(345 g). The final purification step involved preparative HPLC using a Waters Prep Pak/500 unit. The phyllanthoside (22 injections of approximately 17 g per 100 mL of methylene chloride) was applied to a system containing two precolumns (30.5 × 5.1 and 61 × 5.1 cm) dry packed with Davisil 633 silica gel and two Waters μ-Porasil cartridges. Elution with methylene chloride–methanol–water (97.7:2.1:0.2) and analysis of fractions by analytical HPLC gave phyllanthoside (214 g, 98% purity). Treatment of this material in 600 mL of HPLC grade methylene chloride with carbon black (Darco G-60, 10 g) followed by filtration through prewashed Celite 545, gave analytically pure phyllanthoside (191.4 g). A further 24.2 g of pure compound was isolated by using similar chromatographic procedures.

Acknowledgment. For very necessary support of this investigation we acknowledge assistance provided by Contracts N01-CM-97297 and N01-CM-07300 with the Division of Cancer Treatment, NCI, National Institutes of Health, DHH, Grant Nos. CA-16049-06-08 by the National Cancer Institute, DHH, Mary Dell Pritzlaff, the Olin Foundation (Spencer T. and Ann W.), the Fannie E. Rippel Foundation, the Robert B. Dalton Endowment Fund, Jack W. Whiteman, and the National Science Foundation Regional Facility at the University of South Carolina (CH78-18723). We are also pleased to thank Dr. R. D. Macfarlane for assistance with obtaining the ^{254}Cf plasma desorption mass spectra.

Registry No. 1, 17951-19-8; **2a**, 82209-93-6; **2b**, 63166-73-4; **2c**, 81558-18-1; **2d**, 62955-96-8; **2e**, 91860-53-6; **2f**, 86826-02-0; **2g**, 62948-37-2; **2h**, 86825-99-2; **3a**, 81558-17-0; **3b**, 87925-07-3; **4a**, 86826-01-9; **4b**, 86826-00-8.

Absolute Stereochemistry and Circular Dichroic Properties of Chiral Triptycenes with an Anthracene Chromophore: Application of the CD Exciton Chirality Method to Nondegenerate Systems

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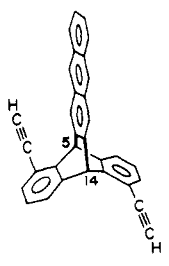
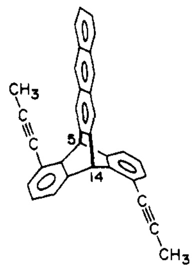
Chiral triptycene compounds with an anthracene chromophore, (5*S*,14*S*)-(+)-1,17-diethynyl-5,14-dihydro-5,14[1′,2′]benzenopentacene (1), (5*S*,14*S*)-(+)-5,14-dihydro-1,17-di-1-propynyl-5,14[1′,2′]benzenopentacene (2), and (5*S*,14*S*)-(+)-dimethyl 5,14-dihydro-5,14[1′,2′]benzenopentacene-1,17-dicarboxylate (3), were synthesized starting from (9*S*,10*S*)-(−)-dimethyl 9,10-dihydro-9,10-ethenoanthracene-1,5-dicarboxylate (4) of known absolute configuration, and their absolute configurations were established on the basis of the chemical correlation. The absolute configurations of the chiral triptycenes were also determined by application of the CD exciton chirality method. The CD spectrum of (+)-1 shows intense positive first and negative second Cotton effects, λ_{ext} 266.4 nm, $\Delta\epsilon$ +203.9, and 228.5 nm, $\Delta\epsilon$ −90.7, which are due to the exciton interaction between the ^1B_b transition of anthracene chromophore and the ^1L_a transitions of two ethynylbenzene chromophores. The positive sign of the first Cotton effect leads to right-handed screw relationships among long axes of the three chromophores. The 5*S*,14*S* absolute configuration of (+)-1 was thus determined in a nonempirical manner. Similar treatments hold for the case of compounds (+)-2 and (+)-3, establishing their absolute configurations on the basis of a chiral exciton coupling mechanism.

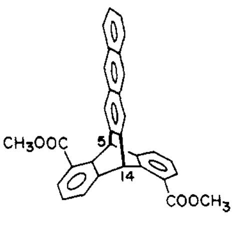
The CD exciton chirality method, a valuable chiroptical tool for determining absolute stereochemistry on the basis of a chiral exciton coupling mechanism, has been extensively applied to various natural and synthetic organic compounds.[1] Recently we applied[2,3] the CD exciton chirality method to synthetic chiral triptycene compounds with three interacting chromophores and achieved chiroptical determination of their absolute configurations in a nonempirical way. In those cases, although the three interacting chromophores were not necessarily identical in structure, the wavelengths of UV absorption maximum of the three chromophores were almost similar to one another; therefore, the compounds were regarded as near-degenerate triple systems. On the other hand, there are many cases of nondegenerate systems in which component



(5S,14S)-(+)-1



(5S,14S)-(+)-2



(5S,14S)-(+)-3

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(3) See also the case of binary systems. (a) Harada, N.; Takuma, Y.; Uda, H. *J. Am. Chem. Soc.* **1976**, *98*, 5408. (b) Harada, N.; Takuma, Y.; Uda, H. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2033. (c) Harada, N.; Takuma, Y.; Uda, H. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 265. (d) Harada, N.; Takuma, Y.; Uda, H. *J. Am. Chem. Soc.* **1978**, *100*, 4029.

