January, 1978] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (1), 265—270 (1978) 265

Synthesis and Absolute Stereochemistry of (+)-7,14-Dihydro-7,14-ethanodibenz[*a*,*h*]anthracene and Its Derivatives

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(Received June 8, 1977)

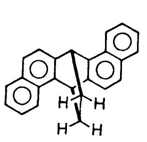
(7*R*,14*R*)-(+)-7,14-Dihydro-7,14-ethanodibenz[*a*,*h*]anthracene (**1**), and the 2,9-dimethyl- (**2**) and 2,4,9,11-tetramethyl- (**3**) derivatives were synthesized from (9*R*,10*R*)-(+)-9,10-dihydro-9,10-ethanoanthracene-1,5-dicarbaldehyde (**4**) of known absolute configuration. The CD spectra of **1**, **2**, and **3** clearly exhibit positive first and negative second Cotton effects due to the coupling of the ^1B_b transitions of two naphthalene chromophores: $\Delta\varepsilon_{237.0}=+326.5$, $\Delta\varepsilon_{224.0}=-180.5$, $A=+507.0$, for **1**; $\Delta\varepsilon_{240.6}=+371.5$, $\Delta\varepsilon_{227.0}=-149.4$, $A=+520.9$, for **2**; $\Delta\varepsilon_{242.0}=+340.3$, $\Delta\varepsilon_{225.0}=-88.0$, $A=+428.3$, for **3**. Since the sign of the A values is positive, positive exciton chirality between the two long axes of the naphthalene moieties is assigned. The (7*R*,14*R*) absolute configuration of **1**, **2**, and **3** is established by both CD exciton chirality and X-ray Bijvoet methods.

The circular dichroic exciton chirality method based on chiral exciton coupling between two or more chromophores enables one to determine the absolute stereochemistry of organic compounds in a nonempirical manner.[1,2] We have reported the synthesis and absolute configuration of (+)-6,15-dihydro-6,15-ethanonaphtho[2,3-*c*]pentaphene determined by the exciton chirality method and chemical correlations, providing definite evidence of the consistency between nonempirical CD and X-ray crystallographic methods.[3,4]

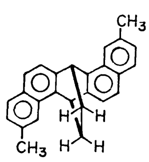
This paper describes the synthesis and absolute stereochemistry of (+)-7,14-dihydro-7,14-ethanodibenz[*a*,*h*]anthracene and its derivatives. The CD spectra of these compounds show typical split Cotton effects due to the chiral exciton coupling between two naphthalene chromophores. The absolute configuration determined by the present CD method is in accord with that obtained by the X-ray Bijvoet method, as in the case of (+)-6,15-dihydro-6,15-ethanonaphtho[2,3-*c*]pentaphene.

Results and Discussion

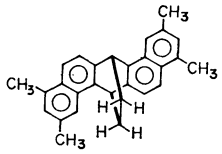
*Synthesis of (7R,14R)-(+)-7,14-Dihydro-7,14-ethanodibenz[a,h]anthracene (**1**) and the 2,9-Dimethyl- (**2**) and 2,4,9,11-Tetramethyl- (**3**) Derivatives.* Compounds **1**, **2**, and **3** were synthesized from (9*R*,10*R*)-(+)-9,10-dihydro-9,10-ethanoanthracene-1,5-dicarbaldehyde (**4**), mp 128.0—129.5 °C, $[\alpha]_D$ +487.3°, the absolute stereochemistry of which has been established by chemical correlations.[3,4)]



(+)-1



(+)-2



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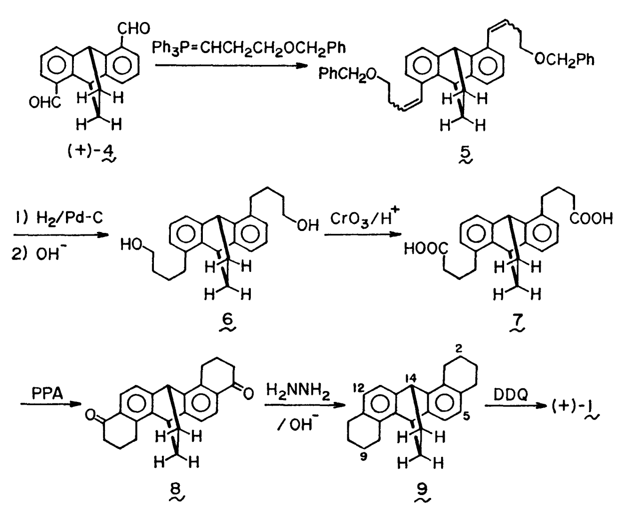
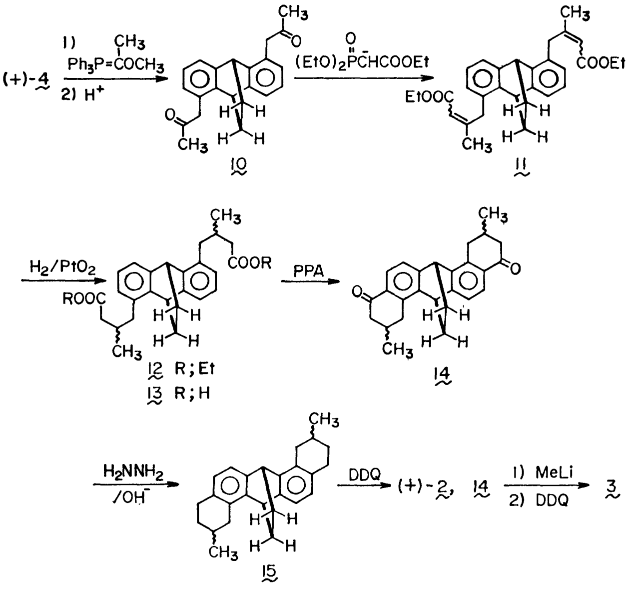
In order to elongate side chains, dialdehyde **4** was subjected to the Wittig reaction with γ-benzyloxypropylenetriphenylphosphorane to afford an isomeric mixture of bisbenzyl ether **5** in an almost quantitative yield (Scheme 1). Catalytic hydrogenation of **5** over palladium on charcoal in acetic acid containing a catalytic amount of sulfuric acid, and successive hydrolysis of the intermediary acetate formed yielded glycol **6**. Oxidation of glycol **6** with Jones reagent, followed by cyclization of the resulting dicarboxylic acid **7** with polyphosphoric acid gave (+)-diketone **8**, $[\alpha]_D$ +184.6°. The Huang-Minlon reduction of **8** afforded hydrocarbon **9**, which was subsequently oxidized with DDQ to yield



