Optical Activity and Absolute Configuration of 5,6,11,12-Tetrahydro-2,3,8,9-tetramethoxy-5,11-methanodibenzo[*a*,*e*]cyclooctatetraene[†]

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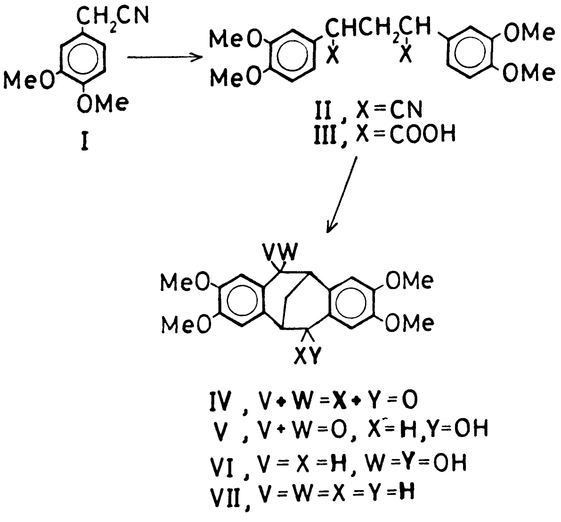
The title compound (VII) was synthesized in an optically active form and the chiroptical properties were recorded. The absolute configuration was determined by chemical correlation method.

The title compound (VII) has a novel type of rigid bicyclo[3.3.1]nonadiene cage skeleton and holds two veratrole chromophores in a twisted spacial position. Formally VII could be transformed to alkaloid argemonine by substituting the methanobridge with an *N*-methyl group. The optical activity of argemonine[1)] was discussed in connection with the absolute configuration[2)] but not fully understood yet. The perfect C_2-symmetry and pure carbocyclic structure make VII one of the best model for the study of chiroptical properties of organic molecules containing two separate aromatic chromophores.

This paper deals with the synthesis, optical resolution and determination of absolute configuration by chemical means concerning VII and its derivatives.

Synthesis and Optical Resolution. The route of synthesis was outlined in Scheme 1. 3,4-Dimethoxyphenylacetonitrile (I) was allowed to react in THF with diiodomethane in the presence of sodium methoxide to yield 2,4-bis(3,4-dimethoxyphenyl)glutaronitrile (II) which was a mixture of racemic and meso forms. Fractional recrystallization of the crude dinitrile from methanol afforded two kinds of crystals. Higher melting crystals were assigned to the racemate and lower melting ones to the meso form on the basis of splitting patterns of methylene proton singnals in their ^{1}H-NMR spectra.[3)] The dicarboxylic acid (III) obtained by alkaline hydrolysis of crude II was cyclized to the diketone (IV) with polyphosphoric acid. Dehydrative cyclization with concd sulfuric acid gave poor results, because of rapid sulfonation to benzene rings activated by two methoxyl groups. The diketone (IV) was reduced to the glycol (VI) with $LiAlH_4$ in THF. The ketol (V) could be obtained along with VI when catalytic reduction of IV over the Adams catalyst was interrupted after one equivalent hydrogen was absorbed.

Optical resolution was carried out *via* camphanate of the ketol (V) or the glycol (VI). Bis-camphanate prepared from (+)-VI and ω-camphanoyl chloride was fractionally recrystallized eleven times from ethanol to yield optically pure crystals. The camphanate derived from (+)-V could be fractionated more effectively than the bis-camphanate of VI. Thus almost optically pure crystals were obtained after one recrystallization from ethanol. Pure (+)-V and (+)-VI were obtained by alkaline hydrolysis of their camphanates. Catalytic reduction of (+)-V over the Adams catalyst afforded



Scheme 1.