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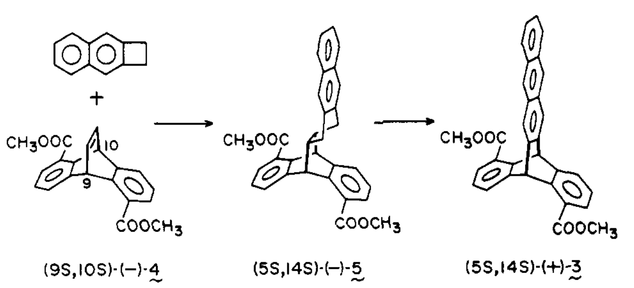
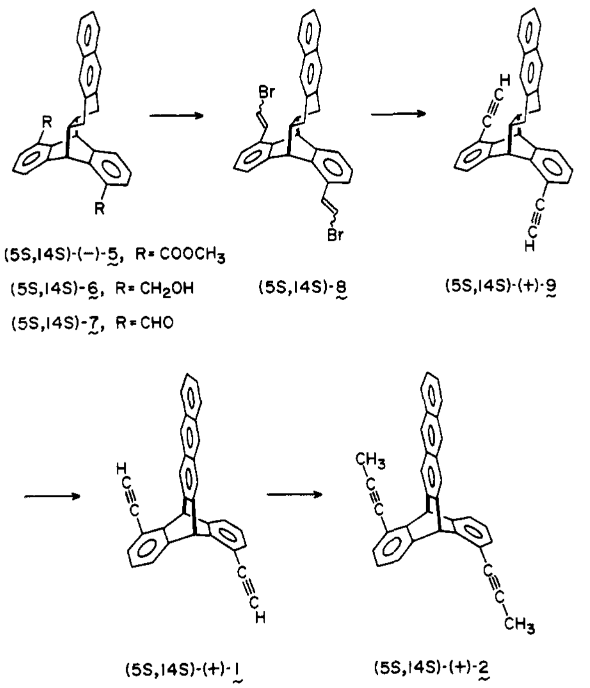
Scheme I



(9S,10S)-(−)-4 (5S,14S)-(−)-5 (5S,14S)-(+)-3

Scheme II



(5S,14S)-(−)-5, R = COOCH₃
(5S,14S)-6, R = CH₂OH
(5S,14S)-7, R = CHO
(5S,14S)-8
(5S,14S)-(+)-9
(5S,14S)-(+)-1
(5S,14S)-(+)-2

chromophores are different, not only in structure but also in the wavelength of UV absorption maximum, from one another. Therefore, it is of significance to study if the CD exciton chirality method can cover such nondegenerate systems.

In this paper, we reveal that the CD exciton chirality method can be satisfactorily extended to nondegenerate systems by exemplifying the case of chiral triptycenes with an anthracene chromophore. Compound 1, (5*S*,14*S*)-(+)-1,17-diethynyl-5,14-dihydro-5,14[1′,2′]benzenopentacene, is quite suitable for studying the mechanism of chromophore–chromophore interaction in nondegenerate systems because the component anthracene chromophore shows an intense ^1B_b absorption band at 265.3 nm and the ethynylbenzene chromophore shows a ^1L_a band of medium intensity at 227.0 nm. Therefore, the gap between the two absorption maxima is about 40 nm in this nondegenerate system. Moreover, the three component chromophores are rigidly fixed to one another by the triptycene skeleton, and hence the exciton chirality between the chromophores can be unambiguously determined. The analysis of the CD data of compound (+)-1 provided good proof that the CD exciton chirality method can be safely applied to nondegenerate systems. Similarly, the data of (5*S*,14*S*)-(+)-5,14-dihydro-1,17-di-1-propynyl-5,14[1′,2′]benzenopentacene (2) and (5*S*,14*S*)-(+)-dimethyl 5,14-dihydro-5,14[1′,2′]benzenopentacene-1,17-dicarboxylate (3) also established the applicability of the CD exciton method to nondegenerate triple systems.

Results and Discussion

Synthesis of Chiral Triptycenes with an Anthracene Chromophore. Compounds 1, 2, and 3 were synthesized starting from (9*S*,10*S*)-(−)-dimethyl 9,10-dihydro-9,10-ethenoanthracene-1,5-dicarboxylate (4) of known absolute configuration,[4] as shown in Schemes I and II. The Diels–Alder reaction of olefin 4 with 1,2-dihydrocyclobuta[*b*]naphthalene[5] was conducted by heating a benzene solution in a sealed tube at 250 °C for 46 h, yielding the adduct (5*S*,14*S*)-(−)-(5), $[\alpha]_D$ −7.7°. The tetrahydroanthracene derivative (−)-5 was dehydrogenated with DDQ in refluxing benzene affording anthracene bis(methyl benzoate) compound (5*S*,14*S*)-(+)-3 as a faintly yellow powder, $[\alpha]_D$ +153.2°.

For the synthesis of acetylenic compounds (+)-1 and (+)-2, the tetrahydroanthracene derivative (−)-5 was employed, instead of (+)-3, in order to avoid possible oxidation of an anthracene moiety. The diester (−)-5 was reduced to the glycol (5*S*,14*S*)-6 with $LiAlH_4$, followed by oxidation with PDC (pyridinium dichromate)[6] under nitrogen, yielding the dialdehyde (5*S*,14*S*)-7 as a white solid material. The dialdehyde 7 was subjected to the Wittig reaction with (bromomethylene)triphenylphosphorane giving a stereoisomeric mixture of the dibromide (5*S*,14*S*)-8. The mixture of the dibromide 8 was employed, without separation, for the next dehydrobromination. Compound 8 was treated with potassium *tert*-butoxide in refluxing THF affording the tetrahydroanthracene bis(ethynylbenzene) compound (5*S*,14*S*)-(+)-9 as a white powder, $[\alpha]_D$ +1.98°. Finally compound (+)-9 was dehydrogenated with DDQ in refluxing benzene, giving the anthracene bis(ethynylbenzene) compound (5*S*,14*S*)-(+)-1 as a white powder, $[\alpha]_D$ +523.8°.

