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Optically Active Triptycenes. V.* Synthesis, Optical Resolution and Absolute Configuration of 2,7-Disubstituted Triptycenes.

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2,7-Dicarboxytriptycene retaining C_2-axis of symmetry was synthesized from 1,5-dichloroanthraquinone. Optical resolution of the triptycene afforded (+)- and (−)-enantiomers. The absolute configuration of (+)-2,7-dicarboxytriptycene was determined as 1R,6R by chemical correlation with (+)-2-methoxy-7-methoxycarbonyltriptycene which has 1R,6S configuration as confirmed by chemical transformation and X-ray structure analysis using the Bijvoet method. Starting from (+)-2,7-dicarboxytriptycene, a series of 2,7-disubstituted triptycenes having 1R,6R configuration has been prepared.

As pointed out in previous papers of this series,[1,2] optically active triptycenes can be regarded as most suitable compounds for the study of rotatory properties in view of their definite molecular geometry and the well-marked electronic transition of benzenoid chromophores.

It is desirable to synthesize simpler and well-defined dissymmetrical systems to facilitate theoretical approaches, since the X-ray analysis of (+)-2,5-dimethoxy-7-dimethylaminotriptycene hydrobromide (XVIII) by the Bijvoet method gave an antipodal absolute configuration[3] to that deduced by the rigorous analysis of CD spectra of this series of trisubstituted triptycenes.[4] If we take into account the effect of substitution on the direction of polarization of the transition of benzenoid chromophore,[5,6] C_2-symmetrical triptycenes having the same substituents at 2,7-positions seem to be favorable model compounds for the present purpose.

The present paper deals with the synthesis, optical resolution and determination of absolute configuration of 2,7-dicarboxytriptycene (VII) and the transformation of VII into various kinds of C_2-symmetrical 2,7-disubstituted triptycenes. The route of synthesis of VII is outlined in Scheme 1. 1,5-Dicarboxyanthraquinone (III) was prepared by acid hydrolysis of dicyano derivative (II) derived from 1,5-dichloroanthraquinone (I). III was reduced to 1,5-dicarboxyanthracene (IV).

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* For preliminary report, see, J. Tanaka, F. Ogura, M. Kuritani, and M. Nakagawa, *Chimia*, **26**, 471 (1972); M. Kuritani, Y. Sakata, F. Ogura, and M. Nakagawa, *ibid.*, **26**, 470 (1972). For Part IV of this series, see Ref. 9.

1) A. Sonoda, F. Ogura, and M. Nakagawa, This Bulletin, **35**, 853 (1962).

2) F. Ogura, Y. Sakata, and M. Nakagawa, *ibid*, **45**, 3646 (1972).

3) N. Sakabe, K. Sakabe, K. Ozeki-Minakata, and J. Tanaka, presented at the 9th International Congress of Crystallography (1972); *Acta Crystallogr.*, **B 28**, 3441 (1972).

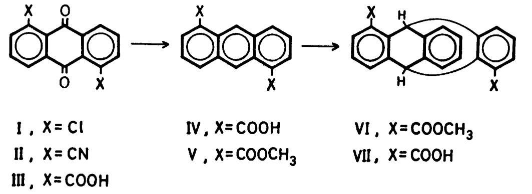
4) J. Tanaka, K. Ozeki-Minakata, F. Ogura, and M. Nakagawa, *Nature, Phys. Sci.*, **241**, 22 (1973).

5) J. R. Platt, *J. Chem. Phys.*, **19**, 263 (1951); J. Petruska, *ibid.*, **34**, 1111 (1961).

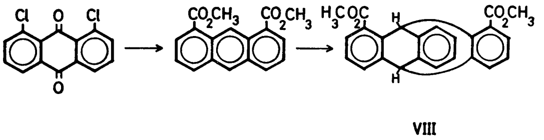
6) A. C. Albrecht and W. T. Simpson, *ibid.*, **23**, 1480 (1955); J. Tanaka, This Bulletin, **36**, 833 (1963).

Treatment of the sodium salt of IV with dimethyl sulfate afforded dimethyl ester (V). 2,7-Dimethoxycarbonyltriptycene (VI) was obtained by the addition of benzyne generated from diazotized anthranilic acid[7] with V.

Isomeric 5,7-dimethoxycarbonyltriptycene (VIII) having a plane of symmetry was prepared as a reference compound by a similar sequence of reaction starting from 1,8-dichloroanthraquinone[8] (Scheme 2).