Scheme 1.



Scheme 2.

the desired hydrocarbon (+)-**1**, mp 234.0—235.5 °C, $[\alpha]_D$ +670.0°.

In the cases of hydrocarbons **2** and **3**, dialdehyde **4** was allowed to react with α-methoxyethylenetriphenylphosphorane to give an isomeric mixture of bisvinyl ether, which was hydrolyzed to diketone **10** (Scheme 2). Diketone **10** was subjected to the second Wittig reaction with triethylphosphonoacetate to yield a *cis,trans* isomeric mixture of diester **11**. Catalytic hydrogenation of the unsaturated diester **11** over platinum oxide and the hydrolysis of ester groups afforded dicarboxylic acid **13**, which was cyclized with polyphosphoric acid yielding diketone **14**. Although the NMR signal of the secondary methyl groups of compound **14** appears as one doublet, diketone **14** could be considered to be a mixture of three possible stereoisomers. Diketone **14** was subjected to the Huang-Minlon reduction giving hydrocarbon **15**, which was oxidized with DDQ to yield the dimethyl derivative (+)-**2**. Methylation of **14** with methyl lithium and successive treatment with DDQ afforded the tetramethyl derivative **3**.

Since the absolute configuration of the ethano-bridge remains unchanged throughout all the reactions, the (7*R*,14*R*) absolute stereochemistry of compounds **1**, **2**, and **3** has been established by the present chemical correlations.

Circular Dichroic Spectra and Absolute Stereochemistry. The linear dichroic properties of electronic transitions of naphthalene chromophore are established as follows. The weak ^1L_b transition around 310 nm (ε 200) and the intense ^1B_b transition around 220 nm (ε 100000) are polarized parallel to the long axis of the chromophore, while the ^1L_a transition of medium intensity around 280 nm (ε 5800) has an electric transition moment along the short axis of the chromophore.[5]

Of these transitions, the allowed ^1B_b transition is ideal for chiral exciton coupling because of its large extinction coefficient value. In fact, hydrocarbon (+)-**1** exhibits strong split Cotton effects due to the exciton coupling between the two ^1B_b transitions: the positive first Cotton effect at 237.0 nm (Δε +326.5) and the negative second one at 224.0 nm (Δε −180.5); $A(\Delta\varepsilon_1-\Delta\varepsilon_2)=+507.0$ (Fig. 1).[6]

Since the sign of the A value is positive, it is established that the hydrocarbon (+)-**1** has positive exciton chirality between the two long axes of the naphthalene moieties (Fig. 1), which corresponds to the (7*R*,14*R*) absolute configuration in line with the chemical correlation results.

Similarly, compounds (+)-**2** and **3** exhibit strong positive first and negative second Cotton effects in the region of the ^1B_b transition (Figs. 2 and 3). As the number of methyl groups increases, the Cotton effects undergo red shift of 4—5 nm corresponding to that of

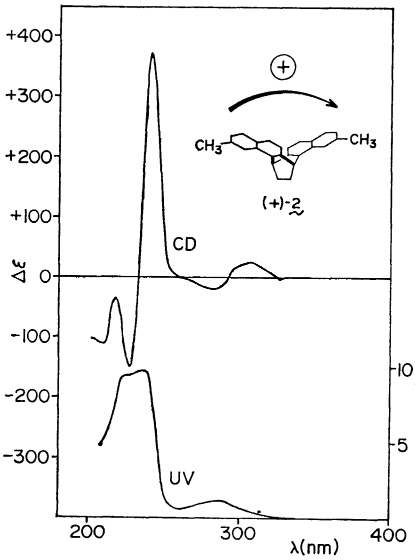


Fig. 2. CD and UV spectra of (7*R*,14*R*)-(+)-7,14-dihydro-2,9-dimethyl-7,14-ethanodibenz[*a*,*h*]anthracene (**2**) (see text for the solvent systems used).