The anthracene bis(1-propynylbenzene) compound (5*S*,14*S*)-(+)-2 was prepared by metalation[7] of compound (+)-1 with *n*-BuLi, followed by quenching with iodomethane: (5*S*,14*S*)-(+)-2, white plate crystals: mp 284.0–287.0 °C; $[\alpha]_D$ +585.5°.

Since the absolute configuration of the bridged molecules remains unchanged throughout all of the above reactions, the 5*S*,14*S* absolute stereochemistry of the dextrorotatory triptycenes with an anthracene chromophore, 1, 2, and 3, was established by the present chemical correlation.

CD Spectra and Chiroptical Determination of Absolute Stereochemistry. The CD and UV spectra of the anthracene bis(ethynylbenzene) compound (+)-1 are shown in Figure 1; the UV spectrum exhibits the intense ^1B_b absorption band (λ_{max} 265.3 nm, ϵ 168 000) of an anthracene moiety, the electric transition moment of which is polarized along the long axis of the anthracene chromophore.[1] The ^1L_a band of the ethynylbenzene chromophore, which is also polarized along the long axis of the chromophore, appears around 227.0 nm (ϵ 54 500).[1] The wavelengths of UV absorption maximum of the component chromophores thus differ from one another, the gap being

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(4) Tatemitsu, H.; Ogura, F.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 915.

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(7) Midland, M M. *J. Org. Chem.* **1975**, *40*, 2250.

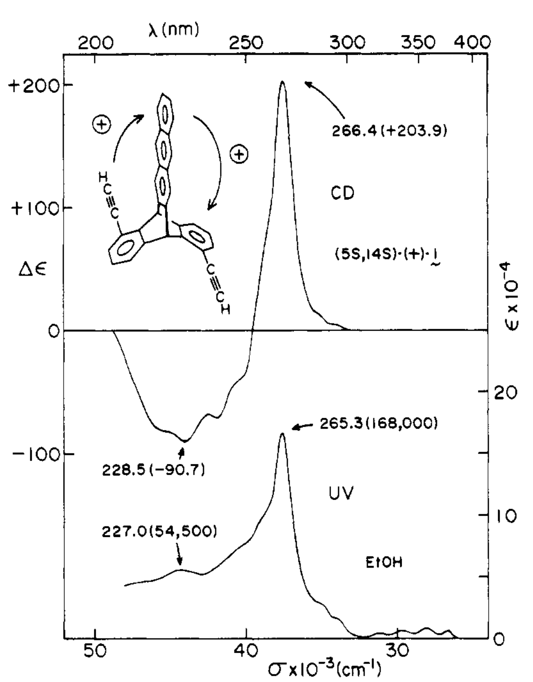


Figure 1. CD and UV spectra of (5*S*,14*S*)-(+)-1,17-diethynyl-5,14-dihydro-5,14[1′,2′]benzenopentacene (**1**) in ethanol.

about 40 nm. Therfore, compound (+)-**1** is one of the representatives of nondegenerate systems.

The CD spectrum of (+)-**1** exhibits very intense exciton split Cotton effects, λ_{ext} 266.4 nm, Δϵ +203.9 and 228.5 nm, Δϵ -90.7 as shown in Figure 1. From the data, it is evident that these Cotton effects are due to the interaction between the ^1B_b exciton of the anthracene moiety and the two ^1L_a excitons of the ethynylbenzene moieties. Since each electric dipole transition moment of these excitons lies along the long axis of the corresponding chromophore, the combination of the long axes of anthracene and one of the ethynylbenzene moieties constitutes a right-handed screw relationship, i.e., a positive exciton chirality, as shown in Figure 1. The same relation holds for the second combination of the anthracene and the other ethynylbenzene because of the C_2-symmetrical nature of the compound, hence leading to a positive chirality. On the other hand, the third combination of the two ethynylbenzene moieties makes no contribution to the CD activity, because the two transition moments located along the long axes of the chromophores are completely parallel to each other. The chiroptical exciton coupling system of (+)-**1** thus consists of two positive exciton chiralities. Accordingly, the observed positive first and negative second Cotton effects lead to an unambiguous chiroptical determination of the 5*S*,14*S* absolute stereochemistry of (+)-**1**. The present conclusion is in accordance with the chemical correlation results described above.

In a similar way, the 5*S*,14*S* absolute stereochemistries of compounds (+)-**2** and (+)-**3** were nonempirically determined from the CD data shown in Figures 2 and 3: (+)-**2**, λ_{ext} 268.7 nm, Δϵ +253.9 and 229.5 nm, Δϵ -111.9; (+)-**3**, λ_{ext} 265.2 nm, Δϵ +136.8 and 221.5 nm, Δϵ -114.0. The assignment of stereochemistry is consistent with the consequence obtained from the syntheses discussed above. The present experimental results thus prove that the CD exciton chirality method for determining absolute stereochemistry is safely applicable to such nondegenerate systems.

In the case of compound (+)-**1**, the ^1L_a transition of the anthracene chromophore is chiroptically inactive, in contrast to the ^1B_b transition. Namely, the ^1L_a absorption band located around 400–320 nm shows no CD Cotton effect, as shown in Figure 1. This phenomenon can be interpreted as follows. The ^1L_a transition of anthracene is polarized along the short axis of the chromophore. Therefore, in the system of compound (+)-**1**, the ^1L_a electric dipole transition moment of the anthracene moiety is completely parallel to the ^1L_a transition moments of the two ethynylbenzene chromophores, the exciton chirality among them being nil. A similar phenomenon was observed in the case of compounds (+)-**2** and (+)-**3**.