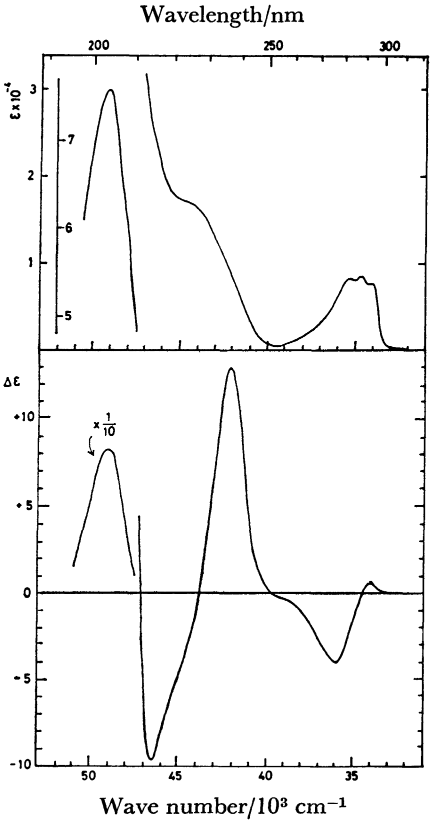


Fig. 1. UV (top) and CD (bottom) spectra of (+)-5,6,11,12-tetrahydro-2,3,8,9-tetramethoxy-5,11-methanodibenzo[*a*,*e*]cyclooctatetraene (VII) in ethanol.

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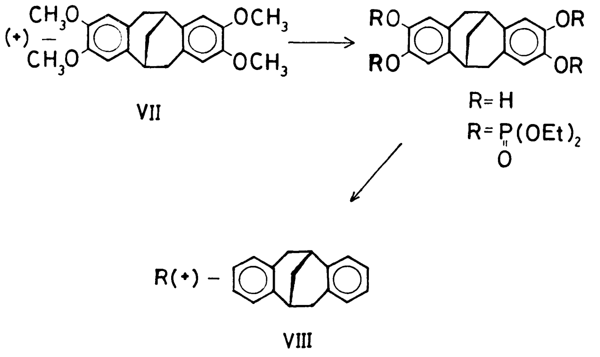
(+)-VI and (−)-IV was obtained from (+)-VI by the Jones oxidation. All of (−)-IV, (+)-V and (+)-VI could be converted easily to the desired compound, (+)-VII, under condition of the Clemmensen reduction.

Optical Activity and Absolute Configuration. The CD spectra of (+)-VII was shown in Fig. 1. Beautiful positive couplets were observed in both α- and p-band regions and a strong positive band appeared in ${}^1E_{1u}$ region.

The absolute configuration was estimated to be *R* by usual exciton theoretical CD analysis, in which the transition moments of each band were assumed to lie in the center and in the direction of the short or long axis of benzene rings according to the spectroscopic moments theory.[4] The molecular structural parameters of VII were assumed to be the same as those of 5,6,11,12-tetrahydro-5,11-methanodibenzo[*a,e*]cyclooctatetraene, VIII.[5]



Scheme 2.

The absolute configuration of (+)-VII was determined to be (*R*) by a chemical correlation (Scheme 2). Demethylation of (+)-VII with BBr_3 followed by diethoxyphosphinylation with diethyl phosphonate afforded a tetrakis-phosphate. The phosphate was reduced by sodium metal in liq ammonia to yield (+)-VIII, whose absolute configuration was proven to be *R*.[3,5] Thus the result of CD analysis was in good agreement with that of the chemical correlation.

Experimental

The melting points were measured on a Mettler FP2 apparatus and are uncorrected. Purified and anhydrous solvents were used, unless otherwise stated. The IR spectra were obtained on a Hitachi EPI-2, EPI-G3, and a JASCO DS-301 spectrometers, electronic spectra on a Hitachi EPS-3T and a Zeiss PMQIIM4QIIId spectrometers, ^{1}H-NMR spectra in deuteriochloroform unless otherwise stated on a Varian XL-100, A-60D or Hitachi R-24 spectrometer using TMS as an internal standard and given in δ-unit. The optical rotations were obtained on a Union Giken High Precision polarimeter PM-71 at 20 °C unless otherwise stated. CD spectra were obtained on a JASCO J-20 spectrometer. Shoulders and inflections are denoted by an asterisk.

3,4-Dimethoxybenzyl Cyanide (I): Veratraldehyde (100 g, 0.6 mol) in ether (500 ml) was added dropwise to an ice-cold ether solution (300 ml) of $LiAlH_4$ (13.7 g). Stirring was continued for further 2 h at room temperature. Ethyl acetate (20 ml) and water (20 ml) were added dropwise with stirring and ice-cooling. The resulting mixture was stirred for a while at room temperature. Colorless gelatinous precipitates formed were removed with suction filtration and washed with ethyl acetate (300 ml). Combined filtrate and washings were concentrated and distilled under reduced pressure to afford 3,4-dimethoxybenzyl alcohol as a colorless oil, bp 155 °C/533 Pa (98 g, 96%).