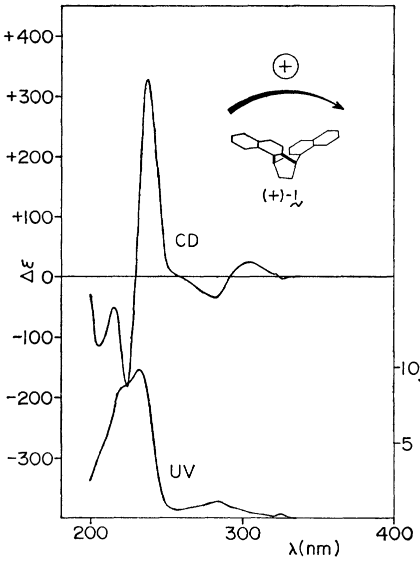


Fig. 1. CD and UV spectra of (7*R*,14*R*)-(+)-7,14-dihydro-7,14-ethanodibenz[*a*,*h*]anthracene (**1**) in ethanol.

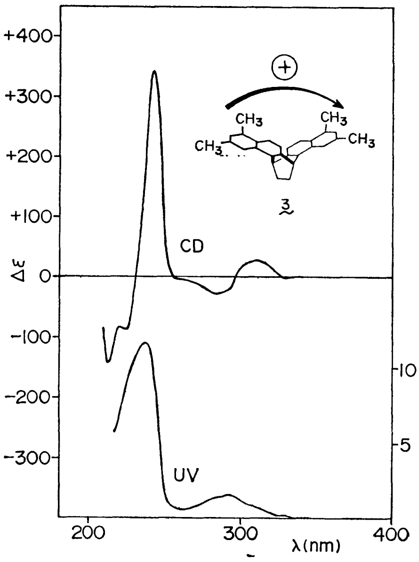


Fig. 3. CD and UV spectra of (7*R*,14*R*)-7,14-dihydro-2,4,9,11-tetramethyl-7,14-ethanodibenz[*a*,*h*]anthracene (**3**) in ethanol.

UV spectrum, the second Cotton effect becoming weaker and the positive first one remaining almost unchanged. On the other hand, the third Cotton effect of negative sign appears around 210 nm, becoming stronger and undergoing red shift as the number of methyl groups increases. In compound **3**, the third and second Cotton effects overlap each other. Although the origin of the third Cotton effect is still unknown, it is obvious that the unsubstituted hydrocarbon **1** is superior to compounds **2** and **3** for observation of exciton split Cotton effects.

In contrast to the case of the intense $^1\mathrm{B}_\mathrm{b}$ transition, the Cotton effects due to other weak transitions can not be assigned in a straightforward manner. Compounds **1**, **2**, and **3** show positive first and negative second Cotton effects of medium intensity ($\Delta\varepsilon$ -27) in the region of a $^1\mathrm{L}_\mathrm{a}$ transition (around 307 and 283 nm), as if they were based on simple exciton coupling mechanism (Figs. 1, 2, and 3). However, the sequence of the sign of the Cotton effects, *i.e.*, positive and negative from longer wavelength side, is in conflict with the negative exciton chirality predicted by a point dipole approximation method. A similar situation was observed for the weak $^1\mathrm{L}_\mathrm{b}$ transition of compound **1** around 325 nm; the sequence of the negative first Cotton effect at 326 nm ($\Delta\varepsilon$ -4.3) and the positive second one at 322 nm ($\Delta\varepsilon$ $+5.0$) disagrees with the positive exciton chirality between the two long axes of the chromophores. The pattern of the Cotton effects also differs from that of (+)-7,14-dihydro-7,14-ethanodibenz[*a*,*h*]anthracene-15,16-dicarboxylic acid.[7] Thus, the weak $^1\mathrm{L}_\mathrm{a}$ and $^1\mathrm{L}_\mathrm{b}$ transitions are unsuitable for the exciton chirality method.

The CD spectrum of diketone **8** is of much interest because of its peculiar behavior in the exciton coupling between the two α-tetralone chromophores; the CD spectrum exhibits split Cotton effects of $\Delta\varepsilon_{275.0}=-17.4$ and $\Delta\varepsilon_{252.0}=+24.7$, correospnding to the intramolecular charge transfer transition at 261.0 nm (ε 28300) (Fig. 4).

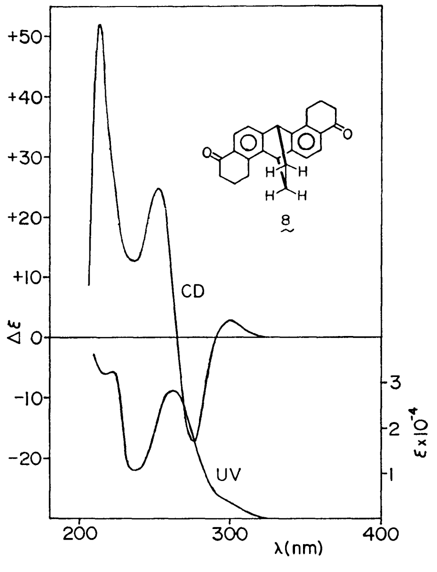


Fig. 4. CD and UV spectra of 1,2,3,7,8,9,10,14-octahydro-7,14-ethanodibenz[*a*,*h*]anthracene-4,11-dione(**8**) in ethanol.