The circular dichroic behavior of tetrahydroanthracene bis(ethynylbenzene) compound (+)-**9** and tetrahydroanthracene bis(methyl benzoate) compound (−)-**5** is also interesting from the viewpoint that the component naph-

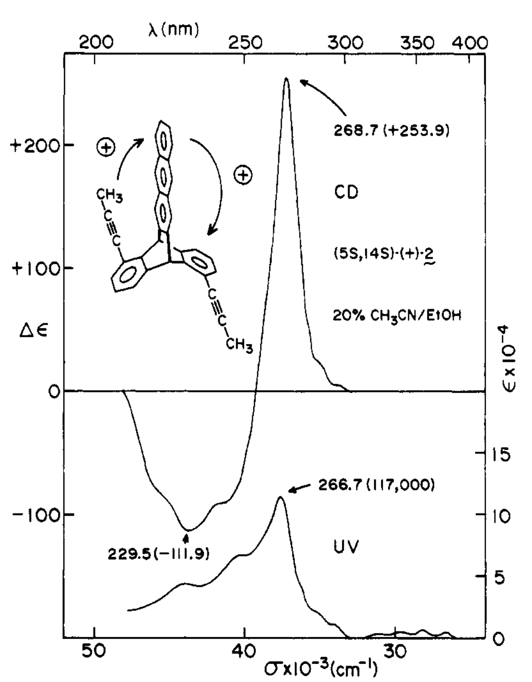


Figure 2. CD and UV spectra of (5*S*,14*S*)-(+)-5,14-dihydro-1,17-di-1-propynyl-5,14[1′,2′]benzenopentacene (**2**) in 20% acetonitrile/ethanol.

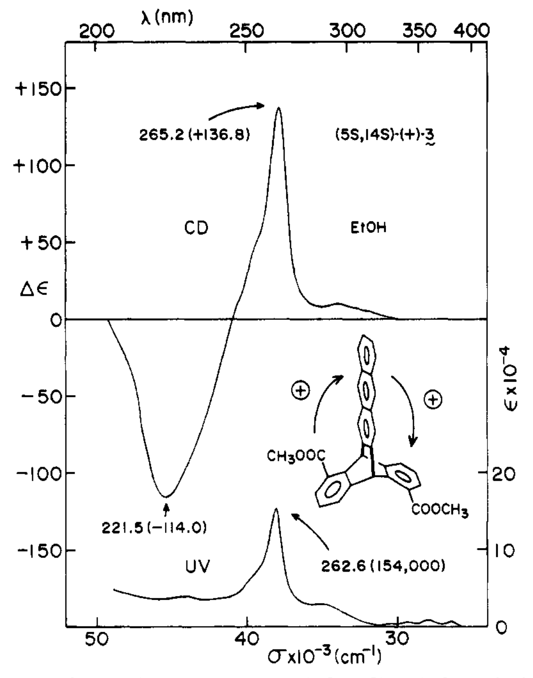


Figure 3. CD and UV spectra of (5*S*,14*S*)-(+)-dimethyl 5,14-dihydro-5,14[1′,2′]benzenopentacene-1,17-dicarboxylate (**3**) in ethanol.

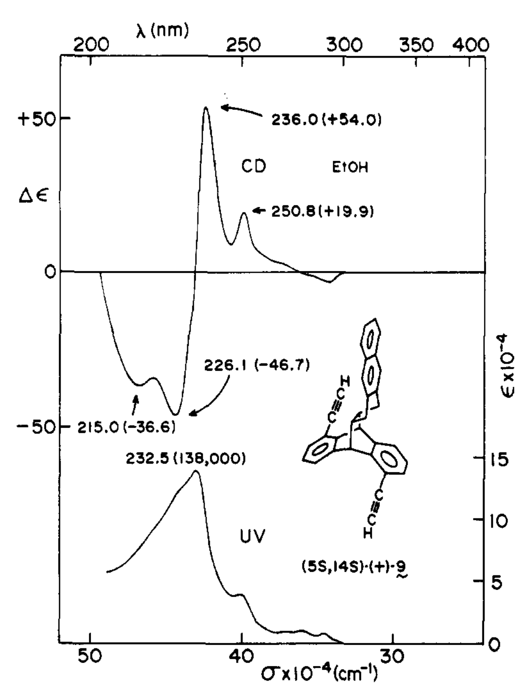
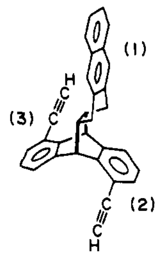


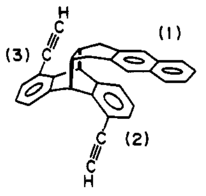
Figure 4. CD and UV spectra of (5*S*,14*S*)-(+)-1,17-diethynyl-5,5a,6,13,13a,14-hexahydro-5,14[1′,2′]benzenopentacene (**9**) in ethanol.

thalene chromophore can interact with the two remaining benzenoid chromophores, in spite of the remote distance between the three chromophores. In fact, the CD spectrum of (+)-**9** exhibits typical exciton split Cotton effects, λ_{ext} 236.0 nm, Δε +54.0 and 226.1 nm, Δε −46.7, which are accompanied by the two side extrema due to the vibrational structure of acetylene groups, λ_{ext} 250.8 nm, Δε +19.9 and 215.0 nm, Δε −36.6 (Figure 4). These Cotton effects originate from the interaction between the ^1B_b exciton of the naphthalene moiety and the two ^1L_a excitons of the ethynylbenzene moieties.