A cold mixture of the alcohol (82.6 g), dichloromethane (100 ml) and concd HCl (100 ml) was stirred vigorously for 20 min at 0—10 °C. Further amount of CH_2Cl_2 (100 ml) was added to the mixture with stirring. The organic layer separated was dried over $CaCl_2$ for 30 min and concentrated under reduced pressure. 3,4-Dimethoxybenzyl chloride obtained was used immediately for further reaction without purification.

Powdered sodium cyanide (48 g) and potassium iodide (6 g) were added to the chloride in acetone (300 ml). The mixture was refluxed for 20 h and filtered with suction after cooling down. The filtrate concentrated under reduced pressure was poured into water and extracted with benzene. The combined extracts were washed with water, dried and concentrated under reduced pressure. Vaccum distillation afforded I as a colorless oil, bp 160 °C/533 Pa (65.0 g, 75%). ^{1}H-NMR (CCl_4): 3.55 (s, 2H, methylene), 3.75 (s, 6H, methoxy), 6.70 (s, 3H, aromatic).

2,4-Bis(3,4-dimethoxyphenyl)glutaronitrile (II): Dry sodium methoxide prepared from sodium (1.8 g, 0.078 g atom) and methanol (100 ml) was suspended in THF (100 ml) and mixed with I (13.5 g, 0.076 mol) and diiodomethane (11.5 g, 0.043 mol). After being refluxed for 1 h with stirring, the mixture was concentrated under reduced pressure and extracted with dichloromethane. After usual work up, the extract was concentrated *in vacuo* to yield a brown oil, which was purified with a column of silica gel (80 g). From benzene–ethyl acetate (1 : 1) eluate, II (8.6 g, 61%) was obtained as a diastereomeric mixture of racemic and meso from. Repeated recrystallization of the crude nitrile from methanol gave racemate as colorless needles and meso form as colorless plates.

Racemate: mp 141—142 °C. ^{1}H-NMR: 2.45 (t, J=8 Hz, 2H, methylene), 3.89, 3.91 (two s, 12H, methoxyl), 4.00 (t, J=8 Hz, 2H, methine), 6.80—6.90 (m, 6H, aromatic). Found: C, 68.64; H, 6.11; N, 7.75%. Calcd for $C_{21}H_{22}O_4N_2$: C, 68.83; H, 6.05; N, 7.65%. *meso*-Isomer: mp 101 °C. ^{1}H-NMR: 2.20—2.90 (m, 2H, methylene), 3.91 (br s, 12H, methoxyl), 3.75 (apparent t, 2H, methine), 6.85—6.90 (m, 6H, aromatic). Found: C, 68.77; H, 6.01; N, 7.68%. Calcd for $C_{21}H_{22}O_4N_2$: C, 68.83; H, 6.05; N, 7.65%.

2,4-Bis(3,4-dimethoxyphenyl)glutaric Acid (III) and Its Methyl Ester: The crude dinitrile (II, 1.0 g) dissolved in 95% ethanol (20 ml) was mixed with KOH (5 g) in 50% EtOH (20 ml) and heated to reflux for 20 h. After removal of ethanol under reduced pressure, the mixture was poured into water (100 ml) and washed three times with dichloromethane. Alkaline aqueous layer was decolorized with active charcoal, and acidified with concd HCl. Precipitates formed were extracted with dichloromethane. After usual work up, a colorless solid of III (0.9 g, 81%) was obtained from the extract. Reflux with methanol and concd sulfuric acid gave colorless crystals of dimethyl ester, mp 116—117 °C (from methanol). ^{1}H-NMR: 1.9—2.9 (m, 2H, methylene), 3.4 (t, 2H, methine), 3.65 (s, 6H, methyl), 3.85 (s, 12H, methoxyl), 6.75 (br s, 6H, aromatic). Found: C, 63.84; H, 6.54%. Calcd for $C_{23}H_{28}O_8$: C, 63.88; H, 6.53%.

