the FAB method. Elemental analyses were performed by a Perkin–Elmer 2400 series analyzer.

3.2. Synthesis

Enantiopure 2,2'-bis(methoxycarbonyl)-9,9'-bianthryl was prepared from 2-chloro-9-anthrone by methods similar to those described in the literature.[5,15] Only modified procedures and additional spectroscopic data are described in Sections 3.2.1, 3.2.2, 3.2.3, 3.2.4 and 3.2.5.

3.2.1. (±)-2,2'-Dichloro-9,9'-bianthryl. To a refluxing suspension of 5.50 g (24.1 mmol) of 2-chloro-9-anthrone[23] and 4.72 g (72.2 mmol) of Zn powder in 55 ml of acetic acid was added 48 ml of conc. HCl dropwise. After refluxing for 2 h, the mixture was poured into 90 ml of water. The insoluble materials were collected by filtration, and washed with water for three times. The organic materials were extracted with dichloromethane. The crude was purified by the chromatography on silica gel with hexane/dichloromethane 50:1 eluent. Recrystallization from hexane/dichloromethane gave pure compound as yellow crystal in 94% yield, mp 292–293°C (lit.[15] 296–298°C); ^{1}H NMR (300 MHz, CDCl₃, rt, TMS): δ 6.99 (d, 2H, *J*=8.0 Hz), 7.01 (s, 2H), 7.16–7.21 (m, 2H), 7.39 (dd, 2H, *J*=2.0, 9.0 Hz), 7.45–7.50 (m, 2H), 8.11 (d, 2H, *J*=9.0 Hz), 8.15 (d, 2H, *J*=8.0 Hz), 8.68 (s, 2H); ^{13}C NMR (75 MHz, CDCl₃, rt, TMS): δ 124.7, 125.7, 126.5, 126.7, 126.8, 127.8, 128.7, 129.6, 130.4, 131.5, 131.6, 131.8, 132.0, 132.1.

3.2.2. (±)-2,2'-Dicyano-9,9'-bianthryl. Yellow crystal (1,4-dioxane), yield 90% (lit.[15] 28%), mp 336–337°C (lit.[15] 342.5–345.5°C); ^{1}H NMR (300 MHz, CDCl₃, rt, TMS): δ 7.04 (d, 2H, *J*=8.4 Hz), 7.22–7.31 (m, 2H), 7.40 (s, 2H), 7.53–7.61 (m, 4H), 8.23 (d, 2H, *J*=8.7 Hz), 8.27 (d, 2H, *J*=8.8 Hz), 8.78 (s, 2H); ^{13}C NMR (75 MHz, CDCl₃, rt, TMS): δ 109.7 (CN), 119.2, 124.6, 126.5, 127.3, 127.6, 128.5, 128.9, 129.8, 130.4, 131.4, 132.4, 133.2, 133.2, 133.7.

3.2.3. (±)-9,9'-Bianthryl-2,2'-dicarboxylic acid. Yellow crystal (acetone), yield 99%, mp 406–407°C (dec.) (lit.[15] 412–417°C); ^{1}H NMR (300 MHz, acetone-*d₆*, rt, TMS): δ 7.04 (d, 2H, *J*=8.7 Hz), 7.26–7.32 (m, 2H), 7.57–7.63 (m, 2H), 7.90 (s, 2H), 8.04 (dd, 2H, *J*=1.4, 7.3 Hz), 8.34 (d, 2H, *J*=8.7 Hz), 8.40 (d, 2H, *J*=8.8 Hz), 8.99 (s, 2H); ^{13}C NMR (75 MHz, acetone-*d₆*, rt, TMS): δ 125.3, 125.3, 127.4, 127.8, 128.0, 129.0, 129.1, 130.75, 130.82, 131.6, 133.1, 133.7, 134.1, 135.6, 167.4 (COOH).