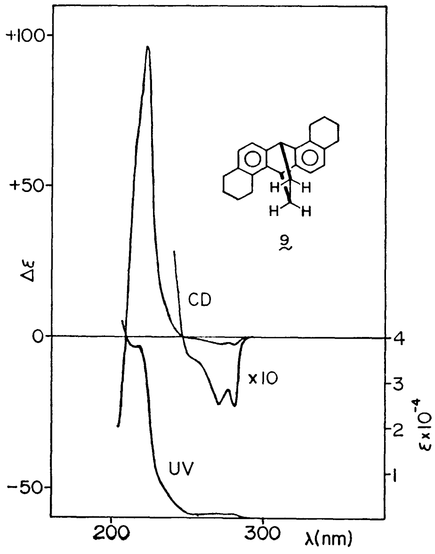


Fig. 5. CD and UV spectra of 1,2,3,4,7,8,9,10,11,14-decahydro-7,14-ethanodibenz[*a*,*h*]anthracene (**9**) in ethanol.

Since the intramolecular charge transfer band has a transition moment along the direction from benzene to carbonyl group,[8] positive exciton chirality is predicted by projection of molecular models. However, the observed sequence of the Cotton effects, *i.e.*, negative and positive, is the reverse of this prediction. A similar case has been reported for (−)-9,10-dihydro-9,10-ethanoanthracene-2,6-diamine.[7] It seems that the homoconjugation effect between the two chromophores makes dominant contribution to the sequence of energy levels.

Hydrocarbon **9** shows a strong positive Cotton effect at 222.5 nm ($\Delta\varepsilon$ $+96.4$) and a negative one below 209 nm (Fig. 5). Although the extremum of the negative Cotton effect could not be observed, these Cotton effects are presumably due to the exciton coupling of the allowed $^1\mathrm{L}_\mathrm{a}$ transition of the benzene chromophores. However, the transition is unsuitable for the exciton chirality method because of the ambiguity of polarization of tetra-alkylated benzene chromophore. Moreover, in the region of a forbidden $^1\mathrm{L}_\mathrm{b}$ transition around 280 nm, compound **9** merely exhibits one negative Cotton effect with vibronic structure. It is therefore impossible to determine the absolute configuration of **9** on the basis of these Cotton effects.

For determination of absolute stereochemistries by the circular dichroic method, it is important to chose a suitable electronic transition of suitable chromophores for chiral exciton coupling.

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-01 SG-2 mass spectrometer; UV: Hitachi EPS-3T spectrophotometer; CD: Jasco J-20 spectropolarimeter; optical rotations: Jasco DIP-4 spectropolarimeter.

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

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

(3-Benzyloxypropyl)triphenylphosphonium Bromide. To a solution of 2.88 g (11.0 mmol) of triphenylphosphine in 5 ml of dry xylene and 25 ml of ligroine was added 2.29 g (10.0 mmol) of benzyl 3-bromopropyl ether.[9] The reaction mixture was refluxed for 5.5 days under stirring, during which time white crystals deposited. After being cooled to room temp, the crystals were filtered, washed with petroleum ether, and dried *in vacuo*, giving 2.760 g (56%) of the phosphonium salt: IR (KBr) ν_{max} 3025, 2850, 1580, 1480, 1435, 1120, 750, 740, 720, 700 cm^{-1}.

1,5-Bis(4-benzyloxyl-1-butenyl)-9,10-dihydro-9,10-ethanoanthracene (5). To a suspension of 20 g (40.7 mmol) of (3-benzyloxypropyl)triphenylphosphonium bromide in 100 ml of dry THF cooled at −70 °C was added dropwise, over 10 min, 25 ml (1.55 mmol/ml, 38.75 mmol) of a solution of butyl lithium in hexane under nitorgen atmosphere and vigorous stirring. After the dark red reaction mixture had been stirred for 15 min at −70 °C, a solution of 731 mg (2.79 mmol) of (9*R*,10*R*)-(+)-9,10-dihydro-9,10-ethanoanthracene-1,5-dicarbaldehyde (**4**),[4] mp 128.0—129.5 °C, $[\alpha]_D$ +487.3°, in 30 ml of THF was added dropwise. The reaction mixture was stirred overnight, during which time the temperature was allowed to rise to room temp. After addition of water, the mixture was extracted with ethyl acetate and the organic layer was washed with water and brine. Evaporation of the solvent afforded 11.623 g of syrup containing a large amount of triphenylphosphine oxide, which was chromatographed on silica gel giving 1.729 g (*ca.* 100%) of bisbenzyl ether **5**: IR ($CHCl_3$) ν_{max} 3000, 2950, 2850, 1450, 1360, 1100, 700cm^{-1}; NMR (60 MHz, $CDCl_3$) δ 1.63 (4H, br s, ethane bridge), 2.13—2.80 (4H, m, allylic), 3.33—3.77 (4H, m, α protons of ether), 4.45—4.56 (4H, m, benzylic), 5.43—6.37 (2H, m, bridge head), 6.67—7.46 ppm (20H, m, vinyl and aromatic).