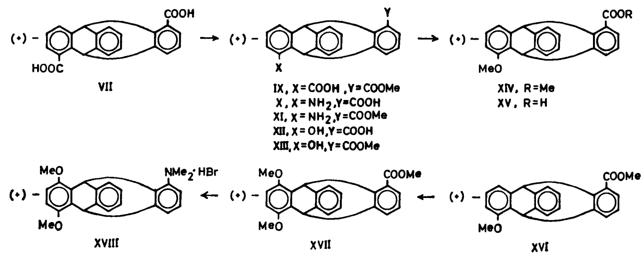
Scheme 1.



Scheme 2.

After several experiments, the optical resolution of VII obtained from VI was attained with equimolar cinchonidine and cinchonine. Optically pure (+)-dicarboxylic acid (VII) was obtained from the cinchonidine salt by decomposition with acetic acid. On the other hand, the cinchonine salt afforded (—)-VII.

(+)-Dicarboxylic acid (VII) was converted into acid sodium salt by the action of equimolar methanolic sodium methoxide (Scheme 3). The reaction of excess dimethyl sulfate with the acid salt afforded (+)-half ester (IX). (+)-Half ester was converted into (+)-2-amino-7-carboxytriptycene (X) by the Curtius reaction *via* acid chloride, acid azide and isocyanate. The diazonium salt derived from (+)-amino derivative (X) was hydrolyzed to yield (+)-2-hydroxy-7-carboxy triptycene (XII). The reaction of dimethyl sulfate with (+)-XII afforded (+)-2-methoxy-7-methoxycarbonyltriptycene (XIV). The methoxy-methyl ester (XIV) was found to be identical with the authentic (+)-2-methoxy-7-methoxycarbonyltriptycene (XVI) prepared by a different route and proved to have 1R, 6R absolute configuration by chemical correlation with (+)-2,5-dimethoxy-7-substituted-triptycenes (XVIII and XVII).[2,9] (+)-XIV and (+)-XVI showed identical IR, NMR, UV, and CD spectra, and the mixed melting point showed no depression. Consequently, the absolute configuration of (+)-2,7-dicarboxytriptycene (VII) was demonstrated to be 1R,6R. The UV and CD spectra of (+)-XIV and (+)-XVI are given in Fig. 1.



Scheme 3.

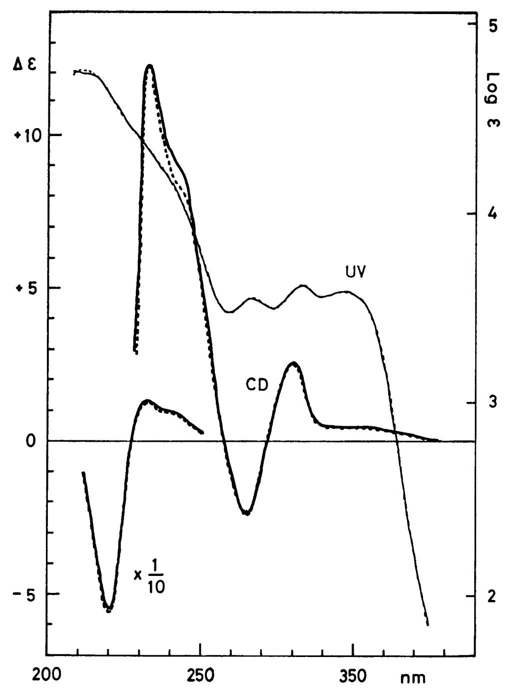


Fig. 1. UV and CD spectra of (+)-XIV (——) and (+)-XVI (------) in dioxane.

The reaction sequence of transformation of (+)- or (—)-VII into C_2-symmetrical 2,7-disubstituted triptycenes is outlined in Scheme 4. (+)-Diaminotriptycene (XIX) was prepared from (+)-VII by the Curtius reaction *via* acid chloride, acid azide and isocyanate. Methylation of (+)-XII with trimethyl phosphate afforded (+)-dimethylamino derivative (XX). (—)-Dinitrotriptycene (XXI) could be prepared by the pertrifluoroacetic acid oxidation of (—)-diamine (XIX). The reaction of nitrosobenzene with (—)-XIX in acetic acid gave bis-phenylazo derivative (XXII). (+)-Difluoro derivative (XXIII) was prepared by the Schiemann reaction of (+)-XIX. Hydrolysis of diazonium salt derived from (+)-XIX yielded (+)-dihydroxytriptycene (XXIV) which was converted into (+)-diacetate (XXV) and (+)-dimethoxy derivative (XXVI). Diacid amide prepared from (+)-dicarboxylic acid (VII) was dehydrated with thionyl chloride in dimethylformamide to give (+)-dicyanotriptycene (XXVII). (+)-Dimethoxycarbonyltriptycene (VI) obtained from (+)-VII was reduced with lithium aluminum hydride to yield (+)-bis(hydroxymethyl)-triptycene (XXVIII) which could be oxidized to (+)-diformyl derivative (XXIX) with chromium trioxide-pyridine complex. The reaction of thionyl chloride with (+)-glycol (XXVIII) afforded bis-chloromethyl derivative which gave (+)-dimethyltriptycene

