Synthesis and Absolute Stereochemistry of (+)-6,15-Dihydro-6,15-ethanonaphtho[2,3-*c*]pentaphene as Determined by Exciton Chirality and X-Ray Bijvoet Methods[1)]

Nobuyuki HARADA, Yuki TAKUMA, and Hisashi UDA

Chemical Research Institute of Nonaqueous Solutions, Tohoku University, Katahira, Sendai 980

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(6*R*,15*R*)-(+)-6,15-Dihydro-6,15-ethanonaphtho[2,3-*c*]pentaphene (**1**) was synthesized from (9*R*,10*R*)-(+)-dimethyl 9,10-dihydro-9,10-ethanoanthracene-1,5-dicarboxylate, the absolute configuration of which has been established by the X-ray Bijvoet method and chemical correlations. The CD spectrum of **1** clearly exhibits very strong positive first and negative second Cotton effects due to coupling of the ^1B_b transitions ($\Delta\varepsilon_{268.0}=+931.3$ and $\Delta\varepsilon_{249.7}=-720.8$; $A(=\Delta\varepsilon_1-\Delta\varepsilon_2)=+1652.1$), the positive sign of the A value being in accord with the positive exciton chirality between the two long axes of the anthracene moieties in **1**. The results demonstrate an ideal case of chiral exciton coupling in CD spectra, and provide evidence of the consistency between nonempirical CD exciton chirality and X-ray Bijvoet methods.

The circular dichroic Cotton effects due to a chiral exciton coupling between two or more chromophores enable one to determine the absolute stereochemistry in a nonempirical manner, as does the X-ray crystallographic Bijvoet method. The present circular dichroic method has been extensively studied in the fields of biopolymers,[2)] inorganic complexes,[3)] physical chemistry,[4,5)] synthetic organic compounds,[6)] as well as in natural products.[7)] In the cases of steroidal glycol dibenzoates and several natural products, we have quantitatively calculated the coupled Cotton effects on the basis of the molecular exciton theory, obtaining excellent agreement between observed and calculated Cotton effects. Not only the sign of a Cotton effect but also its amplitude, location, and shape were satisfactorily reproduced based on the quantum mechanical calculation.[8)]

Although the optical circular dichroic exciton chirality and X-ray crystallographic Bijvoet methods are independent of each other, the two nonempirical methods should give the same absolute stereochemistry. The X-ray Bijvoet method utilizes the anomalous dispersion effect by heavy atoms, and is therefore applicable to all compounds containing a heavy atom. Actually, the X-ray Bijvoet method has been employed for various chemical compounds, since the first determination of the absolute configuration of (+)-tartaric acid was reported by Bijvoet *et al.* in 1951.[9)]

On the other hand, the circular dichroic exciton chirality method is based on the Cotton effects due to the chiral exciton coupling between two or more chromophores. The assignment of Cotton effects should be unambiguous and reliable in view of a nonempirical quantum mechanical calculation. Thus for the determination of the absolute stereochemistry by the application of the present optical method, it is important to choose a proper electronic transition of proper chromophores which satisfy the following requirements of a chiral exciton coupling: (i) Large extinction coefficient values in UV spectra; (ii) isolation of the band in question from other strong absorptions; (iii) established direction of the electric transition moment in the geometry of the chromophore; (iv) unambiguous determination of the exciton chirality in space, inclusive of configuration and conformation; (v) negligible molecular orbital overlapping between the chromophores.

The syntheses and chiroptical properties of optically active triptycene derivatives and 1,5-disubstituted 9,10-dihydro-9,10-ethanoanthracenes have been extensively studied by Nakagawa *et al.*[10)] They determined the absolute configurations of two key compounds, (1*R*,6*S*)-(+)-2,5-dimethoxy-7-aminotriptycene hydrobromide (**2**) and (9*S*,10*S*)-(−)-9,10-dihydro-9,10-ethanoanthracene-1,5-diamine dihydrobromide (**3**) by the X-ray Bijvoet method (Fig. 1).[11)] The absolute stereochemistry of other compounds has been established by the chemical correlations to these key compounds.[10,12)] For example, (+)-dimethyl 9,10-dihydro-9,10-ethanoanthracene-1,5-dicarboxylate (**6**) was converted into the antipode of (−)-diamino derivative (**3**), which corroborated the

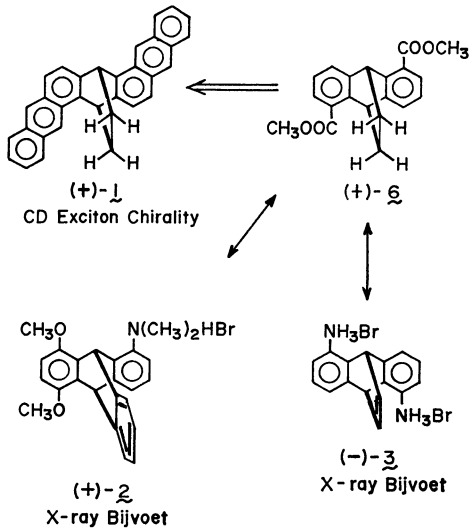


Fig. 1. Correlations between absolute stereochemistries of 9,10-dihydro-9,10-ethanoanthracene derivatives; absolute configurations of (+)-**2** and (−)-**3** have been determined by Tanaka, *et al.*,[11)] using the X-ray Bijvoet method. The arrow (↔) indicates the chemical correlations made by Nakagawa, *et al.*[10,11b)] The synthesis indicated by the arrow (⇐) and the absolute stereochemistry of (+)-**1** as determined by the CD exciton chirality method are described in this paper.