5,6,11,12-Tetrahydro-2,3,8,9-tetramethoxy-5,11-methanodibenzo[a,e]*cyclooctateraene-6,12-dione (IV)*: *a) With Polyphosphoric Acid*: Crude dicarboxylic acid (III, 1.8 g, 0.0049 mol) was mixed with polyphosphoric acid (30 g) and stirred for

5 min at 80 °C. The reaction mixture was poured onto ice (100 g) and precipitates separated were extracted with CH_2Cl_2. Combined extracts were washed with brine, 10% aq NaOH, and brine, successively, and dried over $MgSO_4$. Solvent was removed under reduced pressure to yield IV as a colorless solid, which was recrystallized from dichloromethane–ethanol, mp 261—262 °C. ^{1}H-NMR: 3.0 (t, $J=3$ Hz, 2H, methylene), 3.95, 3.85 (two s, 12H, methoxyl, signals of methine protons (2H) were overlapped with those signals), 6.9, 7.4 (two s, 4H aromatic). IR (Nujol mull): 1670 ($\nu_{\text{C=O}}$) cm^{-1}. Found: C, 68.18; H, 5.46%. Calcd for $C_{21}H_{20}O_6$: C, 68.47; H, 5.47%.

b) With Concd Sulfuric Acid: Crude III (0.6 g) was dissolved in concd sulfuric acid and cooled to −15 °C. The mixture was stirred for 2 h at the temperature and mixed with water (30 ml). Precipitated product was extracted with benzene. Combined extracts were washed with water, 5% aq $NaHCO_3$, and water, successively, and dried over Na_2SO_4. Evaporation of solvent *in vacuo* and trituration with ethanol afforded crude crystals (0.15 g, 27%), whose spectroscopic properties were identical with those of the authentic diketone (IV). The acidic component obtained from the above mentioned $NaHCO_3$ washings were converted with a usual procedure to methyl ester, mp 159—160 °C. ^{1}H-NMR: 2.35—2.80 (m, 2H, methylene), 3.75 (s, 3H, methyl), 3.8, 3.9 (two s, 12H, methoxyl), 3.5—4.2 (m, 2H, methine), 6.7—6.8 (m, 4H, aromatic), 7.5 (s, 1H, aromatic). Found: C, 65.77; H, 6.06%. Calcd for $C_{22}H_{24}O_7$: C, 65.99; H, 6.04%. The ester was assigned to methyl 3-(3,4-dimethoxyphenyl)-4-oxo-6,7-dimethoxy-1,2,3,4-tetrahydro-1-naphthoate on the basis of its ^{1}H-NMR spectra.

12-Hydroxy-5,6,11,12-tetrahydro-2,3,8,9-tetramethoxy-5,11-methanodibenzo[a,e]*cyclooctatetraen-6-one (V)*: Diketone IV (2.164 g, 0.0057 mol) dissolved in dichloromethane (70 ml) and ethanol (100 ml) was catalytically reduced over the Adams catalyst at room temperature. In 40 min *ca.* 165 ml of hydrogen was absorbed and the catalyst was removed to stop the reduction.

Evaporation of solvents under reduced pressure yielded a colorless solid, which was chromatographed on a column of silica gel (50 g) with dichloromethane. Recovered IV (0.380 g, 17%), desired ketol (V, 1.28 g, 59%) and the diol (VI, 0.500 g, 23%) were eluted successively. Recrystallization from methanol afforded colorless needles of V, mp 206 °C. ^{1}H-NMR: 1.6 (d, 1H, OH), 2.5 (m, 2H, methylene), 3.6 (m, 2H, bridgehead methine), 3.7—3.9 (four singlets, 12H, methoxyl), 5.0 (q, 1H, methine), 6.7—7.4 (four singlets, 4H, aromatic) IR (Nujol mull): 3400 (ν_{OH}), 1655 ($\nu_{\text{C=O}}$) cm^{-1}. Found: C, 67.94; H, 5.94%. Calcd for $C_{21}H_{22}O_6$: C, 68.09; H, 5.99%.