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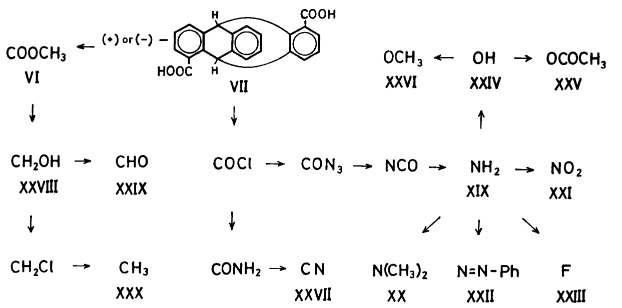
[7] L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, **85**, 1549 (1963).

[8] S. Akiyama, S. Misumi, and M. Nakagawa, This Bulletin, **35**, 1829 (1962).

[9] Y. Sakata, F. Ogura, and M. Nakagawa, *ibid.*, **36**, 611 (1973).



Scheme 4.

(XXX) on treatment with lithium aluminum hydride in boiling tetrahydrofuran.

In view of the method of preparation and the stable cage structure of triptycene skeleton, it is evident that (+)-series of 2,7-disubstituted triptycenes thus prepared has the same absolute configuration as (+)-VII (1R,6R) and (−)-series has an antipodal configuration.

Experimental

All the melting points are not corrected. Purified anhydrous solvents were used unless otherwise stated. Ligroin with bp 60—80°C was used. The IR spectra were measured with Hitachi EPI-2 and JASCO DS-301 spectrophotometers. The NMR spectra were obtained on a Varian A-60 spectrometer using TMS as an internal standard. Chemical shifts are recorded in τ unit. The UV spectra were measured with a Hitachi EPS-3T spectrophotometer. The optical rotations were measured with Rudolf 200S-80 and Yanagimoto ORD-185 spectropolarimeters at 15°C unless otherwise stated. The CD spectra were obtained on a Roussel-Jouan Dichrograph B, II-CD-185 and JASCO J-20 spectropolarimeter with CD attachments. The inflections and shoulders are indicated with an asterisk. The measurements of UV and CD spectra in an acidic medium were performed in methanol containing 10 vol% of 0.1M hydrochloric acid (abbreviated as MeOH-HCl). The experimental procedures referred to the optically active substances unless otherwise stated.

1,5-Dicyanoanthraquinone (II).[10] A mixture of I (50 g, 0.18 mol), cuprous cyanide (40 g, 0.45 mol) and phenylacetonitrile (460 ml) was refluxed for 70 min. The insoluble material was washed with benzene and digested with boiling 4M nitric acid to give II (44.5 g, 95.5%), mp >360°C, IR (Nujol mull): 2200 ($\nu_{C\equiv N}$) cm^{-1}.

1,5-Dicarboxyanthraquinone (III).[10] Water (200 ml) was added to a solution of II (86.0 g, 0.333 mol) in concentrated sulfuric acid (1000 ml) under ice-cooling. After being heated to 160°C for 1.5 hr, the mixture was poured onto water (1500 ml) to give dark brown crystals of III (80.5 g, 85.1%), mp >360°C, IR (Nujol mull): 1690 ($\nu_{C=O}$) cm^{-1}.

1,5-Dicarboxyanthracene (IV). A solution of III (27.16g, 0.0955 mol) in 15% aqueous ammonia (1200 ml) was treated with zinc dust (52 g) under stirring at 85—95°C. Stirring was continued for 5 hr at the same temperature under occasional addition of zinc dust and ammonia. The filtrate was treated with charcoal and acidified with 12M hydrochloric acid to afford IV as yellow crystals, mp >360°C, IR (Nujol mull): 1690 ($\nu_{C=O}$) cm^{-1}.