(9*R*,10*R*) absolute configuration of diester (+)-**6**.

Theoretical determination of the absolute stereochemistry of these compounds in view of the chiral exciton coupling mechanism was attempted by Tanaka *et al.*[11b,13] Their analyses of circular dichroic spectra led to the antipodal absolute configurations, contradictory with X-ray Bijvoet data. On the other hand, the absolute stereochemistry calculated by Hagishita and Kuriyama,[14] and others[15–17] is consistent with the X-ray Bijvoet data. Therefore, it is necessary to determine the absolute configurations of these cage compounds on the basis of reliable and unambiguous assignment of exciton coupled Cotton effects. It is also of significance to clarify the applicability of the present optical method.

This paper reports the synthesis and the (6*R*,15*R*) absolute stereochemistry of (+)-6,15-dihydro-6,15-ethanonaphtho[2,3-*c*]pentaphene (**1**) as determined by both circular dichroic exciton chirality and X-ray Bijvoet methods (Fig. 1). Hydrocarbon **1** was found to be the ideal compound satisfying the requirements of a chiral exciton coupling. It should be emphasized that the results obtained by the exciton chirality method are consistent with those by the X-ray Bijvoet method.

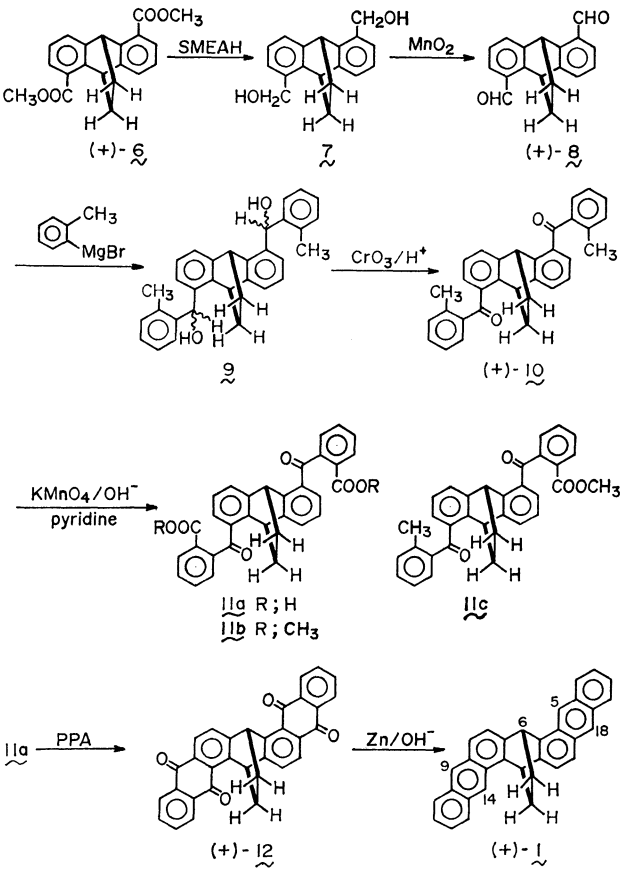
Results and Discussions

*Synthesis of (6*R*,15*R*)-(+)-6,15-Dihydro-6,15-ethanonaphtho[2,3-*c*]pentaphene (1).* The hydrocarbon (+)-**1** was synthesized from (9*R*,10*R*)-(+)-dimethyl 9,10-dihydro-9,10-ethanoanthracene-1,5-dicarboxylate (**6**), the absolute configuration of which has been established by the X-ray Bijvoet method and chemical correlations (Scheme 1).[10–12]

The diester (+)-**6**, mp 120.0—120.5 °C, $[\alpha]_D$ +359.2°, was quantitatively reduced to 9,10-dihydro-9,10-ethanoanthracene-1,5-dimethanol (**7**) with sodium bis(2-methoxyethoxy)aluminumhydride (SMEAH), followed by oxidation with activated manganese (IV) oxide under nitrogen giving (+)-9,10-dihydro-9,10-ethanoanthracene-1,5-dicarbaldehyde (**8**), mp 128.0—129.5 °C, $[\alpha]_D$ +487.3°. Since dialdehyde **8** was air-sensitive the crude product was immediately used for the subsequent Grignard reaction. Dialdehyde **8** was treated with excess *o*-tolylmagnesium bromide at room temperature to afford an epimeric mixture of 9,10-dihydro-α,α′-bis(*o*-tolyl)-9,10-ethanoanthracene-1,5-dimethanol (**9**). Since the additional chiralities of the secondary alcoholic moiety collapse at the next stage, the epimeric mixture of glycol **9** was used without separation. The Jones oxidation of glycol **9** afforded (+)-9,10-dihydro-9,10-ethanoanthracene-1,5-diylbis(*o*-tolyl)methanone (**10**), mp 151.0—152.5 °C, $[\alpha]_D^{20}$ +177°, (56% yield from (+)-dialdehyde **8**).