3.2.4. Enantiomer resolution of 9,9'-bianthryl-2,2'-dicarboxylic acid. The enantiomer resolution was carried out by formation of diastereomeric salts of (+)-quinidine in acetone. The easily crystallized salt was collected, of which composition was **3**:quinidine:acetone=1:2:2. Analytical data of the salt; mp 217.5–219.0°C (lit.[15] 236–237°C); $[\alpha]_D^{25}=+20$ (*c* 0.01, acetone); Anal. Found: C, 75.81; H, 6.54; N, 4.69%. Calcd for C₃₀H₁₆O₄·2(C₂₀H₂₅N₂O₂)·2(C₃H₆O): C, 75.60; H, 6.51; N, 4.64%. The treatment of this salt with HCl afforded practically enantiopure (−)-acid as yellow crystal in 70% yield (35% from the racemate). The absolute stereochemistry of this enantiomer was determined to be *M* by X-ray analysis of the quinidine salt. (*M*)-(−)-9,9'-Bianthryl-2,2'-dicarboxylic acid; mp 376–377°C (dec); $[\alpha]_D^{25}=-115$ (*c* 0.25, acetone) [lit.[15] −115 (*c* 0.30, acetone)]; CD (THF): λ ($\Delta\varepsilon$) 242 (−126), 260 (26), 271 (−5), 386 (−3), 407 (−9) nm; UV (THF): λ (ε) 262 (173000), 364 (13000), 385 (17000), 408 (21000) nm; MS (FAB HR) [M+H]⁺ calcd for C₃₀H₁₈O₄: 443.1283, found 443.1237. The enantiomeric purity was >99% confirmed by the NMR measurements in the presence of enantiopure shift reagent, Eu(hfc)₃ (europium tris-[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate]).

3.2.5. (*M*)-(−)-2,2'-Bis(methoxycarbonyl)-9,9'-bianthryl. Yellow crystals; yield 86%; mp 238–240°C (lit.[15] 232–233°C); $[\alpha]_D^{25}=-123$ (*c* 0.20, acetone); CD (THF): λ ($\Delta\varepsilon$) 242 (−149), 258 (27), 272 (−7), 391 (−6), 408 (−12) nm; UV (THF): λ (ε) 262 (157000), 365 (17000), 387

(19000), 409 (22000) nm; ^{1}H NMR (300 MHz, CDCl$_3$, rt, TMS): δ 3.67 (s, 6H), 6.97 (dd, 2H, J=0.9, 8.9 Hz), 7.16 (dt, 2H, J=1.2, 6.5 Hz), 7.50 (dt, 2H, J=1.1, 6.5 Hz), 7.84 (s, 2H), 8.01 (dd, 2H, J=1.6, 8.9 Hz), 8.17 (d, 2H, J=8.7 Hz), 8.21 (d, 2H, J=8.6 Hz), 8.73 (s, 2H); ^{13}C NMR (75 MHz, CDCl$_3$, rt, TMS): δ 52.0 (OMe), 124.1, 126.48, 126.51, 126.9, 127.6, 127.7, 128.6, 129.1, 130.2, 130.6, 132.2, 132.5, 132.9, 134.8, 166.9 (C=O). After the pure enantiomer was heated in nitrobenzene-d_5 at 210°C for 3 days, another enantiomer could not be detected by ^{1}H NMR spectrum measured in the presence of Eu(hfc)$_3$. Cf. Data of racemate: mp 279.5–280.5°C; MS (FAB HR) calcd for C$_{32}$H$_{22}$O$_4$: [M+H]$^+$ 471.1596, found 471.1479.