1,5-Dimethoxycarbonylanthracene (V). Thoroughly dried acid (IV, 99.8 g, 0.775 mol) was mixed with a methanolic sodium methoxide (from sodium, 23 g and methanol, 1400 ml) and the mixture was refluxed for 2 hr. Freshly distilled dimethyl sulfate (130 g, 1.031 mol) was added dropwise to the solution. After refluxing for 22 hr, the reaction mixture was concentrated under reduced pressure. Yellow crystals (107.1 g, 97.1%) obtained on addition of water (100 ml) to the concentrated mixture were recrystallized from methyl acetate and from benzene to yield pure V, yellow rods, mp 200—201°C, IR (KBr-disk): 1702 ($\nu_{C=O}$) cm^{-1}, NMR (CDCl$_3$): 0.28 (s, 2H, C^{9,10}-H), 1.58—2.58 (m, 6H, C$^{2-4}$-H and C$^{6-8}$-H), 5.91 (s, 6H, -CO$_2$CH$_3$), UV: $\lambda_{\max}^{\text{dioxane}}$ (ε) 406 (8360), 385 (9820), 365 (7730), 348* (4060), 260.5 (12100), 224.4* (19400), 221.5 (19800) nm.

Found: C, 73.46; H, 4.80%. Calcd for $C_{18}H_{14}O_4$: C, 73.78; H, 4.80%.

When IV was treated with phosphorus pentachloride at 150—160°C and the product was mixed with methanol, V was obtained in a 35% yield along with 1,5-dimethoxycarbonyl-9-methoxyanthracene, greenish yellow rods, mp 135°C (8.5%).[11]

2,5-Dimethoxycarbonyltriptycene (VI) and the Adduct of Maleic Anhydride with 1,5-Dimethoxycarbonylanthracene (V). To a stirred solution of V (24.7 g, 0.084 mol) under gentle reflux was added dropwise a solution of anthranilic acid (12.4 g, 0.091 mol) in tetrahydrofuran (300 ml) over a period of 8 hr. Isoamyl nitrite (5.0 g, 0.038 mol) and anthranilic acid (5.0 g, 0.036 mol) were then added and the mixture was refluxed for further 2 hr. Brownish yellow solid (57.0 g) obtained by concentration of the reaction mixture was mixed with xylene (320 ml) and maleic anhydride (15.0 g) and refluxed for 1 hr. Water and dichloromethane (each 200 ml) were added to the reaction mixture and the organic layer was washed successively with 5% aqueous potassium hydroxide and water and dried. The brown residue obtained from the organic layer was dissolved in benzene and chromatographed on alumina. Crystalline solid (26.67 g, 85.8%) obtained from the benzene eluate was recrystallized from methanol and then sublimed *in vacuo* to afford pure VI, mp 209—209.5°C, IR (KBr-disk): 1717 ($\nu_{C=O}$) cm^{-1}, NMR (CCl$_4$): 2.21—3.11 (m, 12H, aromatic and bridgehead), 3.94 (s, 6H, -CO$_2$CH$_3$), UV: $\lambda_{\max}^{\text{dioxane}}$ (ε) 298 (7270), 288* (6590), 222 (39200) nm.

Found: C, 77.61; H, 4.89%. Calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90%.

The adduct was isolated on acidification of the alkaline washings. The adduct, after recrystallization from acetone, was sublimed *in vacuo* to yield pure material, mp 258°C, IR (KBr-disk): 1862, 1782 ($\nu_{C=O}$, anhydride), 1718 ($\nu_{C=O}$, -CO$_2$CH$_3$) cm^{-1}, UV: $\lambda_{\max}^{\text{dioxane}}$ (ε) 222.5 (broad, 24000), 289 (4140) nm.

Found: C, 66.58; H, 4.08%. Calcd for $C_{22}H_{16}O_7$: C, 67.34; H, 4.11%.

2,7-Dicarboxytriptycene (VII). A solution of VI (18.09 g) in acetic acid (300 ml) containing 3M sulfuric acid (4 ml) was refluxed for 21 hr to precipitate fairly pure VII (16.6 g) in a quantitative yield. Recrystallization of VII from acetic acid yielded pure crystals containing 1 mol of acetic acid, mp 325°C (decomp.) (sublimed at 260°C).

Found: C, 71.71; H, 4.51%. Calcd for $C_{22}H_{14}O_4 \cdot C_2H_4O_2$: C, 71.63; H, 4.51%.