Compound (+)-**9** can adopt two possible conformations as illustrated in **9a** and **9b**. In this case, it is reasonable



9a



9b

to consider that the conformer **9b** is scarcely populated in comparison with **9a** because of the steric repulsion[8] between aromatic moieties. In the molecular structure of **9a**, the combination of the ^1B_b electric transition moment of the naphthalene chromophore 1 and the ^1L_a transition moment of the ethynylbenzene chromophore 2 constitutes a right-handed screwness, i.e., a positive exciton chirality. Similarly, the second combination of the ^1B_b transition moment of the naphthalene 1 and the ^1L_a transition moment of the other ethynylbenzene chromophore 3 constitutes a positive exciton chirality. The third combination of the ^1L_a transition moments of the two ethynylbenzenes 2 and 3 gives rise to no exciton chirality, as in the case of compound (+)-**1**. Although the two exciton chiralities thus obtained are not identical with each other because of the lack of C_2 symmetry in the structure, they are of the same sign. Accordingly, compound (+)-**9** has two positive exciton chiralities. The observed CD spectrum of Figure 4 thus leads to the absolute stereochemical assignment of (5*S*,14*S*)-(+)-**9**, in line with the chemical correlation results.

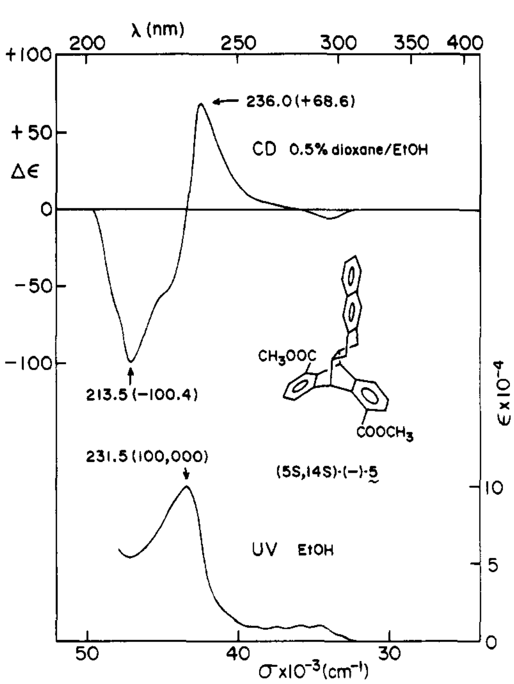
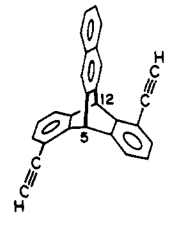


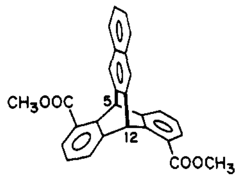
Figure 5. CD and UV spectra of (5*S*,14*S*)-(−)-dimethyl 5,5a,6,13,13a,14-hexahydro-5,14[1′,2′]benzenopentacene-1,17-dicarboxylate (**5**). Solvent: CD, 0.5% dioxane in ethanol; UV, ethanol.

In the case of the tetrahydroanthracene bis(methyl benzoate) compound (−)-**5**, the CD spectrum shows positive first and negative second Cotton effects, λ_{ext} 236.0 nm, Δε +68.6 and 213.5 nm, Δε −100.4, as shown in Figure 5. From the observed positive sign of the exciton chirality, the 5*S*,14*S* absolute stereochemistry was assigned to (−)-**5** in a straightforward manner.

It is worthy of comment that the comparison of the CD data of the tetrahydroanthracene bis(ethynylbenzene) compound (+)-**9** with that of (5*R*,12*R*)-(−)-1,15-diethynyl-5,12-dihydro-5,12[1′,2′]benzenonaphthacene (**10**)[2]



(5R,12R)-(−)-10



(5S,12S)-(+)-11

provides a valuable information on the mechanism of the exciton coupling circular dichroism. Both compounds have one naphthalene and two ethynylbenzene moieties as the component chromophores. In the case of compound (+)-**9**, the naphthalene chromophore is more remote from the two ethynylbenzene moieties than in the case of compound (−)-**10**. Therefore, it is expected that the CD amplitude of (+)-**9** is weaker than that of (−)-**10**, because it is theoretically clarified that the intensity of exciton split Cotton effects is inversely proportional to the square of inter-

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[8] The shortest distance between the naphthalene and ethynylbenzene planes in the conformer **9b** was estimated from a molecular model to be about 2.9 Å, which is smaller than twice (3.4 Å) the van der Waals radius of aromatics. Because of the steric repulsion between these two aromatic moieties, the conformer **9b** is less stable.

chromophoric distance.[9] In fact, this expectation is satisfied by the observed CD data: (+)-**9**, $A = \Delta\epsilon_1 - \Delta\epsilon_2 = +100.7$; (−)-**10**, λ_{ext} 245.5 nm, Δε −138.2 and 215.0 nm, Δε +113.6, $A = -251.8$. Although the signs of the *A* values are opposite to each other because of the mirror image relationship between the two compounds, the *A* value of compound (+)-**9** is considerably smaller than that of (−)-**10**, in agreement with the theoretical expectation.

A similar phenomenon was also observed in the case of compound (−)-**5** and (5*S*,14*S*)-(+)-dimethyl 5,12-dihydro-5,12[1′,2′]benzenonaphthacene-1,15-dicarboxylate (**11**):[2] (5*S*,14*S*)-(−)-**5**, $A = +169.0$; (5*S*,12*S*)-(+)-**11**, λ_{ext} 243.0 nm, Δε +151.1 and 220 nm, Δε −177.8, $A = +328.9$. The concept that a more remote interchromophoric distance leads to smaller exciton split Cotton effects is again evidenced here.

