Absolute Stereochemistry and Chiroptical Properties of Chiral Tribenzotriptycene and Benzotriptycenes

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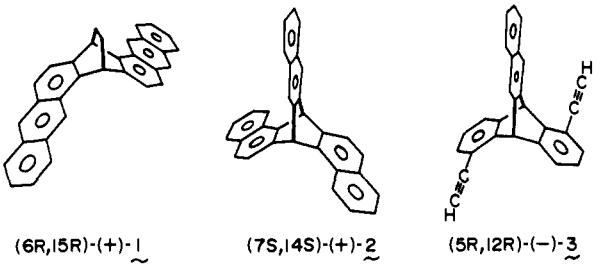
Abstract: The unequivocal and nonempirical chiroptical determination of the absolute configuration of chiral triptycenes, (5*R*,12*R*)-(−)-1,15-diethynyl-5,12-dihydro-5,12[1′,2′]benzenonaphthacene (**3**) and (5*S*,12*S*)-(+)-5,12-dihydro-5,12[1′,2′]-benzenonaphthacene-1,15-dicarbonitrile (**15**), was achieved by applying the CD exciton chirality method. The CD spectrum of (−)-**3** clearly exhibited, around 240 nm, intense negative first and positive second Cotton effects due to the negative exciton coupling between the long-axis-polarized ^1B_b transition of naphthalene and the long-axis-polarized ^1L_a transitions of two ethynylbenzene chromophores. The result that (−)-**3** consists of negative chirality led to unambiguous determination of the (5*R*,12*R*) absolute configuration of (−)-**3**. The same was true for compound (+)-**15**. On the other hand, chiral tribenzotriptycene, (7*S*,14*S*)-(+)-7,14-dihydro-7,14[1′,2′]naphthalenobenzo[*a*]naphthacene (**2**), showed four CD Cotton effects around 200–300 nm, which were unexpected from the simple exciton coupling mechanism. The complex pattern of the CD curve of (+)-**2** was satisfactorily explicable by the terms of an interchromophoric homoconjugation effect.

Recently we reported the ideal chiral exciton coupling of a cage compound, (6*R*,15*R*)-(+)-6,15-dihydro-6,15-ethanonaphtho[2,3-*c*]pentaphene (**1**),[1] a binary system composed of two anthracene chromophores, which demonstrated the consistency between the CD exciton chirality and X-ray Bijvoet

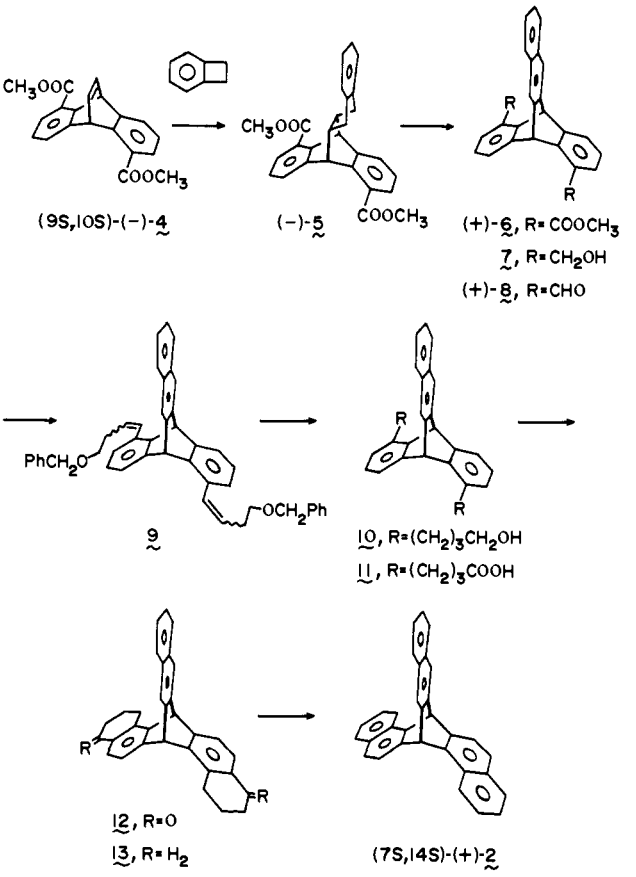


methods for determining absolute stereochemistry. Because of its nonempirical nature, the CD exciton chirality method is powerful for determining the absolute configuration of organic compounds. For example, a recent application of the CD exciton chirality method to insect antifeeding clerodane diterpenes revised the previously accepted absolute configuration of clerodin which had been proposed by X-ray crystallographic studies.[2]

As in the case of binary systems, the present CD exciton method has been successfully applied to triple systems of sugar and steroidal tribenzoates for configurational and conformational studies.[3] Chiral triptycenes are also suitable cage compounds for investigating the extension of the CD exciton method to triple systems, because of rigid spatial arrangement of three chromophores. In fact, a number of chiral triptycenes have been studied to date.[4] However, no ideal triptycene compound permitting unambiguous and reliable chiroptical determination of absolute configuration has yet been reported.

This paper reports the first unambiguous and nonempirical determination of the absolute configuration of chiral triptycenes, (5*R*,12*R*)-(−)-1,15-diethynyl-5,12-dihydro-5,12-[1′,2′]benzenonaphthacene (**3**) and (5*S*,12*S*)-(+)-5,12-dihydro-5,12-[1′,2′]benzenonaphthacene-1,15-dicarbonitrile (**15**), achieved by applying the CD exciton chirality method, and also describes the important role of the interchromophoric homoconjugation effect in the circular dichroism of chiral tribenzotriptycene, (7*S*,14*S*)-(+)-7,14-dihydro-7,14[1′,2′]naphthalenobenzo[*a*]naphthacene (**2**),[5] an inherently dissymmetrical triptycene compound composed of three naphthalenes.[6]

Scheme I



Results and Discussion

Synthesis and Absolute Stereochemistry. Chiral tribenzotriptycene **2** was synthesized as shown in Scheme I starting from (9*S*,10*S*)-(−)-dimethyl 9,10-dihydro-9,10-ethenoanthracene-1,5-dicarboxylate (**4**),[1,7] the absolute configuration of which had been established by the X-ray Bijvoet[8] and CD exciton chirality[1] methods and chemical correlations.[9]

The Diels–Alder reaction[10] of (9*S*,10*S*)-(−)-**4** with benzocyclobutene[11] in a sealed tube at 250 °C gave the adduct (5*S*,12*S*)-(−)-**5**, $[\alpha]_D$ −126.9°, in quantitative yield, which was dehydrogenated with DDQ at 200 °C affording (5*S*,12*S*)-(+)-dimethyl 5,12-dihydro-5,12[1′,2′]benzenonaphthacene-1,15-dicarboxylate (**6**),[12] $[\alpha]_D$ +123.2°. The