Optical Resolution of 12-Hydroxy-5,6,11,12-tetrahydro-2,3,8,9-tetramethoxy-5,11-methanodibenzo[a,e]*cyclooctatetraen-6-one (V)*: *dl*-Ketol (V, 3.8 g, 0.01 mol) dissolved in pyridine (50 ml) was mixed with freshly prepared ω-camphanoyl chloride (2.40 g) and stirred overnight at room temperature. The mixture was poured into water (100 ml) and extracted with dichloromethane (50 ml) and ether (100 ml). Combined extracts were washed thoroughly with 1 M HCl, brine, saturated aq $NaHCO_3$, and brine, successively. After being dried over Na_2SO_4, solvents were removed under reduceds pressure to yield a colorless solid. The solid was recrystallized four times from ethanol or dichloromethane–ethanol to give (−)-camphanate of V with constant optical rotations as colorless needles (1.68 g). Mp 235—237 °C, $[\alpha]^{15}_{\text{D}}-15.8°$, $[\alpha]^{15}_{405}-192.8°$ (*c* 0.448, $CHCl_3$). Found: C, 67.42; H, 6.32%. Calcd for $C_{31}H_{34}O_9$: C, 67.62; H, 6.22%.

Pure(−)-camphanate (1.68 g) was heated to reflux for 1 h with aq methanolic KOH. Evaporation of methanol afforded crude crystals of (+)-V (1.09 g, 96%). Recrystallization from ethanol yielded colorless needles. Mp 222 °C, $[\alpha]^{18}_{\text{D}}+26°$, $[\alpha]^{18}_{405}-258°$ (*c* 0.270, $CHCl_3$), ^{1}H-NMR: Identical with the racemate, UV: $\lambda^{\text{EtOH}}_{\text{max}}$ (ε) 360 (1000), 321 (8200), 280 (11000) 237 (28400), 204.5 (40800) nm, CD: $\lambda^{\text{EtOH}}_{\text{max}}$ ($\Delta\varepsilon$) 359 (−1.72), 348 (−1.43), 326 (−3.94), 287 (−6.74), 267 (+11.1), 242 (+26.9), 229 (−18.7), 208 (+45.9) nm. Found: C, 67.82; H, 6.00%. Calcd for $C_{21}H_{22}O_6$: C, 68.09; H, 5.99%.

(+)-5,6,11,12-Tetrahydro-2,3,8,9-tetramethoxy-5,11-methanodibenzo[a,e]*cyclooctatetraene-6,12-diol (VI)*: (+)-Ketol (V, 0.120 g, 0.320 mmol) dissolved in acetic acid (20 ml) and ethanol (30 ml) was catalytically reduced over the Adams catalyst for 3 h under ordinary pressure and temperature. After the catalyst was removed by filtration and the residue was chromatographed on a column of silica gel (20 g) with CH_2Cl_2 and ethyl acetate. Recovered (+)-ketol (0.055 g) and (+)-VI (0.060 g) were eluted successively. (+)-Diol was recrystallized from ethanol. mp 220 °C, $[\alpha]^{18}_{\text{D}}+115,°$ $[\alpha]^{18}_{405}+327°$ (*c* 0.163, $CHCl_3$), ^{1}H-NMR: identical with racemate, UV: $\lambda^{\text{EtOH}}_{\text{max}}(\varepsilon)$ 289 (6600), 284 (6900), 280 (6200), 234 (15300), 207 (70700) nm, CD: $\lambda^{\text{EtOH}}_{\text{max}}$ ($\Delta\varepsilon$) 289 (+3.0), 243 (+16.0), 213 (+34.8), 199 (−44.0) nm. Found: C, 67.54: H, 6.42%. Calcd for $C_{21}H_{21}O_3$: C, 67.73: H, 6.50%.

5,6,11,12-Tetrahydro-2,3,8,9-tetramethoxy-5,11-methanodibenzo[a,e]*cyclooctatetraene-6,15-diol (VI)*: A THF solution (150 ml) of the diketone IV (1.5 g, 0.004 mol) was added dropwise to an ice-cold THF solution (120 ml) of $LiAlH_4$ (1.0 g). The mixture was stirred for 3 h at room temperature and decomposed with ethyl acetate (2 ml), water (2 ml) and saturated aq ammonium chloride successively. Gelatinous precipitates formed were removed by suction filtration and the filtrate was concentrated under reduced pressure. The crude product obtained was recrystallized from benzene to yield colorless needles (1.45 g, 95%) of *dl*-VI, mp 210—211 °C, ^{1}H-NMR: 1.6 (d, 2H, OH), 2.4 (t, 2H, methlene), 3.3 (m, 2H, bridgehead methine), 3.8, 3.9 (s, 12H, methoxyl), 4.9 (q, 2H, methine) 6.7, 7.0 (s, 4H aromatic), IR (Nujol mull): 3350 (ν_{OH}) cm^{-1}. Found: C, 67.57; H, 6.51%. Calcd for $C_{21}H_{24}O_6$: C, 67.73; 6.50%.