9,10-Dihydro-9,10-ethanoanthracene-1,5-dibutanol (6). A mixture of 1.720 g (3.27 mmol) of bisbenzyl ether **5**, 110 ml of acetic acid, 1.0 ml of concd H_2SO_4, and 1.5 g of 5% palladium on charcoal was magnetically stirred under hydrogen atmosphere at room temp, for 35 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 (0.990 g) was added a solution of 2.5 g of KOH in 50 ml of ethanol, and the mixture was gently refluxed for 3 h. After being cooled to room temp, the reaction mixture was poured into water and extracted with ethyl acetate. The organic solution was washed with brine, and evaporated to dryness yielding 0.789 g of syrup, which was subjected to preparative TLC on silica gel ($CHCl_3$-MeOH 20 : 1) giving 315 mg (28%) of glycol **6**: IR ($CHCl_3$) ν_{max} 3600, 3525—3100, 2995, 2920, 2850, 1460, 1425, 1140, 1045 cm^{-1}; NMR (100 MHz, $CDCl_3$) δ 1.68 (14H, m, hydroxyl, ethane bridge, and β and γ protons to hydroxyl group), 2.80 (4H, m, benzylic), 3.68 (4H, m, α protons to hydroxyl group), 4.58 (2H, s, bridge head), 6.82—7.28 ppm (6H, m, aromatic).

9,10-Dihydro-9,10-ethanoanthracene-1,5-dibutyric Acid (7). To a solution of 283 mg (0.807 mmol) of glycol **6** in 35 ml of acetone was added dropwise, under ice-cooling, 2.5 ml (10.03 mmol of oxygen equivalent) of Jones reagent. After being stirred at 0 °C for 3 h, water was added and the mixture was extracted with ethyl acetate. The organic layer was washed with brine, and dried over anhyd Na_2SO_4. Evaporation of the solvent gave 264 mg (86%) of dicarboxylic acid **7** as white solid: IR ($CHCl_3$) ν_{max} 3500—2400, 2930, 1700, 1270, 1140 cm^{-1}; NMR (60 MHz, $CDCl_3$) δ 1.50—2.23 (8H, m, ethane bridge and β protons to carboxyl group), 2.47 (4H, t, J=7.0 Hz, α protons to carboxyl group), 2.83 (4H, t, J=7.0 Hz, benzylic), 4.0 (2H, br s, bridge head), 6.87—7.76 ppm (8H, m, aromatic and carboxyl).

(+)-1,2,3,7,8,9,10,14-Octahydro-7,14-ethanodibenz[a,h]*anthracene-4,11-dione (8).* A mixture of 213 mg (0.563 mmol) of dicarboxylic acid **7** in 3 ml of polyphosphoric acid (prepared by dissolving 10 g of P_2O_5 in 10 ml of 85% H_3PO_4) was heated at 90—100 °C for 3.5 h under stirring. After being cooled to room temp, the reaction mixture was poured into ice-water and extracted with ethyl acetate. The organic layer was washed with brine and dried over anhyd Na_2SO_4. Evaporation of the solvent yielded 178 mg (92%) of diketone **8**: IR ($CHCl_3$) ν_{max} 2950, 1680, 1590, 1330, 1290 cm^{-1}; NMR (100 MHz, $CDCl_3$) δ 1.72 (4H, s, ethane bridge), 2.16 (4H, br quintet, J=7.0 Hz, β protons to carbonyl), 2.62 (4H, dd, J=7.0 and 6.0 Hz, α protons to carbonyl), 3.12 (4H, t, J=6.0 Hz, benzylic), 4.70 (2H, s, bridge head), 7.24 (2H, d, J=7.6 Hz, aromatic meta to carbonyl), 7.88 ppm (2H, d, J=7.6 Hz, aromatic ortho to carbonyl); $[\alpha]_D$ +184.6° (c 0.00325, $CHCl_3$); UV (EtOH) λ_{max} 261.0 (ε 28300), λ_{max} 221.5 nm (ε 32700); CD (EtOH) $\Delta\varepsilon_{330.0}=+0.4$, $\Delta\varepsilon_{302.0}=+2.3$ $\Delta\varepsilon_{293.0}=0.0$, $\Delta\varepsilon_{275.0}=-17.4$, $\Delta\varepsilon_{264.5}=0.0$, $\Delta\varepsilon_{252.0}=+24.7$, $\Delta\varepsilon_{213.5}=+51.9$.

1,2,3,4,7,8,9,10,11,14-Decahydro-7,14-ethanodibenz[a,h]*anthracene (9).* A mixture of 145 mg (0.423 mmol) of diketone **8**, 0.75 ml of hydrazine hydrate, and 5 ml of diethylene glycol was heated at 100 °C for 1 h. Potassium hydroxide (900 mg) was added and the reaction mixture was heated at 200 °C for 2 h, during which time volatile materials were removed by distillation. After being cooled to room temp, the reaction mixture was poured into ice-water, acidified to pH 1 with 2M HCl, and extracted with ethyl acetate. The organic layer was washed with water and brine, and dried over anhyd Na_2SO_4. Evaporation of the solvent afforded 226 mg of syrup, which was chromatographed on silica gel (EtOAc-hexane 1 : 20) giving 35 mg (26%) of hydrocarbon **9**: IR ($CHCl_3$) ν_{max} 2920, 1450, 1430, 1140, 910 cm^{-1}; NMR (60 MHz, $CDCl_3$) δ 1.53—2.03 (12H, m, ethane bridge and methylene), 2.57—3.07 (8H, m, benzylic), 4.51 (2H, s, bridge head), 6.73 and 6.97 ppm (2H each, d, J=7.5 Hz, aromatic): UV (EtOH) λ_{max} 280.0 (ε 900), λ_{max} 270.7 (ε 900), λ_{max} 263.0 (ε 900), λ_{max} 217.5 nm (ε 37900); CD (EtOH) $\Delta\varepsilon_{280.5}=-2.3$, $\Delta\varepsilon_{270.0}=-2.2$, $\Delta\varepsilon_{246.0}=0.0$, $\Delta\varepsilon_{222.5}=+96.4$, $\Delta\varepsilon_{209.0}=0.0$; MS m/e 314 (M^+).