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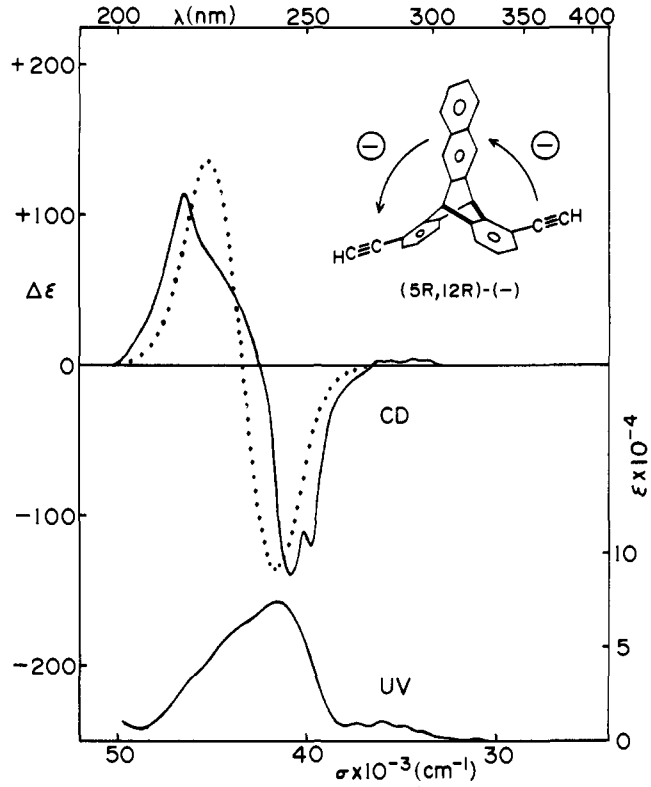


Figure 1. UV and CD spectra of (5*R*,12*R*)-(−)-**3** in EtOH: UV, λ_{max} 241.0 nm (ε 75 000); CD, λ_{ext} 245.5 nm (Δε −138.2) and 215.0 (+113.6). Dotted line shows the CD spectrum calculated[17] by the application of the CD exciton chirality method: λ_{ext} 240.0 nm (Δε −135.5) and 221.0 (+135.3).

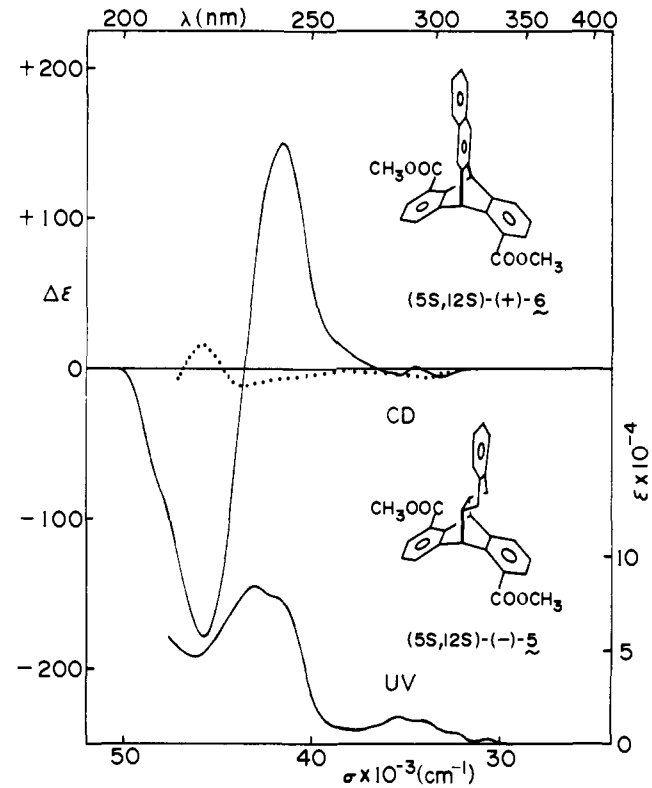
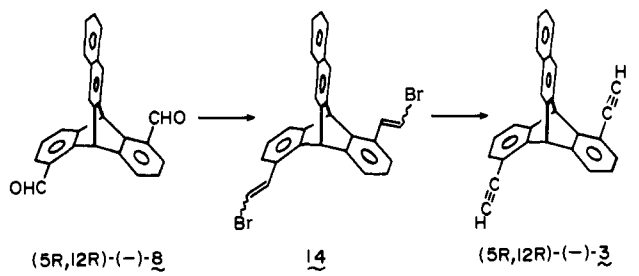
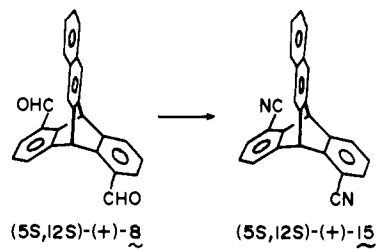


Figure 2. Comparison of CD spectra of (5*S*,12*S*)-(+)-**6** and (5*S*,12*S*)-(−)-**5**: UV and CD of (+)-**6** in EtOH (solid lines), λ_{max} 232.5 nm (ε 83 800), λ_{ext} 242.5 nm (Δε +151.1) and 219.6 (−177.8); CD of (−)-**5** in EtOH (dotted line), λ_{ext} 229.0 nm (Δε −10.1) and 219.0 (+12.8).

Scheme II



Scheme III



diester **6** was quantitatively reduced to the glycol **7** with $LiAlH_4$ at room temperature, followed by oxidation with activated MnO_2 under nitrogen giving (5*S*,12*S*)-(+)-5,12-dihydro-5,12[1′,2′]benzenonaphthacene-1,15-dicarbaldehyde (**8**), $[\alpha]_D$ +199.4°. In contrast to air-sensitive 9,10-dihydro-9,10-ethanoanthracene-1,5-dicarbaldehyde,[1b] the dialdehyde **8** was stable and could be stored in air. The dialdehyde **8** was subjected to the Wittig reaction with excess triphenyl[3-(phenylmethoxy)propylidene]phosphorane[1b] at −70 °C under nitrogen, yielding a stereoisomeric mixture of the bis(benzyl ether) **9.** Catalytic hydrogenation of the bis(benzyl ether) **9** over palladium on charcoal in $AcOH/H_2SO_4$ and successive alkaline hydrolysis of the intermediary acetate formed afforded the glycol **10.** The glycol **10** was oxidized with Jones reagent to the dibutyric acid **11** in quantitative yield, followed by cyclization of the dibutyric acid **11** with polyphosphoric acid yielding the diketone **12** of the tribenzotriptycene skeleton. The Huang-Minlon reduction of the diketone **12** afforded the hydrocarbon **13,** which was subsequently dehydrogenated with DDQ in refluxing benzene to give the desired (7*S*,14*S*)-(+)-tribenzotriptycene (**2**), $[\alpha]_D$ +239.8°, in good yield.