3.2.6. (*M*)-(−)-2,2′-Dichloro-9,9′-bianthryl. To a suspension of 44.6 mg (0.101 mmol) of (*M*)-(−)-9,9′-bianthryl-2,2′-dicarboxylic acid in 16 ml of dichloromethane in a flask covered by aluminium foil was added a solution of 28.0 mg (0.223 mmol) of 2-mercaptopyridine-1-oxide and 46.0 mg (2.40 mmol) of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride in a small amount of dichloromethane. The mixture was stirred at 0°C for 5.5 h. The solvent was removed by evaporation, and the residue was chromatographed on silica gel with ethyl acetate eluent to give 72.0 mg (99%) of the corresponding ester as yellow solid. This material was used in the next reaction without further purification. Bis[2-(1*H*)-thioxo-1-pyridyl] (*M*)-9,9′-bianthryl-2,2′-dicarboxylate; mp 176–178°C (dec.); ^{1}H NMR (500 MHz, CDCl$_3$, rt, TMS): δ 6.54 (dt, 2H, J=1.8, 7.0 Hz), 7.06 (d, 2H, J=8.8 Hz), 7.13 (ddd, 2H, J=1.5, 7.1, 8.9 Hz), 7.24 (ddd, 2H, J=0.5, 7.1, 8.9 Hz), 7.52–7.61 (m, 6H), 8.11 (s, 2H), 8.13 (dd, 2H, J=1.5, 8.8 Hz), 8.19 (d, 2H, J=8.5 Hz), 8.27 (d, 2H, J=8.8 Hz), 8.76 (s, 2H). In 20 ml of tetrachloromethane, 70.5 mg (0.100 mmol) of the ester was dissolved. The solution was refluxed under irradiation with a light bulb (100 W) for 2 h. The solvent was evaporated, and the residue was chromatographed on silica gel with hexane/dichloromethane 1:1 eluent. Recrystallization from hexane afforded the enantiopure dichloride as yellow solid (48%). mp 288–290°C; $[\alpha]_D^{25}=-32$ (c 0.14, acetone); CD (THF): λ ($\Delta\varepsilon$) 239 (−14), 243 (−11), 250 (−14), 261 (16), 270 (−6), 375 (−2), 394 (−2) nm; UV (THF): λ (ε) 228 (50000), 261 (200000), 355 (14000), 374 (17000), 395 (19000) nm; MS (FAB HR) calcd for C$_{28}$H$_{16}$^{35}Cl$_2$: [M+H]$^+$ 422.0629, found 422.0679; Anal. Found: C, 79.07; H, 3.77%. Calcd for C$_{28}$H$_{16}$Cl$_2$: C, 79.44; H, 3.81%. The NMR data are identical with those of the racemate. The enantiopurity was checked by the chiral HPLC (Daicel Chiralcel OD, hexane/2-propanol 200:1 eluent). Whereas the racemate afforded two peaks at the retention times of 20 and 28 min, only the latter was observed for the product, >99% ee.

3.3. X-Ray analysis of 4

A crystal used for the analysis was obtained by crystallization of diastereomerically pure (+)-quinidine salt of (−)-9,9′-bianthryl-2,2′-dicarboxylic acid from acetone. The crystal dimensions were 0.30×0.10×0.10 mm. The diffraction data were collected on a Rigaku RAXIS-IV

imaging plate diffractometer with Mo Kα radiation (λ=0.71070 Å) to a maximum 2θ value of 55.1° at −50°C. A total of 18×5.50° oscillation images were collected, each being exposed for 150.0 min. The reflection data were corrected for the Lorentz-polarization effects and secondary extinction (coefficient=5.303×10^{-8}). The crystal-to-detector distance was 100.0 mm with the detector at the zero swing position. The readout was performed in the 0.100 mm pixel mode. 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 7201 observed reflections, 5639 reflections (I>2.0$\sigma(I)$) were used for the refinement of 824 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=0.0200). Formula C$_{76}$H$_{78}$N$_4$O$_{10}$= C$_{30}$H$_{16}$O$_4$·2(C$_{20}$H$_{25}$N$_2$O$_2$)·2(C$_3$H$_6$O), F. W. 1207.47, Orthorhombic, Space group $P2_12_12_1$, a=23.126(2), b=25.2107(2), c=10.913(1) Å, V=6362.8(6) Å^3, Z=4, D_{calcd}=1.260 g/cm^3, μ(Mo Kα)=0.83 cm^{-1}, R=0.067, R_w=0.095, Goodness of fit 1.27. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 202181. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

3.4. Theoretical CD and UV calculations

The calculations were performed by the Gaussian 98 program[24] on a Linux computer. The molecular structures of (*M*)-**1** and (*M*)-**2** were optimized by the hybrid DFT calculation at the B3LYP/3-21G* level. (*M*)-**1** afforded three optimized conformers, of which free energies were calculated from the thermodynamic data obtained by the vibrational analyses. The calculation of excited states were carried out by the TDDFT method at the same level or by the ZINDO method to give the excitation energies E (in au), oscillator strengths f, transition velocity dipole moment **v**, and transition magnetic dipole moments **m** for the lowest 35 excited states. The dimensionless reduced rotatory strength [R_i] for each excitation was obtained according to the following equation:

$$[R_i]=508.3\frac{\mathbf{v}_i\cdot\mathbf{m}_i}{E_i}$$

where subscript i expresses values for i-th exited state. UV spectra were simulated by using the output values of E and f. CD spectra were simulated by using those of E and [R_i]. Each excitation was treated as Gaussian type function in an ordinary manner: the value of 1800 cm^{-1} was applied for the half band width to reproduce the experimental CD and UV band shape. The treatment and analysis of the calculated data are described in detail in the literature.[10,11,21,22]

Acknowledgements

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