(+)-7,14-Dihydro-7,14-ethanodibenz[a,h]*anthracene (1).* A solution of 35 mg (0.111 mmol) of hydrocarbon **9** and 300 mg (1.32 mmol) of DDQ in 10 ml of benzene was gently refluxed for 4 h. After being cooled to room temp, excess DDQ and hydroquinone formed were removed by chromatography on silica gel. Evaporation of the solvent gave 29 mg (85%) of compound **1**: mp 234.0—235.5 °C from ethanol; IR (KBr) ν_{max} 3025, 2950, 2850, 1620, 1510 1380, 1170, 1150, 1140, 820, 805, 755, 740, 680, 535, 445 cm^{-1}; NMR (100 MHz, $CDCl_3$) δ 1.82 (4H, s, ethane bridge), 5.34 (2H, s, bridge head), 7.26—7.86 (10 H, m, aromatic), 8.28 ppm (2H, br d, J=8.0 Hz, aromatic); $[\alpha]_D$ +670.0° (c 0.02030, $CHCl_3$); UV (EtOH) λ_{max} 325.0 (ε 2500), λ_{max} 283.5 (ε 11100), λ_{max} 232.3 nm (ε 98200); CD (EtOH) $\Delta\varepsilon_{326}=-4.3$, $\Delta\varepsilon_{324}=0.0$, $\Delta\varepsilon_{322}=+5.0$, $\Delta\varepsilon_{304.5}=+25.5$, $\Delta\varepsilon_{291.5}=0.0$, $\Delta\varepsilon_{283.0}=-35.6$, $\Delta\varepsilon_{259.0}=0.0$, $\Delta\varepsilon_{237.0}=+326.5$, $\Delta\varepsilon_{229.5}=0.0$, $\Delta\varepsilon_{224.0}=-180.5$, $\Delta\varepsilon_{205.0}=-115.0$; MS m/e (relative intensity) 306 (30, M^+), 278 (100, $M-C_2H_4$).

Found: m/e 306.1410. Calcd for $C_{24}H_{18}$: M, 306.1409.

1,1′-(9,10-Dihydro-9,10-ethanoanthracene-1,5-diyl)di-2-propanone (10). To a cooled (−70 °C) suspension of 3.5 g (8.05 mmol) of (1-methoxyethyl)triphenylphosphonium chloride in 30 ml of dry THF was added dropwise, over 10 min, 5.4 ml (1.49 mmol/ml, 8.05 mmol) of a solution of *n*-butyl lithium in hexane under nitrogen with vigorous stirring. After the dark red reaction mixture had been stirred for 20 min at −70 °C, a solution of 175 mg (0.67 mmol) of dialdehyde (+)-**4** in 10 ml of THF was added dropwise. The reaction mixture was stirred for 14 h, during which time the temperature was allowed to rise to room temp. After addition of water, the mixture was extracted with chloroform. The organic layer was washed with water and brine, and evaporated to dryness giving 2.975 g of syrup. The syrup was dissolved in 20 ml of methanol contaning 1 ml of 0.1 M HCl, and the mixture was refluxed for 1 h. After being cooled to room temp, the reaction mixture was poured into water, and extracted with ethyl acetate. The organic layer was washed with water and brine, and evaporated to afford 3.624 g of syrup, which was chromatographed on silica gel in order to remove triphenylphosphine and triphenylphosphine oxide formed. The eluate was evaporated to dryness and the residue was subjected to preparative TLC (EtOAc–hexane, 1 : 4) giving 146 mg (69%) of crystalline diketone **10**: mp 136.5—137.5 °C from ethanol; IR (KBr) ν_{max} 2960, 2950, 1715, 1700, 1360, 1160, 785 cm^{-1}; NMR (100 MHz, $CDCl_3$), δ 1.65 (4H, s, ethane bridge), 2.09 (6H, s, methyl), 3.82 (4H, s, benzylic), 4.49 (2H, s, bridge head), 7.28 (2H, dd, J=7.0 and 2.3 Hz, aromatic), 7.40 (2H, t, J=7.0 Hz, aromatic), 7.55 ppm (2H, dd, J=7.0 and 2.3 Hz, aromatic).

Found: C, 82.99, H, 7.13%. Calcd for $C_{22}H_{22}O_2$: C, 82.98; H, 6.96%.

Diethyl 9,10-Dihydro-β,β′-dimethyl-9,10-ethanoanthracene-1,5-dicrotonate (11). To a suspension of 331 mg (13.8 mmol) of sodium hydride in dry THF was added dropwise under nitrogen and ice-cooling a solution of 4.65 g (20.7 mmol) of triethylphosphonoacetate in 2 ml of dry THF. After the clear brown reaction mixture had been stirred at room temp for 30 min, a solution of 438 mg (1.38 mmol) of diketone **10** in 1 ml of THF was added dropwise, and the mixture was stirred overnight. After addition of water, the reaction mixture was extracted with ether. The ethereal solution was washed with water and brine, and dried over anhyd Na_2SO_4. Evaporation of the solvent gave 757 mg of syrup, which was chromatographed on silica gel in order to remove excess triethylphosphonoacetate, giving 356 mg (56%) of diester **11** as syrup: IR (neat) ν_{max} 2950, 1733, 1711, 1215, 1145, 1045 cm^{-1}; NMR (60 MHz, $CDCl_3$) δ 1.05—1.45 (6H, m, methyl), 1.50—1.75 (4H, br s, ethane bridge), 1.45—2.30 (6H, m, vinyl methyl), 3.03—3.62 (4H, m, benzylic), 3.90—4.20 (6H, m, bridge head and methylene of ethoxyl group), 5.30—5.85 (1H, m, vinyl), 6.40—7.40 ppm (7H, m, vinyl and aromatic). Thus, the NMR spectrum indicates that diester **11** is a *cis,trans* isomeric mixture.