The diethynyl compound (5*R*,12*R*)-(−)-**3** was synthesized as shown in Scheme II from the levorotatory dialdehyde, (5*R*,12*R*)-(−)-**8,** which was obtainable by the optical resolution[12] of the dicarboxamide prepared from racemic 5,12[1′,2′]benzenonaphthacene-1,15-dicarboxylic acid and (*S*)-(−)-α-phenylethylamine.[13] The Wittig reaction of (5*R*,12*R*)-(−)-**8** with (bromomethylene)triphenylphosphorane[14] gave the dibromide **14,** the NMR spectrum of which indicated that the product was a stereoisomeric mixture of the double bonds. The dibromide **14** was dehydrobrominated by refluxing in THF with potassium *tert*-butoxide, affording the diethynyl compound (−)-**3,** $[\alpha]_D$ −270.9°, in good yield.[15]

The dinitrile compound (5*S*,12*S*)-(+)-**15,** $[\alpha]_D$ +234.4°, was prepared from the dialdehyde (5*S*,12*S*)-(+)-**8** by oxime formation and successive dehydration in refluxing acetic anhydride (Scheme III).

Since the absolute configuration of the bridge system remains unchanged throughout all of the above reactions, the absolute stereochemistries of tribenzotriptycene **2** and benzotriptycenes **3** and **15** have been established by the present chemical correlations.

Chiral Exciton Coupling in the CD of Benzotriptycenes and Chiroptical Determination of Absolute Stereochemistry. The CD spectrum of chiral diethynylbenzotriptycene (−)-**3** clearly exhibits, around 240 nm, intense negative first and positive second Cotton effects, λ_{ext} 245.5 nm (Δε −138.2) and 215.0 (+113.6); A ($\Delta\epsilon_1 - \Delta\epsilon_2$) = −251.8, due to the exciton cou-

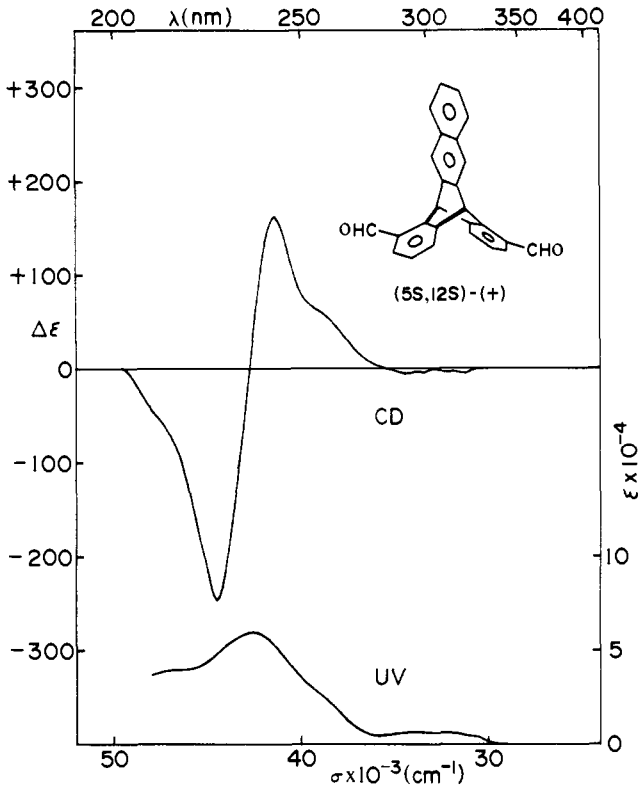


Figure 3. UV and CD spectra of (5*S*,12*S*)-(+)-**8** in EtOH.

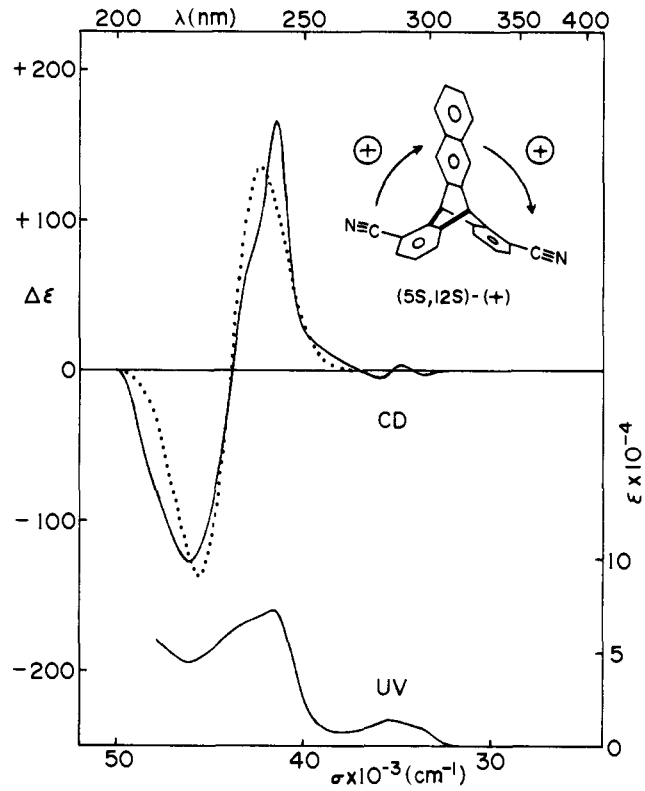


Figure 4. UV and CD spectra of (5*S*,12*S*)-(+)-**15** in EtOH: UV, λ_{max} 241.0 nm (ϵ 72 400); CD, λ_{ext} 241.0 nm ($\Delta\epsilon$ +166.0) and 217.0 (−127.3). Dotted line shows the CD spectrum calculated[17] by the CD exciton chirality method: λ_{ext} 236.0 nm ($\Delta\epsilon$ +136.2) and 219.0 (−136.2).

pling between the ^1B_b transition of naphthalene and the intramolecular charge transfer or ^1L_a transition of two ethynylbenzene chromophores (Figure 1).