The selective oxidation of two aromatic methyl groups of diketone (+)-**10** was achieved by refluxing with $KMnO_4$ in aqueous NaOH–pyridine to give 2,2′-(9,10-dihydro-9,10-ethanoanthracene-1,5-diyldicarbonyl)dibenzoic acid (**11a**) contaminated with a small amount of monocarboxylic acid. The oxidation occurred exclusively on the aromatic methyl groups, the bridge head hydrogens remaining unchanged. The stability of the bridgehead hydrogens to oxidation can be accounted for by the fact that the carbon-hydrogen bond is perpendicular to the π-orbitals of the aromatic moiety and the rigidity of the molecular frame prevents the enolization of the bridgehead hydrogens. The structure of dibenzoic acid **11a** was characterized by the physical data of diester **11b**, and also by those of monoester **11c** derived from the intermediate monocarboxylic acid.

Cyclization of dibenzoic acid **11a** in polyphosphoric acid yielded (+)-6,15-dihydro-6,15-ethanonaphtho[2,3-*c*]pentaphene-5,9,14,18-tetrone (**12**), mp 268.0—268.5 °C, $[\alpha]_D^{20}$ +1000°, as the sole product (64% from diketone (+)-**10**). Finally, reduction of quinone (+)-**12** with zinc powder and successive dehydration catalyzed with acetic acid gave a very strong fluorescent hydrocarbon, (+)-6,15-dihydro-6,15-ethanonaphtho[2,3-*c*]-pentaphene (**1**), $[\alpha]_D$ +1157°, in solid masses.



Scheme 1.

Since the configuration of the ethano-bridge remains unchanged throughout all the reactions, it is concluded that the (6*R*,15*R*) absolute stereochemistry of hydrocarbon (+)-**1** has been established by the X-ray Bijvoet method and chemical correlations.

Circular Dichroic Spectra and Absolute Stereochemistries. The characterization of the electronic spectra of polyacene chromophores has been established by theoretical and experimental studies since the discovery of quantum mechanics. For example, anthracene exhibits at least four absorptions above 200 nm wavelength: the ^1L_a transition of medium-intensity around 380—300 nm

(ε 7600) with vibrational structures, the weak ^1L_b transition buried under the ^1L_a band, the intense ^1B_b transition at 251.9 nm (ε 204000), and the ^1C_b transition around 200 nm. Among these transitions, the allowed ^1B_b transition has been well established to have the electric transition moment along the long axis of the chromophore, while the ^1L_a transition has been assigned to be polarized parallel to the short axis, as illustrated in Fig. 2.[18]

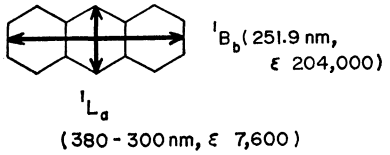


Fig. 2. Polarizations of the electric transition moments of anthracene.

The electronic spectrum of (+)-**1** resembles that of anthracene; it exhibits the ^1L_a transition around 410—300 nm (ε 11200) with five peaks, the very strong ^1B_b transition at 267.2 nm (ε 268600) with an inflection around 250 nm, and the broad ^1C_b transition around 220 nm (ε 34200) (Fig. 3).

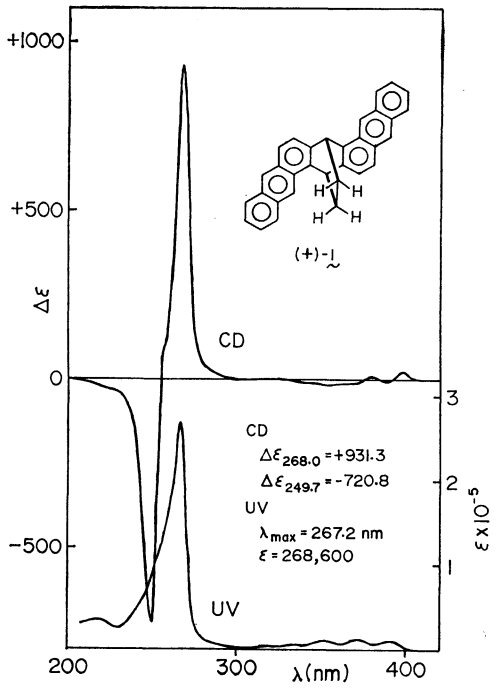


Fig. 3. CD and UV spectra of (6R,15R)-(+)-6,15-dihydro-6,15-ethanonaphtho[2,3-c]pentaphene (**1**) (see text for the solvent systems).