The comparison of the *A* values discussed above also supports the conclusion that conformer **9a** is conformationally stabler than **9b**. In the case of conformer **9b**, the naphthalene chromophore 1 is very close to the ethynylbenzene moiety 2 but far from the other ethynylbenzene moiety 3. Therefore, the CD activity is governed by the positive exciton chirality between chromophores 1 and 2 rather than by the negative one between chromophores 1 and 3. The interchromophoric distance between moieties 1 and 2 of conformer **9b** is much shorter than the corresponding distance of (−)-**10**. Therefore, if conformer **9b** is predominant in the conformational equilibrium, much stronger split Cotton effects are expected. However, the observed *A* value of (+)-**9** is considerably smaller than that of (−)-**10**, as discussed above. The conformational preponderance of **9a** was thus confirmed.

In conclusion, the present studies clarified that the CD exciton chirality method can be safely applied to nondegenerate systems in which component interacting chromophores differ, not only in chemical structure but also in the wavelength of UV absorption maximum, from one another. In this paper, the absolute configurations of nondegenerate chiral triptycenes with an anthracene chromophore were nonempirically and unequivocally determined by application of the CD exciton chirality method.

Experimental Section

General Methods. Melting points were taken on a Yamato capillary melting point apparatus and are uncorrected. IR spectra were obtained as KBr disks or as solutions in $CHCl_3$ on a JASCO A-3 or a Hitachi EPI-G2 spectrophotometer. ^1H NMR spectra were recorded on a JEOL PMX60 or a JEOL JNMPS-100 spectrometer, employing tetramethylsilane as an internal standard. Optical rotations $[\alpha]_D$ were determined on a JASCO DIP-4S spectropolarimeter. UV and CD spectra were obtained on a JASCO UVDEC-505 spectrophotometer and a JASCO J-400X spectropolarimeter, respectively. Mass spectra were obtained on a Shimadzu LKB-9000 spectrometer.

The following CD data are those of the extrema and zero-line intersections.

(5*S*,14*S*)-(−)-Dimethyl 5,5a,6,13,13a,14-Hexahydro-5,14-[1′,2′]benzenopentacene-1,17-dicarboxylate (5). A solution of (9*S*,10*S*)-(−)-dimethyl 9,10-dihydro-9,10-ethenoanthracene-1,5-dicarboxylate (**4**,[2-4] 1.486 g, 4.639 mmol) and 1,2-dihydrocyclobuta[*b*]naphthalene[5] (2.199 g, 14.3 mmol) in dry benzene (25 mL) was heated at 250 °C in a sealed tube for 46 h. The reaction mixture was cooled and evaporated in vacuo to dryness. The residue was chromatographed on silica gel (hexane/EtOAc, 7:1), yielding 0.503 g of the starting material **4** and 1.039 g (48%) of the adduct **5** as a white solid material. Recrystallization from hexane/EtOAc gave an analytical sample: mp 207.0–208.0 °C; IR (KBr) ν_{max} 1720, 1440, 1280, 1145, 1035, 885, 765, 750 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 1.90–2.50 (4 H, m, H-5a,6,13,13a), 2.70–3.20 (2 H, m, H-6,13), 3.96 and 3.98 (3 H each, s, OCH_3), 5.58 and 5.68 (1 H each, s, H-5,14), 7.02–7.88 (12 H, m, Ar); $[\alpha]_D$ −7.7° (*c* 0.10006, $CHCl_3$); UV (EtOH) λ_{max} 287.5 nm (ε 8760), 277.8 (9550), 267.0 (8760), 231.5 (100 000); CD (0.5% dioxane in EtOH) λ_{ext} 294.0 nm (Δε −6.4), 275.0 (0.0), 236.0 (+68.6), 231.0 (0.0), 213.5 (−100.4); MS, *m/e* 474 (parent).

(5*S*,14*S*)-(+)-Dimethyl 5,14-Dihydro-5,14[1′,2′]benzenopentacene-1,17-dicarboxylate (3). A mixture of the adduct (5*S*,14*S*)-(−)-**5** (0.380 g, 0.801 mmol) and DDQ (0.520 g, 2.291 mmol) in dry benzene (40 mL) was refluxed under nitrogen for 21 h. After being cooled to room temperature, a precipitate of DDQ and its reduced species was removed by passing the mixture through a short alumina column and by eluting with $CHCl_3$. The eluate was evaporated to dryness and subjected to preparative TLC on silica gel (benzene), affording 0.119 g (32%) of the diester **3** as a faintly yellow powder: IR (KBr) ν_{max} 1720, 1675, 1440, 1300, 1280, 1195, 1145, 1025, 760, 680 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 4.00 (6 H, s, OCH_3), 7.07 (2 H, s, H-5,14), 7.11 (2 H, t, *J* = 7.5 Hz, H-3,19), 7.38 (2 H, dd, *J* = 3.5, 6.5 Hz, H-9,10), 7.72 (4 H, d, *J* = 7.5 Hz, H-2,4,18,20), 7.92 (2 H, dd, *J* = 3.5, 6.5 Hz, H-8,11), 7.99 (2 H, s, H-6,13), 8.23 (2 H, s, H-7,12); $[\alpha]_D$ +153.2° (*c* 0.10055, $CHCl_3$); UV (EtOH) λ_{max} 375.7 nm (ε 5960), 355.7 (8170), 338.1 (5520), 322.0 (3760), 262.6 (154 000), 228.0 (39 100); CD (EtOH) λ_{ext} 295.0 nm (Δε +9.7), 265.2 (+136.8), 247.5 (0.0), 221.5 (−114.0); MS, *m/e* 470 (parent).