The polarization properties of UV transitions of naphthalene and monosubstituted benzene chromophores are well established.[16] For example, the allowed ^1B_b transition of 2,3-dimethylnaphthalene (λ_{max} 226 nm, ϵ 92 500) and the intramolecular charge transfer or ^1L_a transition of ethynylbenzene (λ_{max} 234 nm, ϵ 15 000) are polarized parallel to the long axis of the chromophores, respectively. In the case of (−)-**3**, these two transitions occupy the ideal chiral position for generating the exciton coupling CD activity. Namely, the combination of the long axes of the naphthalene and one ethynylbenzene moieties makes negative exciton chirality as shown in Figure 1. The same is true for the second combination of the naphthalene and the other ethynylbenzene. On the other hand, the third combination of two ethynylbenzene chromophores does not contribute to the CD activity, because these two transitions are parallel to each other, the exciton chirality between them being nil. After all, the diethynyl compound (−)-**3** consists of two negative exciton chiralities. Thus, the observed negative sign of the first Cotton effect leads to unequivocal and nonempirical determination of the (5*R*,12*R*) absolute configuration of (−)-**3**, in line with the chemical correlation results.

As discussed in the following paper, the numerically calculated CD spectrum[17] of (−)-**3** based on the chiral exciton coupling mechanism and empirical parameters taken from the UV spectra of ethynylbenzene and 2,3-dimethylnaphthalene is in excellent agreement with the observed one, establishing the above assignment in a quantitative manner (Figure 1).

The present chiral exciton coupling mechanism is confirmed by comparison of the CD spectra of the benzotriptycene diester (+)-**6** and the hexahydrobenzotriptycene diester (−)-**5** (Figure 2). The diester (+)-**6** exhibits typical and strong exciton Cotton effects of positive chirality, λ_{ext} 242.5 nm ($\Delta\epsilon$ +151.1) and 219.6 (−177.8); A = +328.9, as (−)-**3** does. On the other hand, (−)-**5** shows 14 times smaller Cotton effects, λ_{ext} 229.0 nm ($\Delta\epsilon$ −10.1) and 219.0 (+12.8), than those of (+)-**6**, because (−)-**5** lacks the ^1B_b transition of naphthalene responsible for constitution of exciton chirality. Similarly, the dialdehyde (+)-**8** and the dinitrile (+)-**15** exhibit typical exciton Cotton effects of positive chirality, λ_{ext} 241.0 nm ($\Delta\epsilon$ + 163.0) and 225.0 (−244.4); A = +407.4, and λ_{ext} 241.0 nm ($\Delta\epsilon$ +166.0) and 217.0 (−127.3); A = +293.3, respectively, confirming the above configurational assignment (Figures 3 and 4). However, for rigorous application of the CD exciton method, the diester **6** and the dialdehyde **8** are less suitable than the diethynyl compound **3** and the dinitrile **15** because of conformational ambiguity around the single bond connecting benzene and ester or aldehyde group. Thus, the diethynyl compound (−)-**3** and the dinitrile (+)-**15** of definite conformation are quite ideal for application of the CD exciton chirality method.

Circular Dichroism of Tribenzotriptycene. Unlike the case of the diethynyl compound (−)-**3** and the dinitrile (+)-**15**, the CD spectrum of tribenzotriptycene (+)-**2** exhibits very complex CD Cotton effects around 200–300 nm, which were entirely unexpected from the simple exciton coupling mechanism (Figure 5). Since tribenzotriptycene (+)-**2** consists of two positive and one negative exciton chiralities between three ^1B_b transitions of naphthalene moieties, two Cotton effects of positive first and negative second signs were expected in the ^1B_b transitional region, from the viewpoint of chiral exciton interaction.[18] However, the observed CD spectrum showed four Cotton effects in the corresponding region.

The UV spectrum also reflects the complex electronic structural features of compound (+)-**2**. A new absorption band of medium intensity appears at 264.5 nm (ϵ 35 800) which is not observable in the UV spectrum of naphthalene itself. These phenomena imply the considerable contribution of the interchromophoric homoconjugation effect[19] to the CD and UV activity. In fact, as discussed in the following paper, the SCF-CI-dipole velocity molecular orbital calculation in-

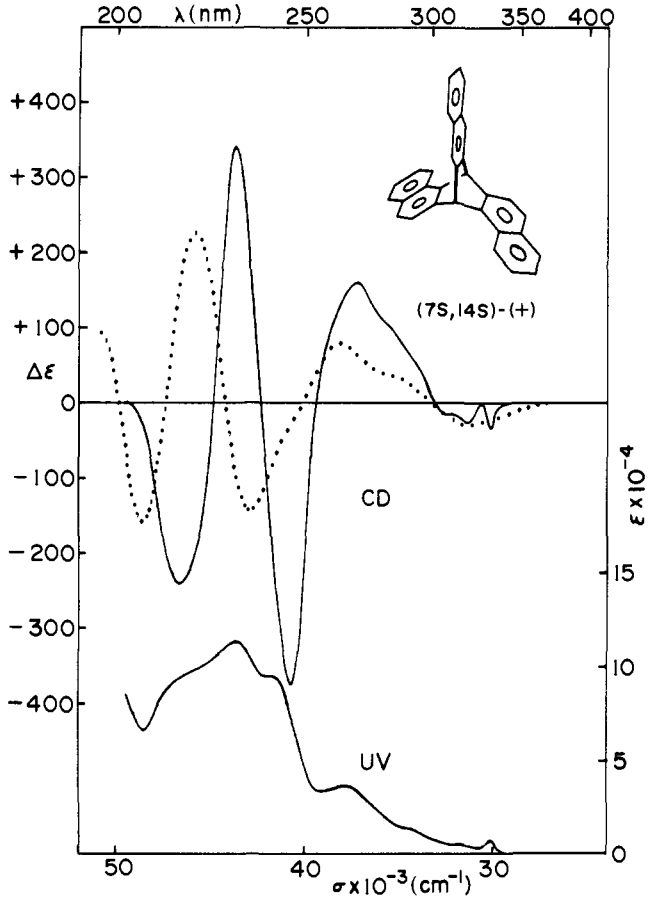


Figure 5. UV and CD spectra of (7*S*,14*S*)-(+)-**2** in 0.2% dioxane/EtOH: UV, λ_{max} 331.0 nm (ϵ 7900), 264.5 (35 800), 241.5 (95 500), 229.0 (113 800), 214.0 (96 800); CD, λ_{ext} 331.5 nm ($\Delta\epsilon$ −32.6), 317.0 (−24.6), 267.5 (+160.8), 244.5 (−381.9), 229.0 (+344.9), 213.0 (−246.4). Dotted line is the CD curve calculated[17] by the SCF-CI-dipole velocity method including the interchromophoric homoconjugation effect between three naphthalenes: λ_{ext} 320.5 nm ($\Delta\epsilon$ −29.0), 261.8 (+78.4), 232.5 (−142.0), 218.3 (+226.2), 205.7 (−157.3).

cluding the interchromophoric homoconjugation effect gave the good agreement between the calculated and observed CD spectra (Figure 5).[17] Thus, the absolute configuration of tribenzotriptycene (+)-**2** is assignable by the SCF-CI-DV molecular orbital calculation.