From these electronic properties and the rigidity of the molecular frame, it is obvious that the hydrocarbon **1** meets the requirements of the exciton chirality method: Namely, (i) the allowed ^1B_b transition of the component chromophore of **1**, *i.e.*, anthracene, exhibits a very strong ε value of the order of 10^5, (ii) the location of the present band around 260 nm is sufficiently separated from the weak ^1L_a and ^1L_b transitions around 400—300 nm and also from the ^1C_b transition so that the contribution of the weak absorption bands can be neglected, (iii) the polarization of the ^1B_b transition in anthracene is well established, (iv) because of the rigidity of the present cage compound **1**, the positive exciton chirality in space can be definitely determined, and (v) there is no direct conjugation between the two component chromophores, and the contribution of homoconjugation if any, is negligible[19] because of the large exciton dipole-dipole coupling term.

As expected, the circular dichroic spectrum of (+)-**1** clearly exhibits very strong positive first and negative second Cotton effects due to the coupling of the ^1B_b transitions ($\Delta\varepsilon_{268.0}=+931.3$, and $\Delta\varepsilon_{249.7}=-720.8$; $A(\Delta\varepsilon_1-\Delta\varepsilon_2)=+1652.1$) (Fig. 3). These Cotton effects are about one hundred times larger than those of common organic compounds.

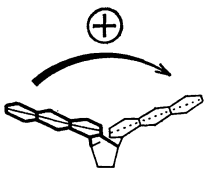


Fig. 4. Positive exciton chirality between the two axes of the anthracene moieties in hydrocarbon (+)-**1**.

Since the sign of the *A* value is positive, it is concluded that the hydrocarbon (+)-**1** has a positive exciton chirality, *i.e.*, a clockwise screwness, between the two long axes of the anthracene moieties, which corresponds to the (6*R*,15*R*) absolute stereochemistry in consistency with the X-ray data (Fig. 4). The present data thus not only determine the absolute configuration of (+)-**1** in a nonempirical manner, but also provide *definite evidence of the consistency between nonempirical circular dichroic and X-ray Bijvoet methods.*

In contrast to the case of intense absorption, the simple exciton coupling mechanism is not always applicable to the Cotton effects due to a weak absorption. For example, the ^1L_a transition of (+)-**1** exhibits weak and complicated Cotton effects around 400—300 nm, which are of positive sign at longer wavelength side and of negative sign at shorter wavelength side, in conflict with the signs expected from the negative exciton chirality between the two short axes of anthracene moieties (Fig. 3). It seems that the homoconjugation effect between the two chromophores and/or the mixing of the ^1L_a transition with the intense ^1B_b transition[20] make a dominant contribution to these weak Cotton effects.

A similar situation was observed for dialdehyde (+)-**8**; both the ^1L_b transition at 307.5 nm and the intramolecular charge transfer band at 252.5 nm exhibit only weak positive Cotton effects instead of split ones (Fig. 5). The circular dichroism of (+)-**10** also shows a simple pattern; two weak positive Cotton effects of the ^1L_b and intramolecular charge transfer bands and a negative one at 228 nm (Fig. 6). The small amplitude ($\Delta\varepsilon\simeq 10$) of these Cotton effects can be ascribed to the complicated polarization spectra of benzophenone chromophore[21] and to the conformational flexibility of the *o*-toluoyl group.

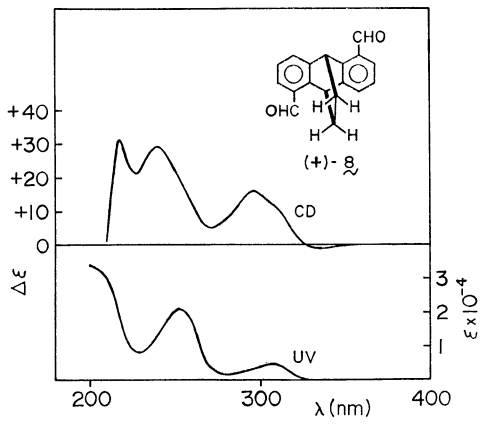


Fig. 5. CD and UV spectra of (+)-9,10-dihydro-9,10-ethanoanthracene-1,5-dicarbaldehyde (**8**)(see text for the solvent systems).

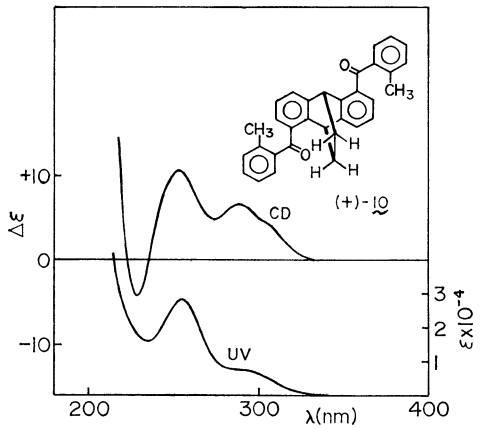


Fig. 6. CD and UV spectra of (+)-9,10-dihydro-9,10-ethanoanthracene-1,5-diylbis(*o*-tolyl)methanone (**10**) (see text for the solvent systems).