Crystals of VII free from acetic acid could be obtained on heating at 80°C for 6 hr *in vacuo*, mp 332—335°C (decomp.) (sublimed at 260°C), IR (KBr-disk): 1685 ($\nu_{C=O}$) cm^{-1}, NMR (DMSO-d_6): 2.23—3.18 (m, aromatic and bridgehead), UV: $\lambda_{\max}^{\text{EtOH}}$ (ε) 211 (44400), 287.5 (5600), 299 (6180) nn.

Found: C, 76.81; H, 4.21%. Calcd for $C_{22}H_{14}O_4$: 77.18; H, 4.12%.

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10) *Cf.*, W. Waldmann and A. Oblath, *Ber.*, **71**, 366 (1938).

11) *Cf.*, S. Akiyama, F. Ogura, and M. Nakagawa, This Bulletin, **44**, 3443 (1971).

Optical Resolution of dl-*2,7-Dicarboxytriptycene (VII).* To a hot solution of *dl*-VII (10.058 g, 0.0294 mol) in ethanol (350 ml) was added cinchonidine (8.649 g, 0.0294 mol) and the mixture was refluxed for 1 hr. Colorless solid (mp 188—195°C) obtained by concentration of the mixture was refluxed in methyl acetate (2350 ml) for 6.5 hr.[12] The mixture, on standing overnight in a refrigerator, gave crystals containing 1 mol of methyl acetate, mp 187—194°C, 8.305 g, $[\alpha]_{350}$ $-261.0°$ (*c* 0.528, methanol). The salt was recrystallized 4 times from methyl acetate to give optically pure material, mp 186—189°C, $[\alpha]_{350}$ $-146.3°$ (*c* 0.436, methanol).

Found: C, 74.62; H, 5.96; N, 4.19%. Calcd for $C_{41}H_{36}N_2O_5 \cdot C_3H_6O_2$: C, 74.35; H, 5.96; N, 3.94%.

Decomposition of the optically pure salt with acetic acid (150 ml) yielded (+)-VII (1.053 g) as colorless crystals, mp 342.5—350.0°C (decomp.) (sublimed at 260°C), ORD: $[\alpha]_{600}$ $+33.33°$, $[\alpha]_D$ $+33.3°$, $[\alpha]_{500}$ $+54.81°$, $[\alpha]_{400}$ $+140.7°$, $[\alpha]_{350}$ $+328.1°$ (*c* 0.540, methanol), CD: $\lambda_{\max}^{\text{MeOH}}$ ($\Delta\varepsilon$) 304 (+1.6), 282 (+5.3), 259 (−1.7), 244 (−4.0), 233 (+6.0), 219 (−49.7) nm.

Found: C, 76.81; H, 4.21%. Calcd for $C_{22}H_{14}O_4$: C, 77.18; H, 4.12%.

The initial mother liquor was mixed with acetic acid to afford (−)-VII with a low optical purity, mp 321—328°C (decomp.) (sublimed at 275°C), $[\alpha]_{350}$ $-129.4°$ (*c* 0.4325, methanol).

Starting from *dl*-VII (11.338 g, 0.033 mol), ethanol (350 ml) and cinchonine (9.749 g, 0.033 mol), crude cinchonine salt was prepared by an essentially similar procedure with (+)-enantiomer. A suspension of the salt in methyl acetate (2000 ml) was refluxed for 3 hr, and then concentrated to 800 ml. Crystals deposited on standing the solution in a refrigerator overnight were recrystallized 4 times from the same solvent to yield optically pure salt, $[\alpha]_{500}^{12}$ $+112.1°$ (*c* 0.5925, methanol). The crystals obtained on treatment of the optically pure salt with acetic acid were recrystallized from acetic acid to afford pure (−)-VII, 1.227 g, mp 342—350°C (decomp.) (sublimed at 260°C), ORD: $[\alpha]_{600}$ $-33.2°$, $[\alpha]_D$ $-33.9°$, $[\alpha]_{500}$ $-56.8°$, $[\alpha]_{400}$ $-141.9°$, $[\alpha]_{350}$ $-332.9°$ (*c* 0.5425, methanol).

Found: C, 77.04; H, 4.15%. Calcd for $C_{22}H_{14}O_4$: C, 77.18; H, 4.12%.