Optical Tesolution of 5,6,11,12-Tetrahydro-2,3,8,9-tetramethoxy-5,11-methanodibenzo[a,e]*cyclooctatetraene-6,12-diol (VI)*: *dl*-Diol (VI, 0.50 g, 1.6 mmol) dissolved in pyridine (3 ml) was mixed with freshly prepared ω-camphanoyl chloride (1.0 g) and the mixture was stirred overnight at room temperature. Water was added to the mixture and extracted with dichloromethane and ether. Combined extracts were washed thoroughly with 1 M HCl and brine. After being dried over magnesium sulfate, solvents were removed under reduced pressure to yield a colorless oil (0.88 g, 90%), which was crystallized by trituration with ethanol.

Repeated fractional recrystallization (11 times) afforded optically pure (−)-bis-camphanate of VI as colorless needles (0.08 g). $[\alpha]^{18}_{\text{D}}-25°$, $[\alpha]^{18}_{405}-45°$ (*c* 0.910, $CHCl_3$). Pure (−)-bis-camphanate obtained was heated to reflux in aq methanolic KOH solution. Crystals appeared on evaporation of methanol were collected by suction filtration and recrystallized from EtOH to yield optically pure (+)-VI (0.030 g), mp 220 °C. $[\alpha]^{18}_{\text{D}}+110°$, $[\alpha]^{18}_{405}+330°$ (*c* 0.370, $CHCl_3$).

(−)-5,6,11,12-Tetrahydro-2,3,8,9-tetramethoxy-5,11-methanodibenzo[a,e]*cyclooctatetraene-6,12-dione (IV)*: Chromium trioxide (0.4 g) in water (2 ml) was added dropwise at room temperature to a well stirred solution of (+)-ketol (VI, 0.430 g, 1.3 mmol) in acetic acid (30 ml). The mixture was diluted with water (50 ml) and extracted with dichloromethane.

Combined extracts were washed with water, saturated aq $NaHCO_3$, and water, successively, and dried over sodium sulfate. On concentration under reduced pressure, a yellow solid was obtained. A dichloromethane solution of the solid was passed through a short column of silica gel (10 g) to remove colored impurities. Recrystallization from ethanol afforded colorless crystals of (−)-IV (0.270 g, 63%). Mp 222—223 °C, $[\alpha]_D^{18}-246°$, $[\alpha]_{405}^{18}-3290°$ (*c* 0.06, $CHCl_3$), UV: $\lambda_{max}^{dioxane}(\varepsilon)$ 366* (1050), 348* (3070), 339* (3940), 316 (13600), 284 (19800), 270 (29600), 240 (24700) nm. $\lambda_{max}^{EtOH}(\varepsilon)$ 340* (4700), 315 (12900), 285* (21000), 271 (26900), 238 (23600), 206 (26300) nm. CD: $\lambda_{max}^{dioxane}(\Delta\varepsilon)$ 365 (−13.8), 347 (−50.7), 336.5 (−47.3) 313 (+36.7), 285 (+55.8), 254 (−19.8), 230 (−26.6), 210 (+40.4) nm. λ_{max}^{EtOH} $(\Delta\varepsilon)$ 340 (−52.9), 310 (+31.8), 285 (+56.7), 253 (−16.9), 230 (−22.2), 209 (+40.7) nm. Found: C 68.57; H, 5.49%. Calcd for $C_{21}H_{20}O_6$: C, 68.47; H, 5.47%.

(+)-5,6,11,12-Tetrahydro-2,3,8,9-tetramethoxy-5,11-methanodibenzo[a,e]*cyclooctatetraene (VII)*: Granules of zinc (1.0 g) was amalgamated by a standard method6) and used immediately as follows. A benzene solution of (−)-diketone IV (50 mg) was added to a stirred mixture of the amalgamated zinc, water (0.5 ml), and concd HCl (1 ml). The mixture was refluxed for 4 h, diluted with water, and extracted with dichloromethane and ether. Combined extracts were washed with water, saturated aq $NaHCO_3$ and water, successively, and dried over Na_2SO_4. Solvents were removed under reduced pressure and the residue was passed through a short column of silica gel (10 g) as a CH_2Cl_2 solution. A colorless oil (34 mg, 74%) obtained was crystallized in methanol. Mp 209—210 °C, UV: $\lambda_{max}^{EtOH}(\varepsilon)$ 292 (7700), 288 (8600), 283 (8300), 223* (17300), 204 (76000) nm. CD: $\lambda_{max}^{EtOH}(\Delta\varepsilon)$ 294 (+1.0), 267.5 (−4.0), 237.5 (+13.0), 216 (−9.7), 204 (+82.5) nm. Found: C, 73.66; H, 7.10%. Calcd for $C_{21}H_{24}O_4$: C, 74.09: H, 7.11%.