In contrast to (+)-**8** and (+)-**10**, quinone (+)-**12** exhibits relatively strong Cotton effects over 400—200 nm ($\Delta\varepsilon$ −44—+133) (Fig. 7). The polarization of the electronic transitions of 9,10-anthraquinone is established on the basis of the polarized phosphorescence spectrum;[22] the π-π^* transition (I) at 360—300 nm, the transition (II) at 300—260 nm, and the transition (III) at 260—240 nm are polarized along long, short, and long axes, respectively, of the chromophores. On the basis of the present polarization spectra, we have tentatively assigned the CD spectrum of (+)-**12** as follows: The positive Cotton effect at 360 nm and the negative one at 324 nm are attributable to the coupling of transition I, corresponding to the positive exciton chirality. In a similar way, the negative exciton coupling of transition II and the positive one of transition III give rise to the negative/positive and positive/negative Cotton effects, respectively, in which the two positive Cotton effects overlap each other at 260 nm. The present assignment is not definite because of the proximity of the two intense transitions II and III, and the weak intensity of transition I. It is difficult to determine the absolute stereochemistry of (+)-**10** based on the circular dichroic data.

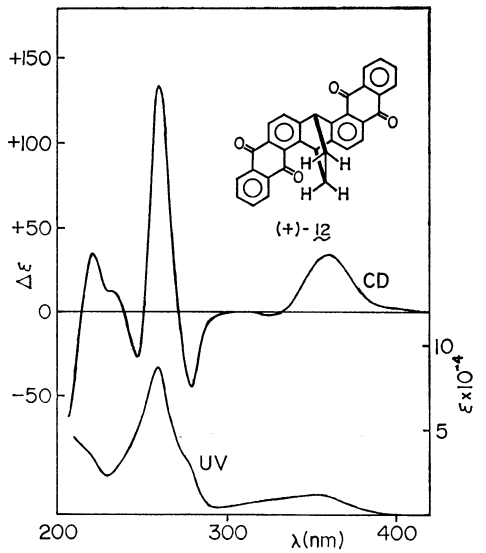


Fig. 7. CD and UV spectra of (+)-6,15-dihydro-6,15-ethanonaphtho[2,3-*c*]pentaphene-5,9,14,18-tetrone (**12**) (see text for the solvent systems).

As in the case of hydrocarbon (+)-**1**, the ^1B_b transition of polyacenes is ideal for the nonempirical determination of absolute stereochemistry on the basis of a chiral exciton coupling. On the other hand, the use of chromophores which exhibit weak transitions and/or complicated polarization spectra is undesirable for the present purpose. Therefore *one should choose a proper electronic transition of proper chromophores which satisfy the requirements of the exciton chirality method*, if one wish to determine absolute stereochemistry on sound grounds.

Experimental

General Procedures. Melting points are uncorrected. Spectral data were recorded on the following instruments: NMR, Jeol C-60HL, PMX60, and JNMPS-100 spectrometers; IR, Hitachi EPI-G2 infrared spectrophotometer; MS, Jeol JMS-01SG-2 mass spectrometer; UV, Hitachi EPS-3T spectrophotometer; CD, Jasco J-20 spectropolarimeter;optical rotations, Jasco DIP-4 and ORD/UV-5 spectropolarimeters.

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

Elemental analyses were carried out in the microanalytical laboratories of our institute.

Both (+)- and (−)-dimethyl 9,10-dihydro-9,10-ethanoanthracene-1,5-dicarboxylate (6) were prepared according to the reported procedure;[10e] 9,10-dihydro-9,10-ethenoanthracene-1,5-dicarboxylic acid (**4**) was optically resolved with (−)-strychnine. The crystalline salt of (−)-**4** and (−)-strychnine was recrystallized four times from ethanol to afford a salt of constant rotation, $[\alpha]_D$ −305.1° (*c* 0.20059, pyridine). The optically pure salt was treated with 50% acetic acid to give (−)-diacid **4**, which was esterified by refluxing in methanol containing concd H_2SO_4, followed by recrystallization three times from methanol giving (−)-dimethyl 9,10-dihydro-9,10-ethenoanthracene-1,5-dicarboxylate (**5**) of constant rotation: mp 149.5—150.0°C; $[\alpha]_D$ −350.0° (*c* 0.30048, methanol), $[\alpha]_{405}$ −1016° (*c* 0.03100, methanol) (lit,[10e] mp 151.5—151.8 °C; $[\alpha]_{405}$ −1160° (*c* 0.00546, methanol)).

Catalytic hydrogenation of (−)-**5** over PtO_2 in tetrahydrofuran and recrystallization three times from methanol yielded

optically pure diester (−)-**6**: mp 121.0—121.5 °C; $[\alpha]_D$ −360.4° (*c* 0.30032, methanol), $[\alpha]_{405}$ −1064° (*c* 0.03055, methanol) (lit,[10e] mp 121.8—122.4 °C; $[\alpha]_{405}$ −1170° (*c* 0.00600, methanol)).