In conclusion, in order to determine the absolute stereochemistry of triple systems by applying the CD exciton chirality method in a reliable and nonempirical manner, it is necessary to choose ideal systems which satisfy the following requirements: (1) combination of three chiralities of same sign or of two chiralities of same sign and one zero chirality; namely, combination of plus/plus/plus or plus/plus/zero is more favorable than that of plus/plus/minus; (2) negligible interchromophoric homoconjugation effect. It should be emphasized that diethynyl (−)-**3** and dinitrile (+)-**15** benzotriptycenes composed of definite exciton chirality enabled, for the first time, unambiguous and reliable chiroptical determination of absolute stereochemistry of chiral triptycenes.

Experimental Section

General. All melting points are uncorrected. Spectral data were recorded on the following instruments: NMR, JEOL PMX60 and JNMPS-100 spectrometers; IR, Hitachi EPI-G2 infrared spectrophotometer; MS, JEOL JMS-01SG-2 mass spectrometer; UV, Hitachi EPS-3T and Jasco UVIDEC-505 spectrophotometers; CD, Jasco J-20 spectropolarimeter; optical rotations, Jasco DIP-4S spectropolarimeter.

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

(5*S*,12*S*)-(−)-Dimethyl 5,5a,6,11,11a,12-Hexahydro-5,12[1′,2′]-benzenonaphthacene-1,15-dicarboxylate (5). A solution of (9*S*,10*S*)-(−)-dimethyl 9,10-dihydro-9,10-ethenoanthracene-1,5-dicarboxylate (**4**,[1,7] 113 mg, 0.35 mmol) and benzocyclobutene[11] (109 mg, 1.05 mmol) in toluene (5 mL) was heated at 250 °C in a sealed tube for 16 h. The reaction mixture was cooled and evaporated in vacuo to dryness. The residue was separated by preparative TLC on silica gel (hexane/EtOAc, 4:1) yielding 160 mg (100%) of the adduct **5** as a syrup: IR (film) ν_{max} 3000, 2950, 1720, 1435, 1280, 1150, 780 cm^{-1}; NMR (100 MHz, $CDCl_3$) δ 1.72–2.50 ppm (4 H, m, H-5a, 6, 11, 11a), 2.68–2.96 (2 H, m, H-6,11), 3.96 and 3.98 (3 H each, s, OCH_3), 5.54 and 5.63 (1 H each, s, H-5,12), 6.99–7.80 (10 H, m, aromatic); $[\alpha]_D$ −126.9° (*c* 0.1497, EtOH); UV (EtOH) λ_{max} 293.0 nm (ϵ 5100), λ_{infl} 272.0 (2400), λ_{infl} 235.0 (20 000); CD (EtOH) λ_{ext} 298.0 nm ($\Delta\epsilon$ −4.9), 262.0 (−1.8), 229.0 (−10.1), 223.5 (0.0), 219.0 (+12.8); MS *m/e* 424 (parent).

(5*S*,12*S*)-(+)-Dimethyl 5,12-Dihydro-5,12[1′,2′]benzenonaphthacene-1,15-dicarboxylate (6). A solution of the adduct **5** (100 mg, 0.236 mmol) and DDQ (300 mg, 1.414 mmol) in dry benzene (10 mL) was heated at 200 °C in a sealed tube for 5 h. A precipitate of reduced DDQ deposited upon cooling to room temperature. The reaction 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, 4:1) affording 67 mg (68%) of the diester **6**: mp 237.0–238.0 °C from ethanol; IR (KBr) ν_{max} 3000, 2940, 1710, 1435, 1275, 1145, 1020, 750 cm^{-1}; NMR (100 MHz, $CDCl_3$) δ 4.03 ppm (6 H, s, OCH_3), 7.01 (2 H, s, H-5,12), 7.06 (2 H, t, J = 7.7 Hz, H-3,17), 7.34 (2 H, m, H-8,9), 7.65 (4 H, d, J = 7.7 Hz, H-2,4,16,18), 7.69 (2 H, m, H-7,10), 7.87 (2 H, s, H-6,11); $[\alpha]_D$ +123.2° (*c* 0.099 87, $CHCl_3$); UV (EtOH) λ_{max} 323.5 nm (ϵ 2500), 282.5 (14 000), 232.5 (83 800), 210.0 (55 000); CD (EtOH) λ_{ext} 300 nm ($\Delta\epsilon$ −5.1), 292 (0.0), 290 (+0.8), 289 (0.0), 283 (−3.8), 273 (0.0), 243 (+151.1), 229 (0.0), 220 (−177.8); MS molecular ion at *m/e* 420.1390 (calcd, 420.1363).

5,12-Dihydro-5,12[1′,2′]benzenonaphthacene-1,15-dimethanol (7). To a suspension of $LiAlH_4$ (54 mg, 1.42 mmol) in dry THF (20 mL) was added dropwise under nitrogen a solution of the diester (+)-**6** (204 mg, 0.485 mmol) in dry THF (30 mL). After stirring at room temperature for 1 h, the reaction mixture was quenched with ethyl acetate and a minimum amount of water to precipitate hydroxides. The organic layer was evaporated to dryness giving 177 mg (100%) of the glycol **7** as a syrup: NMR (60 MHz, $CDCl_3$) δ 2.77 ppm (2 H, s, OH), 4.67 (4 H, s, $-CH_2O-$), 5.93 (2 H, s, H-5,12), 6.77–7.73 (12 H, m, aromatic).