Diethyl 9,10-Dihydro-β,β′-dimethyl-9,10-ethanoanthracene-1,5-dibutyrate (12). A mixture of 356 mg (0.778 mmol) of diester **11** and 20 mg of PtO_2 in 20 ml of ethanol was magnetically stirred under hydrogen atmosphere at room temp for 4 h. Removal of the catalyst by filtration, and evaporation of the solvent afforded 348 mg (100%) of an epimeric mixture of diester **12** as syrup: IR (neat) ν_{max} 2950, 1715, 1155, 755 cm^{-1}; NMR (60 MHz, $CDCl_3$) δ 0.70—0.96 (6H, m, methyl), 1.05—1.45 (6H, m, methyl of ethoxy), 1.65 (4H, br s, ethane bridge), 2.10—2.85 (10H, m, methylene and methine) 3.85—4.35 (4H, m, methylene of ethoxy), 4.35—4.70 (2H, br s, bridge head), 6.46—7.28 ppm (6H, m, aromatic).

9,10-Dihydro-β,β′-dimethyl-9,10-ethanoanthracene-1,5-dibutyric Acid (13). Diester **12** (348 mg, 0.754 mmol) was dissolved in 20 ml of a 5% ethanolic KOH solution and the solution was gently refluxed for 3.5 h. After being cooled to room temp, the reaction mixture was acidified with 2 M HCl under ice-cooling, and extracted with chloroform. The organic layer was washed with water and brine, and dried over anhyd Na_2SO_4. Evaporation of the solvent yielded 314 mg (100%) of dicarboxylic acid **13** as syrup: IR (CCl_4) ν_{max} 3650—2200, 2950, 1705, 1430, 1405, 1290, 1220, 1140, 940 cm^{-1}: NMR (60 MHz, $CDCl_3$) δ 0.60—1.40 (8H, m, methyl and methine), 1.65 (4H, br s, ethane bridge), 1.90—2.95 (8H, m, methylene), 4.55 (2H, br s, bridge head), 6.50—7.30 (6H, m, aromatic), 8.20—8.90 ppm (2H, br s, carboxyl).

1,2,3,7,8,9,10,14-Octahydro-2,9-dimethyl-7,14-ethanodibenz[a,h]*anthracene-4,11-dione (14).* A mixture of 275 mg (0.678 mmol) of dicarboxylic acid **13** in 9 ml of polyphosphoric acid (prepared in the same way as described for diketone **8**) was heated at 90 °C for 1 h under stirring. After being cooled to room temp, the reaction mixture was poured into ice-water, and extracted with chloroform. The organic layer was washed with water and brine, and dried over anhyd Na_2SO_4. Evaporation of the solvent gave 281 mg of syrup, which was chromatographed on silica gel to yield 135 mg (50%) of diketone **14** as syrup: IR (CCl_4) ν_{max} 2950, 1685, 1595, 1580, 1285, 1110 cm^{-1}; NMR (100 MHz, $CDCl_3$) δ 1.23 (6H, d, J=6.0 Hz, methyl), 1.72 (4H, s, ethane bridge), 2.19—2.79 (8H, m, methylene and/or methine), 3.12—3.48 (2H, m, methylene or methine), 4.72 (2H, s, bridge head), 7.24 (2H, d, J=7.5 Hz, aromatic meta to carbonyl), 7.85 ppm (2H, d, J=7.5 Hz, aromatic ortho to carbonyl).

1,2,3,4,7,8,9,10,11,14-Decahydro-2,9-dimethyl-7,14-ethanodibenz[a,h]*anthracene (15).* A solution of 127 mg (0.342 mmol) of diketone **14** and 5 ml of hydrazine hydrate in 50 ml of diethylene glycol was heated at 100 °C for 30 min. Potassium hydroxide (2.5 g) was added and the reaction mixture was heated at 200 °C for 3 h, during which time volatile substances were distilled. After being cooled to room temp, the reaction mixture was poured into ice-water, acidified with 2 M HCl, and extracted with ether. The ethereal layer was washed with water and brine. Evaporation of the solvent afforded 371 mg of a mixture of yellow crystals and oil, which was recrystallized from methanol giving 68 mg (58%) of hydrocarbon **15**: mp 176.0—177.0 °C; IR (KBr) ν_{max} 2940, 2920, 2360, 1475, 1455, 1435, 825 cm^{-1}; NMR (100 MHz, $CDCl_3$) δ 1.08 (6H, d, J=6.5 Hz, methyl), 1.0—2.0 (6H, m, methylene and methine), 1.62 (4H, s, ethane bridge), 2.31 (2H, dd, J=16.8 and 10.6 Hz, benzylic), 2.73 (4H, m, benzylic), 3.06 (2H, dt, J=16.8 and 4.5 Hz, benzylic), 4.49 (2H, s, bridge head), 6.75 (2H, d, J=7.6 Hz, aromatic), 6.98 ppm (2H, d, J=7.6 Hz, aromatic).