The mother liquor obtained after the first recrystallization of the strychnine salt of (±)-diacid **4** was evaporated to dryness. The residual crystalline salt was acidified and esterified in the same way as described for the (−)-diacid **4**, giving diester (+)-**5**: mp 147.5—148.0 °C from methanol; $[\alpha]_{405}$ +1000.1° (*c* 0.006344, methanol), optical purity 98.4% based on the rotation.

Catalytic hydrogenation of (+)-**5** and recrystallization four times from methanol afforded optically pure diester (+)-**6**: mp 120.0—120.5 °C; $[\alpha]_D$ +359.2° (*c* 0.30037, methanol).

Found: C, 74.59; H, 5.80%. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63%.

9,10-Dihydro-9,10-ethanoanthracene-1,5-dimethanol (7). A 7.0 % solution of sodium bis(2-methoxyethoxy)aluminumhydride in toluene (30.6 ml, 11.0 mmol) was added dropwise to a solution of 1.0 g (3.1 mmol) of diester (+)-**6** in 20 ml of dried benzene under ice-cooling. The ice bath was removed and the solution was stirred at room temp for 2.5 h. The reaction mixture was quenched with a minimum amount of water to precipitate hydroxides. After decantation of the supernatant, the precipitate was washed with ether, and the combined organic solution was dried over anhyd Na_2SO_4. Evaporation of the solvent gave a syrup of dimethanol **7** in a quantitative yield: IR($CHCl_3$) ν_{max} 3580, 3550—3090, 2990, 2940, 2850, 1460, 1435, 1380, 1140, 1000 cm^{-1}; NMR(100 MHz, $CDCl_3$) δ 1.64 (br s, 4H, ethane bridge), 2.60 (br s, 2H, hydroxy), 4.64 (br s, 6H, $-CH_2O-$ and bridgehead), 6.93—7.30 ppm (m, 6H, aromatic).

(+)-9,10-Dihydro-9,10-ethanoanthracene-1,5-dicarbaldehyde (8). A solution of 830 mg of dimethanol **7** in 150 ml of acetone was stirred overnight with 10.0 g of activated MnO_2 at room temp under nitrogen. The reaction mixture was filtered through celite, and MnO_2 was washed with acetone. The filtrate was evaporated to give 791 mg (97%) of crude crystalline dialdehyde (+)-**8**. Since dialdehyde **8** is air sensitive, the crude product was used for the next reaction without purification.

An analytical sample was obtained by recrystallization from ethanol, mp 128.0—129.5 °C; IR(KBr) ν_{max} 2960, 2925, 2850, 1670, 1580, 1460, 1440, 1405, 1240, 1140, 1060, 1030, 790, 770, 750, 730 cm^{-1}; NMR (100 MHz, $CDCl_3$) δ 1.79 (br s, 4H, ethane bridge), 5.75 (s, 2H, bridge head), 7.28 (t, J=7.5 Hz, 2H, aromatic meta to formyl), 7.57 (dd, J= 7.5, 2.0 Hz, 2H, aromatic para to formyl), 7.59 (dd, J= 7.5, 2.0 Hz, 2H, aromatic ortho to formyl), 10.28 ppm (s, 2H, formyl); $[\alpha]_D$ +487.3° (*c* 0.01026, $CHCl_3$); UV(EtOH) λ_{max} 307.5 (ε 4400), 252.5 nm (ε 20200); CD(EtOH) $\Delta\varepsilon_{335.0}=-1.1$, $\Delta\varepsilon_{328.0}=0.0$, $\Delta\varepsilon_{296.5}=+16.0$, $\Delta\varepsilon_{240.0}=+29.4$, $\Delta\varepsilon_{218.5}=+31.2$.

Found: C, 81.97; H, 5.46%. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38%.

9,10-Dihydro-α,α′-bis(o-tolyl)-9,10-ethanoanthracene-1,5-dimethanol (9). A solution of 4.245 g (24.8 mmol) of *o*-bromotoluene in 150 ml of ether was stirred overnight with 603 mg (24.8 mmol) of magnesium filings at room temp under nitrogen. To the greenish black solution of the Grignard reagent of *o*-tolylmagnesium bromide was added dropwise, over a period of 20 min, a solution of 781 mg (3.1 mmol) of dialdehyde (+)-**8** in 50 ml of abs ether. The reaction mixture was stirred for 4 h at room temp, then quenched by addition of wet ether. After addition of water to precipitate hydroxides and decantation of the supernatant, the precipitate was washed with ether and the combined ethereal solution was dried over anhyd Na_2SO_4. Evaporation of the solvent afforded 1.360 g (*ca.* 100%) of crude solid glycol **9**.

Thin layer chromatography of **9** on silica gel ($CHCl_3$–methanol 10: 1) showed partially overlapping three spots, which indicates that glycol **9** is a mixture of epimers (theoretically three epimers are possible). Product **9** was used for the next oxidation reaction, without separation of epimers.