(5*S*,12*S*)-(+)-5,12-Dihydro-5,12[1′,2′]benzenonaphthacene-1,15-dicarbaldehyde (8). A mixture of the glycol **7** (221 mg, 0.592 mmol), activated MnO_2 (2.21 g), and acetone (30 mL) was stirred at room temperature for 23 h under nitrogen. The mixture was passed through a silica gel short column, eluting with ethyl acetate. The eluate was evaporated, affording 155 mg (73%) of the dialdehyde **8** as crystals: mp 249.5–251.0 °C from EtOH; IR (KBr) ν_{max} 1690, 1580, 1440, 1400, 1215, 755 cm^{-1}; NMR (100 MHz, $CDCl_3$) δ 7.08 ppm (2 H, s, H-5,12), 7.19 (2 H, t, J = 7.5 Hz, H-3,17), 7.35 (2 H, dd, J = 3.5, 6.5 Hz, H-8,9), 7.45 (2 H, dd, J = 1.5, 7.5 Hz, H-2,16 or H-4,18), 7.69 (2 H, dd, J = 3.5, 6.5 Hz, H-7,10), 7.71 (2 H, dd, J = 1.5, 7.5 Hz, H-4,18 or H-2,16), 7.88 (2 H, s, H-6,11), 10.26 (2 H, s, aldehyde); $[\alpha]_D$ +199.4° (*c* 0.100 29, $CHCl_3$); UV (EtOH) λ_{max} 282.0 nm (ϵ 1400), 235.5 (59 400); CD (EtOH) λ_{ext} 309.5 nm ($\Delta\epsilon$ −3.2), 303.0 (0.0), 291.5 (−4.2), 284.0 (0.0), 241.0 (+163.0), 234.0 (0.0), 225.0 (−244.4), 202.0 (0.0).

1,15-Bis(4-(phenylmethoxy)-1-butenyl)-5,12-dihydro-5,12[1′,2′]-benzenonaphthacene (9). To a suspension of (3-(phenylmethoxy)-propyl)triphenylphosphonium bromide (5.10 g, 10.4 mmol) in dry THF (25 mL) cooled at −70 °C was added dropwise a solution of *n*-butyllithium in hexane (5.5 mL, 10 mmol) under a nitrogen atmosphere and vigorous stirring. After the dark red reaction mixture had been stirred at −70 °C for 20 min, a solution of the dialdehyde (+)-**8** (266 mg, 0.738 mmol) in THF (15 mL) was added dropwise. The mixture was stirred overnight, during which time the temperature was allowed to rise to room temperature. The reaction mixture was poured into water and extracted twice with ethyl acetate. The combined organic layers were washed with water and brine and evaporated to afford a syrup (3.30 g) containing a large amount of triphenylphosphine oxide. The syrup was chromatographed on silica gel (hexane/

EtOAc, 4:1) giving 396 mg (86%) of the bis(benzyl ether) **9**: IR ($CHCl_3$) ν_{max} 3050, 3000, 2850, 1450, 1360, 1100, 885, 695 cm^{-1}; NMR (100 MHz, $CDCl_3$) δ 2.44 and 2.77 ppm (4 H, q, J = 6.5 Hz, β protons to benzyl ether), 3.52 and 3.72 (4 H, t, J = 6.5 Hz, α protons to benzyl ether), 4.46 and 4.62 (4 H, s, benzylic), 5.71–6.30 (4 H, m, bridgehead and olefinic), 6.71–7.75 (24 H, m, olefinic and aromatic). The NMR spectrum indicates that the product is a mixture of stereoisomers.

5,12-Dihydro-5,12[1′,2′]benzenonaphthacene-1,15-dibutanol (10). A mixture of the bis(benzyl ether) **9** (396 mg, 0.634 mmol), acetic acid (15 mL), concentrated H_2SO_4 (0.25 mL), and 5% palladium on charcoal (500 mg) was magnetically stirred under a hydrogen atmosphere at room temperature for 4 h. After removal of the catalyst, the solution was poured into water and extracted with ethyl acetate. The organic layer was washed with water and brine and evaporated to dryness. To the residue (338 mg) was added a 5% KOH/EtOH solution (30 mL) and the mixture was refluxed for 1.5 h. After cooling to room temperature, the mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with brine and evaporated to dryness, giving 282 mg of syrup, which was subjected to preparative TLC on silica gel ($CHCl_3$/MeOH, 20:1) yielding 157 mg (56%) of the glycol **10**: IR ($CHCl_3$) ν_{max} 3590, 3500–3100, 2980, 2910, 1585, 1450, 1425, 1050, 880 cm^{-1}; NMR (60 MHz, $CDCl_3$) δ 1.68 ppm (10 H, m, β and γ protons to OH and alcoholic), 2.87 (4 H, m, benzylic), 3.60 (4 H, m, α protons to OH), 5.72 (2 H, s, bridgehead), 6.70–7.73 (12 H, m, aromatic).

5,12-Dihydro-5,12[1′,2′]benzenonaphthacene-1,15-dibutyric Acid (11). To a solution of the glycol **10** (157 mg, 0.35 mmol) in acetone (20 mL) under ice cooling was added dropwise Jones reagent (2.7 mL, 7.3 mmol of oxygen equivalent). After stirring at 0 °C for 3 h, the mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, and evaporated to dryness, yielding 167 mg (100%) of the dibutyric acid **11** as a white solid: IR (KBr) ν_{max} 3600–2400, 1690, 1420, 1240, 745 cm^{-1}; NMR (60 MHz, $CDCl_3$) δ 1.67–2.30 ppm (4 H, m, β protons to COOH), 2.50 (4 H, t, J = 7.0 Hz, α protons to COOH), 2.95 (4 H, t, J = 8.0 Hz, benzylic), 5.80 (2 H, s, bridgehead), 6.67–7.83 (14 H, m, aromatic and carboxyl).

1,2,3,7,14,17,18,19-Octahydro-7,14[1′,2′]-naphthalenobenzo-[*a*]naphthacene-4,20-dione (12). A mixture of the dibutyric acid **11** (167 mg, 0.35 mmol) and polyphosphoric acid (6 mL, prepared by dissolving 10 g of P_2O_5 in 10 mL of 85% H_3PO_4) was stirred at 90–110 °C for 3 h. After cooling to room temperature, the mixture was poured into ice–water and extracted with chloroform. The organic layer was washed with brine and evaporated to dryness, affording 87 mg (56%) of the diketone **12** as crystals: mp 320–340 °C dec from EtOH; IR ($CHCl_3$) ν_{max} 3000, 2950, 1670, 1590, 1355, 1325, 1285, 1100, 900 cm^{-1}; NMR (60 MHz, $CDCl_3$) δ 2.13 ppm (4 H, br quintet, J = 6.0 Hz, H-2,18), 2.58 (4 H, br t, J = 6.0 Hz, H-3,19), 3.23 (4 H, br t, J = 6.0 Hz, H-1,17), 5.83 (2 H, s, H-7,14), 7.30 (2 H, d, J = 8.0 Hz, H-6,22), 7.77 (2 H, d, J = 8.0 Hz, H-5,21), 7.23–7.90 (6 H, m, H-8,9,10,11,12,13); UV (EtOH) λ_{max} 323.5 nm (ϵ 1600), 270.0 (33 300), 244.0 (82 600), 239.0 (74 200), 220.0 (59 400); CD (EtOH) λ_{ext} 323.5 nm ($\Delta\epsilon$ +5.3), 320.0 (0.0), 287.5 (+37.8), 279.5 (0.0), 264.0 (−121.2), 248.8 (0.0), 236.5 (+267.0), 223.8 (0.0), 218.0 (−124.7); MS *m/e* 440 (parent).