(+)-7,14-Dihydro-2,9-dimethyl-7,14-ethanodibenz[a,h]*anthracene (2).* A mixture of 67 mg (0.196 mmol) of hydrocarbon **15** and 426 mg (1.88 mmol) of DDQ in 10 ml of benzene was gently refluxed for 4 h. After being cooled to room temp, excess DDQ and hydroquinone were removed by chromatography on silica gel. The eluate was evaporated and the residue was subjected to preparative TLC (petroleum ether–EtOAc 100 : 3) yielding 47 mg (72%) of hydrocarbon **2**: mp 209.5—211 °C from ethanol; IR (KBr) ν_{max} 3040, 2920, 2850, 1625, 830, 557 cm^{-1}; NMR (100 MHz, $CDCl_3$) δ 1.76 (4H, s, ethane bridge), 2.55 (6H, s, methyl), 5.26 (2H, s, bridge head), 7.15 (2H, dd, J=8.2 and 2.0 Hz, 3-H and 10-H), 7.40 and 7.49 (2H each, d, J=9.0 Hz, 5-H, 6-H, 12-H, and 13-H), 7.64 (2H, d, J=8.2 Hz, 4-H and 11-H), 8.01 ppm (2H, br s, 1-H and 8-H); $[\alpha]_D$ +786° (c 0.01005, 10% dioxane in ethanol); UV (0.18% dioxane in ethanol) λ_{max} 326.3 (ε 1000), λ_{max} 286.5 (ε 11700), λ_{max} 236.8 (ε 98100), λ_{max} 226.0 nm (ε 95300); CD (0.18% dioxane in ethanol) $\Delta\varepsilon_{326.5}=-2.3$, $\Delta\varepsilon_{324.5}=0.0$, $\Delta\varepsilon_{307.0}=+25.1$, $\Delta\varepsilon_{292.0}=0.0$, $\Delta\varepsilon_{281.0}=-18.7$, $\Delta\varepsilon_{261.0}=0.0$, $\Delta\varepsilon_{240.6}=+371.5$, $\Delta\varepsilon_{232.8}=0.0$,

$\Delta\varepsilon_{227.0}=-149.4$, $\Delta\varepsilon_{210.0}=-111.3$; MS *m/e* (relative intensity) 334 (35, M^+), 306 (100, $M-C_2H_4$).

Found: *m/e* 334.1727. Calcd for $C_{26}H_{22}$: M, 334.1720. Found: C, 92.82; H, 6.75%. Calcd for $C_{26}H_{22}$: C, 93.37; H, 6.63%.

7,14-Dihydro-2,4,9,11-tetramethyl-7,14-ethanodibenz[a,h]*anthracene (**3**).* To a solution of 30 mg (0.0812 mmol) of diketone **14** in 2 ml of dry THF was added dropwise 4 ml of an ethereal solution of methyl lithium (2.0 mmol) under nitrogen and ice-cooling. The reaction mixture was stirred for 2 h. After addition of ice-water, the mixture was extracted with ether. The ethereal layer was washed with water and brine, dried over anhyd Na_2SO_4, and evaporated to dryness giving 24 mg of syrup. The residue was dissolved in 20 ml benzene, to which 82 mg (0.36 mmol) of DDQ was added. The reaction mixture was gently refluxed for 3 h under stirring. After being cooled to room temp, the mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with water, 1% aq KOH, and brine, and dried over anhyd Na_2SO_4. Evaporation of the solvent afforded 39 mg of syrup, which was subjected to preparative TLC on silica gel (EtOAc-hexane 1 : 20) yielding 5.5 mg (19%) of hydrocarbon **3**: mp 124.0—126.0 °C from ethanol; IR (KBr) ν_{max} 2940, 2850, 1620, 1150, 850 cm^{-1}; NMR (100 MHz, $CDCl_3$) δ 1.82 (4H, s, ethane bridge), 2.54 (6H, s, 2-CH_3 and 9-CH_3), 2.61 (6H, s, 4-CH_3 and 11-CH_3), 5.32 (2H, s, bridge head), 7.10 (2H, s, 3-H and 10-H), 7.53 (2H, d, J=8.3 Hz, 6-H and 13-H), 7.73 (2H, d, J=8.3 Hz, 5-H and 12-H), 7.96 ppm (2H, s, 1-H and 8-H); UV (EtOH) λ_{max} 293.0 (ε 16000), λ_{max} 238.0 nm (ε 116200); CD (EtOH) $\Delta\varepsilon_{311.5}=+27.5$, $\Delta\varepsilon_{296.5}=0.0$, $\Delta\varepsilon_{283.0}=-27.1$, $\Delta\varepsilon_{255.5}=0.0$, $\Delta\varepsilon_{242.0}=+340.3$, $\Delta\varepsilon_{230.5}=0.0$, $\Delta\varepsilon_{225.0}=-88.0$, $\Delta\varepsilon_{212.5}=-139.3$.

The authors thank Dr. Hiroshi Hayashi, Asahi Chemicals Industry, Co., for measurements of the mass spectra. The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education.

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