(5*S*,14*S*)-5,5a,6,13,13a,14-Hexahydro-5,14[1′,2′]benzenopentacene-1,17-dimethanol (6). To a suspension of $LiAlH_4$ (0.315 g, 8.30 mmol) in dry ether (60 mL) was added dropwise under nitrogen a solution of the diester (5*S*,14*S*)-(−)-**5** (0.400 g, 0.843 mmol) in dry THF (20 mL) and dry ether (70 mL). After being stirred at room temperature for 1.5 h, the reaction mixture was quenched with a minimum amount of water to precipitate hydroxides. The organic layer was evaporated to dryness, and the residue was chromatographed on silica gel (ether/$CHCl_3$, 1:2), giving 0.391 g (100%) of the glycol **6** as a syrup: IR ($CHCl_3$) ν_{max} 3600, 1440, 1010, 880 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.9–3.0 (6 H, m, H-5a,6,13,13a), 4.53 (2 H, br s, H-5,14), 4.73 (4 H, br s, CH_2O), 6.9–7.8 (12 H, m, Ar).

(5*S*,14*S*)-5,5a,6,13,13a,14-Hexahydro-5,14[1′,2′]benzenopentacene-1,17-dicarbaldehyde (7). A mixture of the glycol (5*S*,14*S*)-**6** (0.058 g, 0.139 mmol), pyridinum dichromate[6] (PDC, 0.162 g, 0.431 mmol), and dry dichloromethane (2.5 mL) was stirred under nitrogen at room temperature for 5 h. After ether (50 mL) was added, the mixture was passed through a silica gel short column, eluting with ether. The eluate was evaporated to dryness and the residue was chromatographed on silica gel (hexane/EtOAc, 3:1), giving 0.048 g (84%) of the dialdehyde **7** as a white solid material: IR ($CHCl_3$) ν_{max} 1700, 1590, 1445, 1405, 1220, 1165, 880, 660 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.9–3.2 (6 H, m, H-5a,6,13,13a), 5.65 and 5.75 (1 H each, s, H-5,14), 7.1–7.8 (12 H, m, Ar), 10.3 (2 H, br s, aldehyde).

(5*S*,14*S*)-1,17-Bis(2-bromoethenyl)-5,5a,6,13,13a,14-hexahydro-5,14[1′,2′]benzenopentacene (8). To a suspension of (bromomethyl)triphenylphosphonium bromide (5.623 g, 12.9 mmol) in dry THF (90 mL) cooled at 0 °C was added dropwise a solution of *n*-butyllithium in hexane (4.6 mL, 8.4 mmol) under nitrogen. After the dark red reaction mixture had been stirred for 25 min, a solution of the dialdehyde (5*S*,14*S*)-**7** (0.290 g, 0.700 mmol) in dry THF (60 mL) was added dropwise. The mixture was stirred for 1 h, poured into water, and extracted with ethyl acetate. The organic layer was washed with brine and evaporated to dryness. The residue was separated by preparative TLC on silica gel, developing with $CHCl_3$. The crude product obtained was further purified by preparative TLC on silica gel, developing with hexane/EtOAc (10:1), yielding 0.310 g (78%) of the dibromide **8** as a white solid material: IR $(CHCl)_3$ ν_{max} 1610, 1595, 1500, 1470, 1435, 1320, 1170, 940, 880 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.8–2.9 (6 H, m, H-5a,6,13,13a), 4.2–4.8 (2 H, m, H-5,14), 6.3–7.7 (16 H, m, vinyl and Ar); MS, molecular ion at *m/e* (relative intensity) 566 (1), 568 (2), 570 (1). The ^1H NMR data indicated that the product was a mixture of three possible stereoisomers.

(5*S*,14*S*)-(+)-1,17-Diethynyl-5,5a,6,13,13a,14-hexahydro-5,14[1′,2′]benzenopentacene (9). To a solution of potassium *tert*-butoxide in *tert*-butyl alcohol (prepared by dissolving 0.380

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[9] Harada, N.; Chen, S. L.; Nakanishi, K. *J. Am. Chem. Soc.* **1975**, *97*, 5345.

g of potassium metal in 70 mL of *tert*-butyl alcohol) was added dropwise a solution of the dibromide (5*S*,14*S*)-**8** (0.305 g, 0.537 mmol) in dry THF (40 mL). The mixture was refluxed under nitrogen for 11 h. After being cooled to room temperature and addition of water (2 mL), the mixture was evaporated in vacuo to dryness and the residue was partitioned by extracting with ethyl acetate. The organic layer was washed with brine and evaporated. The residue was subjected to preparative TLC on silica gel, developing with hexane/EtOAc (10:1), affording 0.174 g (80%) of the diethynyl compound **9** as a white solid material: IR ($\mathrm{CHCl_3}$) ν_{max} 3320, 2120, 1470, 1435, 1175, 880, 660, 620 cm^{-1}; ^{1}H NMR (100 MHz, $\mathrm{CDCl_3}$) δ 1.9–2.5 (4 H, m, H-5a,6,13,13a), 2.5–3.1 (2 H, m, H-6,13), 3.30 and 3.32 (1 H each, s, acetylenic), 4.76 and 4.82 (1 H each, s, H-5,14), 7.0–7.9 (12 H, m, Ar); $[\alpha]_{\mathrm{D}}$ +1.98° (*c* 0.10122, $\mathrm{CHCl_3}$); UV (EtOH) λ_{max} 277.0 nm (ϵ 9420), 249.5 (39 600), 232.5 (138 000); CD EtOH) λ_{ext} 292.2 nm ($\Delta\epsilon$ −2.82), 276.0 (0.0), 250.8 (+19.9), 236.0 (+54.0), 232.5 (0.0), 226.1 (−46.7), 215.0 (−36.6), 204.0 (0.0); MS, *m/e* 406 (parent).