1,2,3,4,7,14,17,18,19,20-Decahydro-7,14[1′,2′]naphthalenobenzo[*a*]naphthacene (13). A mixture of the diketone **12** (66 mg, 0.15 mmol), hydrazine hydrate (0.5 mL), and di(ethylene glycol) (6 mL) was heated at 100 °C for 1 h. Potassium hydroxide (500 mg) was added and the reaction mixture was heated at 200 °C for 2 h, during which time volatile materials were distilled. After cooling to room temperature, the mixture was poured into ice–water, acidified to pH 1 with 2 M HCl, and extracted with ethyl acetate. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, and evaporated to dryness, affording 158 mg of syrup. The syrup was chromatographed on silica gel (hexane/EtOAc, 20:1) to yield 41 mg (66%) of the hydrocarbon **13**: mp 160.5–161.5 °C from EtOH; IR ($CHCl_3$) ν_{max} 3000, 2925, 2850, 1470, 1430, 1140, 890 cm^{-1}; NMR (60 MHz, $CDCl_3$) δ 1.50–2.00 ppm (8 H, m, H-2,3,18,19), 2.63 (4 H, br t, J = 6.0 Hz, H-4,20), 3.03 (4 H, br t, J = 6.0 Hz, H-1,17), 5.65 (2 H, s, H-7,14), 6.65 (2 H, d, J = 8.0 Hz, H-5,21), 7.03–7.27 (8 H, m, H-6,8,9,10,11,12,13,22); UV (EtOH) λ_{max} 324.0 nm (ϵ 2000), 310.0 (1600), 249.5 (40 100), 224.0 (96 400); CD (EtOH) λ_{ext} 282.6 nm ($\Delta\epsilon$ −8.4), 270.0 (0.0), 255.0 (+56.6), 235.0 (+47.9), 228.5 (0.0), 221.5 (−114.9); MS *m/e* 412 (parent).

(7*S*,14*S*)-(+)-7,14-Dihydro-7,14[1′,2′]naphthalenobenzo[*a*]naphthacene (2). A solution of the hydrocarbon **13** (39 mg, 0.095 mmol) and DDQ (390 mg, 1.72 mmol) in benzene (10 mL) was refluxed for 4 h. After removal of the solvent in vacuo, the residue was chromatographed on silica gel, eluting with hexane/EtOAc (20:1), yielding 35 mg (92%) of chiral tribenzotriptycene **2** as crystals: mp 185.0–186.5 °C prisms from benzene/petroleum ether; IR (KBr) ν_{max} 3040, 2960, 1510, 1475, 1165, 890, 815, 750, 680 cm^{-1}; NMR (100 MHz, $CDCl_3$) δ 6.49 ppm (2 H, s, H-7,14), 7.25–7.93 (16 H, m, aromatic), 8.45 (2 H, d, J = 8.0 Hz, H-5,21); $[\alpha]_D$ +239.8° (c 0.010 01, $CHCl_3$); UV (0.2% dioxane in EtOH) λ_{max} 331.0 nm (ϵ 7900), 264.5 (35 800), 241.5 (95 500), 229.0 (113 800), 214.0 (96 800); CD (0.2% dioxane in EtOH) λ_{ext} 331.5 nm ($\Delta\epsilon$ − 32.6), 317.0 (−24.6), 302.0 (0.0), 267.5 (+160.8), 253.0 (0.0), 244.5 (−381.9), 236.0 (0.0), 229.0 (+344.9), 222.2 (0.0), 213.0 (−246.4); MS molecular ion at *m/e* 404.1570 (calcd, 404.1566).

1,15-Bis(2-bromoethenyl)-5,12-dihydro-5,12[1′,2′]benzenonaphthacene (14). To a suspension of (bromomethyl)triphenylphosphonium bromide[14] (5.0 g, 11.5 mmol) in dry THF (40 mL) cooled at 0 °C was added dropwise a solution of *n*-butyllithium in hexane (5.5 mL, 10 mmol) under nitrogen. After the dark red reaction mixture had been stirred for 20 min, a solution of the levorotatory dialdehyde (5*R*,12*R*)-(−)-**8**[12] (212 mg, 0.588 mmol) in THF (30 mL) was added dropwise. The mixture was stirred for 1.5 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, eluting with hexane/EtOAc (4:1), yielding 243 mg (80%) of the dibromide **14**: NMR (100 MHz, $CDCl_3$) δ 5.63, 5.67, 5.79, 5.83 ppm (2 H, s each, bridgehead), 6.58–7.74 (16 H, m, aromatic and olefinic). The NMR data indicated that the product was a mixture of three stereoisomers, and from the peak intensity of bridgehead proton signals the abundance ratio of cis,cis, cis,trans, and trans,trans isomers was 1:2:1: MS molecular ion at *m/e* (rel intensity) 512 (1), 514 (2), 516 (1).

(5*R*,12*R*)-(−)-1,15-Diethynyl-5,12-dihydro-5,12[1′,2′]benzenonaphthacene (3). To a solution of potassium *tert*-butoxide in *tert*-butyl alcohol (prepared by dissolving 260 mg of potassium metal in 60 mL of *tert*-butyl alcohol) was added dropwise a solution of the dibromide **14** (181 mg, 0.352 mmol) in dry THF (40 mL). The mixture was refluxed under nitrogen for 10 h. After addition of water (2 mL), the solvent was evaporated in vacuo and the residue was extracted with ethyl acetate. The organic layer was washed with brine and evaporated to dryness. The residual syrup (133 mg) was subjected to preparative TLC on silica gel, eluting with hexane/EtOAc (4:1), giving the diethynyl compound **3** (113 mg, 91%) as a white solid: IR (KBr) ν_{max} 3260, 2070, 1720, 1620, 1460, 1420, 1190, 880, 790, 745 cm^{-1}; NMR (100 MHz, $CDCl_3$) δ 3.37 ppm (2 H, s, acetylenic), 6.02 (2 H, s, H-5,12), 6.97 (2 H, dd, J = 6.9, 7.8 Hz, H-3,17), 7.20 (2 H, dd, J = 1.5, 7.8 Hz, H-2,16 or H-4,18), 7.36 (2 H, dd, J = 3.3, 6.3 Hz, H-8,9), 7.45 (2 H, dd, J = 1.5, 6.9 Hz, H-4,18 or H-2,16), 7.70 (2 H, dd, J = 3.3, 6.3 Hz, H-7,10), 7.82 (2 H, s, H-6,11); $[\alpha]_D$ −270.9° (c 0.0812, EtOH); UV (EtOH) λ_{max} 322 nm (ϵ 1500), 308 (1400), 278 (10 300), 268 (8900), 241 (75 000); CD (EtOH) λ_{ext} 290 nm ($\Delta\epsilon$ +3.5), 273.5 (0.0), 245.5 (−138.2), 235 (0.0), 215.0 (+113.6), 200 (0.0); MS *m/e* 352 (parent).