*(*R*)-(+)-5,6,11,12-Tetrahydro-5,11-metahnodibenzo*[a,e]*cyclooctatetraene (VIII)*: As shown in Scheme 2, (+)-VII was converted to (*R*)-(+)-VIII.

Demethylation: A dichloromethane solution (12.5 ml) of (+)-VII (0.431 g, 1.27 mmol) was added with stirring to an ice-cold solution of BBr_3 (1.818 g, 7.26 mmol) in CH_2Cl_2 (15.6 ml). The mixture was stirred overnight at room temperature. Gelatinous precipitates were formed in the case of racemate. After addition of water (30 ml), the reaction mixture was stirred for 30 min and extracted with ether. Combined extracts were washed with saturated aq $NaHCO_3$ and brine, successively, and dried over Na_2SO_4. Upon concentration of the fraction *in vacuo*, the tetrol was obtained as faintly pink powder (0.352 g). Acidification of $NaHCO_3$ washings followed by extraction with ether gave further amount of the tetrol (0.052 g, total 0.404 g quantitative). Alkaline extraction should be avoided because of unstable nature of the phenol. ^{1}H-NMR (acetone-d_6); 2.35—3.27 (m, 8H, methylene and methine), 6.35, 6.62 (two singlets, 4H, aromatic), 7.05 (br s, 4H, OH). The phenol was used directly for further reaction without purification.

Dehydroxylation via *Diethoxyphosphinylation*: The tetrol (0.404 g, 1.421 mmol) was mixed with diethylphosphonate (0.862 g, 8.124 mmol) in CCl_4 (11 ml) and triethylamine (1 ml) and stirred for 48 h at room temperature. Colorless precipitates were formed. The mixture was mixed with water and extracted with chloroform. Combined extracts were wahsed with 1 M HCl, 5% aq $NaHCO_3$ and water, successively, and dried over Na_2SO_4. Evaporation of solvents under reduced pressure afforded a faintly yellow oil (1.42 g) which showed single spot on a TLC plate. The crude phosphate (1.42 g) dissolved in THF (50 ml) was added to liq NH_3 (50 ml). Sodium metal (0.5 g) was added in small pieces to the solution with stirring until blue color of the solution persisted. Crystals of ammonium chloride were added to the mixture to stop the reaction. Ammonia was evaporated by warming up the solution to room temperature. The residue was diluted with water and extracted with ether. Combined extracts were washed with cold 3% aq KOH and brine successively and dried over Na_2SO_4. On evaporation of solvents *in vacuo*, a light yellow solid was obtained. The crude product was dissolved in benzene and passed through a short column of silica gel (10 g).

The crystals obtained were again purified by high pressure liquid chromatography (machine: Hitachi 635; column: 8×500 mm×2 packed with Merck Lichrosorb S2-100; solvent: hexane; flow rate: 2.6 ml/min; pressure: 110 kg/cm^2; retention time: 45 min) and recrystallized from methanol or pentane. mp 100.5—101.5 °C, ^{1}H-NMR: 2.00 (t, J=3 Hz, 2H, methano-bridge), 2.62—3.52 (m, 6H, methine and benzylic methylene), 6.85—7.22 (m, 8H, aromatic), UV: $\lambda_{max}^{isooctane}(\varepsilon)$: 273 (1500), 266 (1230), 261.5 (800), 259.5 (790), 219 (15500), 214 (17800), 196 (66800) nm. CD: $\lambda_{max}^{isooctane}(\Delta\varepsilon)$: 273 (−1.89), 265.5 (−1.69), 260 (−1.02), 225 (+0.90), 222 (−1.81), 218 (+8.00), 214 (+7.29), 195 (+115.0) nm. Found: C, 92.37; H, 7.33%. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32%.

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