(5*S*,14*S*)-(+)-1,17-Diethynyl-5,14-dihydro-5,14[1′,2′]-benzenopentacene (1). A mixture of the tetrahydroanthracene compound (5*S*,14*S*)-**9** (0.125 g, 0.246 mmol) and DDQ (0.170 g, 0.749 mmol) in dry benzene (20 mL) was refluxed under nitrogen for 21 h. After being cooled, the mixture was passed through a short alumina column, eluting with chloroform. The eluate was evaporated to dryness and subjected to preparative TLC on silica gel (hexane/EtOAc, 7:1) affording 0.037 g (30%) of the anthracene compound **1** as a white solid material. Attempts to recrystallize the product from various solvents gave white powders instead of crystals: IR ($\mathrm{CHCl_3}$) ν_{max} 3300, 2120, 1585, 1470, 1430, 1295, 1200, 1160, 910, 715, 660, 650, 620, 480 cm^{-1}; ^{1}H NMR (100 MHz, $\mathrm{CDCl_3}$) δ 3.42 (2 H, s, acetylenic), 6.06 (2 H, s, H-5,14), 7.04 (2 H, t, J = 7.8 Hz, H-3,19), 7.27 (2 H, dd, J = 1.7, 7.8 Hz, H-4,20), 7.43 (2 H, dd, J = 3.5, 7.0 Hz, H-9,10), 7.56 (2 H, dd, J = 1.7, 7.8 Hz, H-2,18), 7.96 (2 H, dd, J = 3.5, 7.0 Hz, H-8,11), 7.96 (2 H, s, H-6,13), 8.27 (2 H, s, H-7,12); $[\alpha]_{\mathrm{D}}$ +523.8° (*c* 0.09259, $\mathrm{CHCl_3}$); UV (EtOH) λ_{max} 374.8 nm (ϵ 7040), 354.8 (9460), 337.2 (6240), 321.4 (3220), 293.2 (17 500), 265.3 (168 000), 227.0 (54 500); CD (EtOH) λ_{ext} 266.4 nm ($\Delta\epsilon$ +203.9), 254.0 (0.0), 240.3 (−70.7), 228.5 (−90.7), 207.0 (0.0); MS, *m/e* 402 (parent).

(5*S*,14*S*)-(+)-5,14-Dihydro-1,17-di-1-propynyl-5,14[1′,2′]-benzenopentacene (2). To a solution of the diethynyl compound (5*S*,14*S*)-(+)-**1** (0.059 g, 0.147 mmol) in dry THF (8 mL) was added, under nitrogen at 0 °C, dropwise a hexane solution of *n*-butyllithium (1.54 M, 0.2 mL, 0.308 mmol). After being stirred for 20 min, a solution of iodomethane (0.200 g, 1.409 mmol) in dry THF (1.5 mL) was added dropwise at 0 °C. The reaction mixture was stirred at room temperature for 1 h, poured into water, and extracted with ether. The organic layer was washed with brine and evaporated to dryness. The residue was subjected to preparative TLC on silica gel (hexane/EtOAc, 10:1), giving a white solid material. The crude product obtained was further purified by recrystallization from hexane/ethyl acetate, yielding 0.038 g (60%) of the di-1-propynyl compound **2** as plate crystals: mp 284–287 °C; IR (KBr) ν_{max} 2250, 1590, 1475, 1430, 1295, 1205, 1160, 905, 800, 760, 750, 690, 650 cm^{-1}; ^{1}H NMR (100 MHz, $\mathrm{CDCl_3}$) δ 2.25 (6 H, s, methyl), 6.00 (2 H, s, H-5,14), 6.99 (2 H, dd, J = 7.0, 7.5 Hz, H-3,19), 7.17 (2 H, dd, J = 1.8, 7.5 Hz, H-4,20), 7.42 (2 H, dd, J = 3.5, 6.5 Hz, H-9,10), 7.44 (2 H, dd, J = 1.8, 7.0 Hz, H-2,18), 7.97 (2 H, dd, J = 3.5, 6.5 Hz, H-8,11), 7.97 (2 H, s, H-6,13), 8.29 (2 H, s, H-7,12); $[\alpha]_{\mathrm{D}}$ +585.5° (*c* 0.0497, $\mathrm{CHCl_3}$); UV (20% $\mathrm{CH_3CN}$ in EtOH) λ_{max} 375.0 nm (ϵ 5180), 354.8 (7360), 337.1 (5180), 293,2 (13 400), 266.7 (117 000), 228.0 (43 600); CD (20% $\mathrm{CH_3CN}$ in EtOH) λ_{ext} 295.0 nm ($\Delta\epsilon$ +6.7), 268.7 (+253.9), 255.2 (0.0), 229.5 (−111.9), 209.1 (0.0); MS, *m/e* 430 (parent).

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Registry No. (5*S*,14*S*)-(+)-**1**, 92011-54-6; (5*S*,14*S*)-(+)-**2**, 92011-55-7; (5*S*,14*S*)-(+)-**3**, 92011-56-8; (9*S*,10*S*)-(−)-**4**, 40443-30-9; (5*S*,14*S*)-(−)-**5**, 92011-57-9; (5*S*,14*S*)-**6**, 92011-58-0; (5*S*,14*S*)-**7**, 92011-59-1; (5*S*,14*S*)-**8**, 92011-60-4; (5*S*,14*S*)-(+)-**9**, 92011-61-5; (bromomethyl)triphenylphosphonium bromide, 1034-49-7.