(5*S*,12*S*)-(+)-5,12-Dihydro-5,12[1′,2′]benzenonaphthacene-1,15-dicarbonitrile (15). To a solution of the dialdehyde (5*S*,12*S*)-(+)-**8** (70 mg, 0.194 mmol) in hot ethanol (40 mL) was added a solution of hydroxylamine (33.6 mg, 0.484 mmol) in water (6 mL) and 0.1 M NaOH (4.8 mL). The reaction mixture was stirred at room temperature for 3.5 h. After removal of the solvent in vacuo and addition of water, the mixture was extracted with ethyl acetate. The organic layer was washed with brine and evaporated to dryness. The residue (87 mg) was dissolved in acetic anhydride (15 mL) and the solution was refluxed for 2 h. After evaporation of the solvent in vacuo, water was added and the mixture was extracted with ether. The ethereal layer was washed with brine, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was subjected to preparative TLC on silica gel, eluting with hexane/EtOAc (4:1), yielding 32 mg (47%) of the dinitrile **15**: mp 241.0–241.5 °C from ethanol; IR (KBr) ν_{max} 3040, 2900, 2220, 1460, 1425, 1200, 795, 755 cm^{-1}; NMR (100 MHz, $CDCl_3$) δ 6.02 ppm (2 H, s, H-5,12), 7.16 (2 H, dd, J = 7.2, 8.2 Hz, H-3,17), 7.36 (2 H, dd, J = 8.2, 1.3 Hz, H-4,18), 7.42 (2 H, dd, J = 6.6, 3.2 Hz, H-8,9), 7.72 (2 H, dd, J = 7.2, 1.3 Hz, H-2,16), 7.76 (2 H, dd, J = 6.6, 3.2 Hz, H-7,10), 7.92 (2 H, s, H-6,11); $[\alpha]_D$ +234.4° (c 0.050 35, $CHCl_3$); UV (EtOH) λ_{max} 323.5 nm (ϵ 770), 282.0

(13 300), 241.0 (72 400); CD (EtOH) λ_{ext} 298 nm ($\Delta\epsilon$ −4.5), 292 (0.0), 288 (+3.0), 283 (0.0), 277 (−5.0), 271 (0.0), 241 (+166.0), 228 (0.0), 217 (−127.3), 201 (0.0).

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Circular Dichroic Power of Chiral Triptycenes

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Abstract: The CD spectra of (5*R*,12*R*)-(−)-1,15-diethynyl-5,12-dihydro-5,12[1′,2′]benzenonaphthacene (**2**) and (5*S*,12*S*)-(+)-5,12-dihydro-5,12[1′,2′]benzenonaphthacene-1,15-dicarbonitrile (**3**) were quantitatively calculated on the basis of chiral exciton coupling between three chromophores. The calculated spectra are in excellent agreement with the observed ones, establishing the absolute stereochemistry in a nonempirical manner. In the case of (7*S*,14*S*)-(+)-7,14-dihydro-7,14[1′,2′]-naphthalenobenzo[*a*]naphthacene (**1**), the complex CD spectrum of which had not been explicable by the simple exciton coupling mechanism, the CD spectrum was computed by the SCF-CI-dipole velocity molecular orbital method including the interchromophoric homoconjugation effect. When the resonance integral ratio β_{hc}/β_{arom} is 32%, the calculated CD curve is in good agreement with the observed one, clarifying the important role of the interchromophoric homoconjugation effect in the circular dichroic power of (+)-**1**.

In the preceding paper,[1] we reported the unequivocal and nonempirical chiroptical determination of the absolute stereochemistry of chiral triptycenes, (5*R*,12*R*)-(−)-1,15-diethynyl-5,12-dihydro-5,12[1′,2′]benzenonaphthacene (**2**) and (5*S*,12*S*)-(+)-5,12-dihydro-5,12[1′,2′]benzenonaphthacene-1,15-dicarbonitrile (**3**), achieved by applying the CD exciton chirality method,[2] and also described the complex circular dichroism of (7*S*,14*S*)-(+)-7,14-dihydro-7,14-[1′,2′]naphthalenobenzo[*a*]naphthacene (**1**) which was not explicable by the simple exciton coupling mechanism.

This paper reports the theoretical calculation results of the CD spectra of diethynylbenzotriptycene (−)-**2** and benzotriptycenedinitrile (+)-**3** obtained by the exciton chirality method.[2] The calculated CD spectra are in excellent agreement with the observed ones, corroborating the previous qualitative configurational assignment. This paper also describes the SCF-CI-dipole velocity molecular orbital calculation results of the UV and CD spectra of chiral tribenzotriptycene (+)-**1**, diethynylbenzotriptycene (−)-**2**, (6*R*,15*R*)-(+)-6,15-dihydro-6,15-ethanonaphtho[2,3-*c*]pentaphene (**4**),[3,4] and (7*R*,14*R*)-(+)-7,14-dihydro-7,14-ethanodibenz[*a*,*h*]anthracene (**5**).[3,5] Good agreement between the calculated and observed curves was obtained, establishing the absolute configurations in a quantitative manner. In the case of tribenzotriptycene (+)-**1**, the SCF-CI-DV molecular orbital calculation clarified the important role of the interchromophoric homoconjugation effect in the circular dichroic power of (+)-**1**.

Methods of Calculation

Molecular Structure. The Cartesian coordinate system for the molecular structure of (7*S*,14*S*)-(+)-tribenzotriptycene **1** was adopted as shown in Figure 1, in which the *z* axis is the C_2 symmetrical axis of the molecule. The coordinates of atoms were calculated[3b] by employing the geometric parameters shown in Figure 1 which were taken from the X-ray crystallographic data of triptycene derivatives.[6]

In the case of the diethynyl compound (−)-**2** and the dinitrile (+)-**3**, the additional parameters for acetylene and nitrile

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