(+)-9,10-Dihydro-9,10-ethanoanthracene-1,5-diylbis(o-tolyl)-methanone (10). To a cold solution of 1.360 g (6.1 mmol of hydroxyl group) of an epimeric mixture of **9** in 40 ml of acetone was added dropwise over 2 min, under ice-cooling, 1.52 ml of Jones reagent (6.1 mmol of oxygen equivalent; a standard solution made by dissolving 26.72 g of CrO_3 in 23 ml of concd H_2SO_4 diluted with water to a volume of 100 ml). The reaction mixture was stirred for 3 min. Addition of ethanol and water, extraction with ether, washing with water and brine, and evaporation of solvent gave 1.193 g of crystalline material, which was recrystallized from ethanol to yield 746 mg (56% from dialdehyde **8**) of diketone (+)-**10**: mp 151.0—152.5 °C from ethanol; IR(KBr) ν_{max} 1662, 1640, 1270, 758, 752, 740 cm^{-1}; NMR(60 MHz, $CDCl_3$) δ 1.72 (br s, 4H, ethane bridge), 2.46 (s, 6H, aromatic methyl), 4.95 (br s, 2H, bridgehead), 6.91—7.56 ppm (m, 14H, aromatic); $[\alpha]_D^{20}$ +177° (*c* 0.02032, ethanol); UV (EtOH) λ_{infl} 298 (ε 6800), λ_{max} 255.1 nm (ε 28200); CD (EtOH) $\Delta\varepsilon_{289.0}=+6.6$, $\Delta\varepsilon_{254.0}=+10.6$, $\Delta\varepsilon_{236.0}=0.0$, $\Delta\varepsilon_{228.0}=-4.1$, $\Delta\varepsilon_{222.5}=0.0$.

2,2′-(9,10-Dihydro-9,10-ethanoanthracene-1,5-diyldicarbonyl)-dibenzoic Acid (11a). A mixture of 231 mg (0.52 mmol) of diketone (+)-**10**, 30 ml of pyridine, 20 ml of 4% aq NaOH, and 4.0 g of $KMnO_4$ was gently refluxed for 2 h. Additional 20 ml of 4% aq NaOH and 4.0 g of $KMnO_4$ were added and the reaction mixture was refluxed for 3 h, during which the reaction was monitored by TLC on silica gel ($CHCl_3$–methanol 10: 1). After cooling to room temp, the reaction mixture was acidified with 6 M HCl, followed by addition of aq satd Na_2SO_3 solution in order to dissolve the brown precipitate of MnO_2. Extraction with ether, washing with brine, and evaporation of solvent afforded 253 mg (96%) of syrup, which was predominantly dibenzoic acid **11a**, contaminated with a small amount of monocarboxylic acid.

Dimethyl 2,2′-(9,10-Dihydro-9,10-ethanoanthracene-1,5-diyldicarbonyl)dibenzoate (11b). The crude dibenzoic acid **11a** (70 mg) was treated with ethereal diazomethane solution under ice-cooling and the reaction mixture was allowed to stand for 30 min. Evaporation of solvent gave 66 mg of syrup, which was subjected to preparative TLC (petroleum ether–ethyl acetate 10: 3) to yield 27 mg (56%) of pure dibenzoate **11b**: IR($CHCl_3$) ν_{max} 1724, 1663, 1282, 1138 cm^{-1}; NMR (100 MHz, $CDCl_3$) δ 1.81 (br s, 4H, ethane bridge), 3.53 (s, 6H, ester methyl), 5.43 (s, 2H, bridgehead), 6.95—7.13 (m, 4H, aromatic), 7.34—7.66 (m, 8H, aromatic), 7.85—8.02 ppm (m, 2H, aromatic).

By preparative TLC, a monoester product, methyl 2-(9,10-dihydro-5-*o*-toluoyl-9,10-ethanoanthracene-1-ylcarbonyl)-benzoate (**11c**) was isolated as a minor product: NMR (60 MHz, $CDCl_3$) δ 1.75 (br s, 4H, ethane bridge), 2.43 (s, 3H, aromatic methyl), 3.49 (s, 3H, ester methyl), 4.90 (br s, 1H, bridgehead 9-H), 5.40 (br s, 1H, bridgehead 10-H), 6.88—7.66 (m, 13H, aromatic), 7.76—7.97 ppm (m, 1H, aromatic).

(+)-6,15-Dihydro-6,15-ethanonaphtho[2,3-c]pentaphene-5,9,14,18-tetrone (12). A mixture of 253 mg of dibenzoic acid **11a** in 26 ml of polyphosphoric acid (prepared by dissolving 100 g of P_2O_5 in 100 ml of 85% H_3PO_4) was heated at 90 °C for 1.5 h under stirring. At the end of the reaction period, TLC on silica gel ($CHCl_3$–acetone 50: 1) revealed only one yellow spot with strong UV absorption. After cooling to room temp, the reaction mixture was poured into ice-water and extracted with ether. The ethereal solution was dried over anhyd

Na_2SO_4; evaporation of the solvent yielded 191 mg of crystals, which were purified by short column chromatography on silica gel giving 157 mg (64% yield from **10**) of quinone (+)-**12**: mp 268.0—268.5 °C from benzene–ether; IR(KBr) ν_{max} 1662, 1588, 1567, 1348, 1325, 1280, 1137, 988, 717 cm^{-1}; NMR (60 MHz, $CDCl_3$) δ 1.85 (br s, 4H, ethane bridge), 6.43 (br s, 2H, bridgehead), 7.53—7.76 (m, 6H, aromatic meta to carbonyl), 7.95—8.22 ppm (m, 6H, aromatic ortho to carbonyl); $[\alpha]_D^{20}$ +1000° (*c* 0.01009, 10% dioxane in ethanol); UV(0.47% dioxane in ethanol) λ_{max} 350.0 (ε 11100), λ_{infl} 278 (ε 30300), λ_{max} 259.2 nm (ε 86500); CD(1.0% dioxane in ethanol) $\Delta\varepsilon_{360}=+33.6$, $\Delta\varepsilon_{332}=0.0$, $\Delta\varepsilon_{324}=-2.1$, $\Delta\varepsilon_{308}=0.0$, $\Delta\varepsilon_{278.5}=-44.1$, $\Delta\varepsilon_{271}=0.0$, $\Delta\varepsilon_{260}=+133.4$, $\Delta\varepsilon_{251}=0.0$, $\Delta\varepsilon_{247}=-26.3$, $\Delta\varepsilon_{239}=0.0$, $\Delta\varepsilon_{232}=+12.3$, $\Delta\varepsilon_{221}=+34.2$, $\Delta\varepsilon_{214.5}=0.0$.

*(+)-6,15-Dihydro-6,15-ethanonaphtho[2,3-c]pentaphene (**1**).* To a solution of 76 mg of quinone (+)-**12** in 20 ml of benzene were added 4.0 g of activated zinc powder, 20 ml of 10% aq NaOH, and 0.5 ml of aq satd $CuSO_4$. The reaction mixture of a deep red color was refluxed under vigorous stirring for 10 h, during which the red color faded.

The reaction was monitored by TLC on silica gel ($CHCl_3$–acetic acid 5: 0.03). In this case, acetic acid in a developing solvent is important for catalyzing the dehydration of hydroxy intermediates which are more polar than the starting material **10**.

After cooling to room temp, zinc metal was filtered and washed with water and benzene. The combined filtrate was neutralized with acetic acid, followed by extraction with ether and evaporation of solvent to give 70 mg of a syrup. The remaining material was dissolved in 30 ml of chloroform containing 0.04 ml of acetic acid and gently refluxed for 3 h to complete the dehydration. The solvent was evaporated *in vacuo*, and the residual matter was subjected to preparative TLC on silica gel (petroleum ether–benzene 10: 3), giving 52 mg (78%) of a strong fluorecent hydrocarbon (+)-**1**. Attempts to carry out recrystallization from various solvents were unsuccessful. Instead, yellow solid masses were obtained from benzene–ethanol. Hydrocarbon **1** was characterized by the following spectral data: IR(KBr) ν_{max} 3040, 2955, 1615, 1150, 874, 740, 467 cm^{-1}; NMR(60 MHz, $CDCl_3$) δ 1.79 (br s, 4H, ethane bridge), 5.41 (br s, 2H, bridgehead), 6.89—8.07 (m, 12H, aromatic), 8.22 (s, 2H, 9-H and 18-H), 8.75 ppm (s, 2H, 5-H and 14-H); $[\alpha]_D$ +1157° (*c* 0.034, dioxane); UV 0.08% dioxane in ethanol) λ_{max} 391.0 (ε 9130), λ_{max} 371.2 (ε 11170), λ_{max} 352.7 (ε 8950), λ_{max} 267.2 (ε 268600), λ_{max} 219.5 nm (ε 34200); CD(0.18% dioxane in ethanol) $\Delta\varepsilon_{397.2}=+26.4$, $\Delta\varepsilon_{390.6}=0.0$, $\Delta\varepsilon_{388.1}=-2.3$, $\Delta\varepsilon_{384.9}=0.0$, $\Delta\varepsilon_{378.0}=+6.3$, $\Delta\varepsilon_{374.5}=0.0$, $\Delta\varepsilon_{370.0}=-9.7$, $\Delta\varepsilon_{362.9}=-9.7$, $\Delta\varepsilon_{352.8}=-14.5$, $\Delta\varepsilon_{330.5}=0.0$, $\Delta\varepsilon_{268.0}=+931.3$, $\Delta\varepsilon_{256.0}=0.0$, $\Delta\varepsilon_{249.7}=-720.8$; MS *m/e* (relative intensity), 406 (39, M^+), 378 (100, $M-C_2H_4$), 188 (29).

Found: *m/e* 406.1718. Calcd for $C_{32}H_{22}$: M, 406.1720.

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