5,7-Dimethoxycarbonyltriptycene (VIII). According to the method used for VI, a solution of anthranilic acid (1.74 g, 0.0127 mol) in tetrahydrofuran was added dropwise to a mixture of 1,8-dimethoxycarbonylanthracene[8] (3.6 g, 0.012 mol), isoamyl nitrite (1.62 g, 0.0138 mol) and dichloromethane (58 ml). Crude crystals obtained after treatment of the reaction mixture with maleic anhydride were recrystallized from methanol to yield fairly pure VIII (2.84 g, 62.7%) which was recrystallized from the same solvent to give pure VIII, mp 176—177°C, IR (KBr-disk): 1720 ($\nu_{C=O}$) cm^{-1}, NMR (CCl_4): 2.04—3.13 (m, 11H, aromatic and C^6-H), 4.62 (s, 1H, C^1-H), 5.99 (s, 6H, -CO_2CH_3). The signal of the bridgehead proton at a proximate position to both ester groups (C^1-H) was shifted to the aromatic region by anisotropy of the ester carbonyl groups. UV: $\lambda_{\max}^{\text{dioxane}}$ (ε) 222 (39600), 286 (5520), 298 (6010) nm.

Found: C, 77.58; H, 4.74%. Calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90%.

(+)-2-Carboxy-7-methoxycarbonyltriptycene (IX). (+)-VII (2.009 g, 5.868 mmol) was mixed with equimolar sodium methoxide in methanol (39 ml) prepared from sodium (0.35 g) and methanol (100 ml). The mixture, after being refluxed for 1 hr, was evaporated under reduced pressure to give monosodium salt. Thoroughly dried acid salt suspended in benzene (70 ml) was mixed with freshly distilled dimethyl sulfate (0.740 g, 5.868 mmol) and the mixture was refluxed. After 4.5 hr, an additional amount of dimethyl sulfate (0.740 g) in benzene (20 ml) was added and refluxing was continued for further 16.5 hr. The reaction mixture was worked up to give a mixture of (+)-VII and (+)-IX as crystalline solid. The mixture was extracted with benzene. (+)-IX (1.604 g, 76.7%) was obtained from the benzene extract and recrystallized from benzene–ligroin, mp 252°C (sublimed at 200°C), [racemate, mp 246—249°C (decomp.) (sublimed at 200°C)], NMR ($CDCl_3$): −0.80 (broad, s, 1H, -COOH), 2.10—3.03 (m, 12H, aromatic and bridgehead), 6.00 (s, 3H, -CO_2CH_3), UV: $\lambda_{\max}^{\text{MeOH}}$ (ε) 298 (6600), 287 (5900), 240* (10500), 207 (62900) nm, CD: $\lambda_{\max}^{\text{MeOH}}$ ($\Delta\varepsilon$) 306 (+1.64), 283 (+4.90), 258 (−1.04), 242 (−2.08), 234 (+2.0) nm.

Found: C, 77.58; H, 4.52%. Calcd for $C_{23}H_{16}O_4$: C, 77.51; H, 4.53%.

The benzene insoluble residue was recovered (+)-VII which was also obtained by acidification of the aqueous layer of the initial extraction (total 26.9% recovery).

(+)-2-Amino-7-carboxytriptycene (X). (+)-IX (4.00 g, 11.2 mmol) in tetrahydrofuran (60 ml) was refluxed with excess thionyl chloride (10 ml) for 2 hr, and the volatile material was removed under reduced pressure to give crude acid chloride [IR (Nujol mull): 1760 ($\nu_{C=O}$, -COCl), 1720 ($\nu_{C=O}$, -CO_2CH_3) cm^{-1}]. A solution of sodium azide (0.900 g in 10 ml of water) was added to an ice-cooled and stirred solution of acid chloride in tetrahydrofuran (40 ml), After being stirred for 3 hr at the same temperature, the reaction mixture was worked up to give acid azide [IR (Nujol moll): 2140 ($\nu_{N=\overset{+}{N}=\overset{-}{N}}$), 1720 ($\nu_{C=O}$, -$CO_2CH_3$), 1685 ($\nu_{C=O}$, -$CON_3$) cm^{-1}]. The azide gave isocyanate [IR (Nujol mull): 2250 ($\nu_{N=C=O}$), 1720 ($\nu_{C=O}$, -CO_2CH_3) cm^{-1}] upon heating to 135°C for 6 hr. A mixture of isocyanate, ethanol (150 ml), potassium hydroxide (20 g) and water (50 ml) was refluxed for 25 hr to give crude amino carboxylic acid (X, 2.109 g, 60.1%). Recrystallization of crude X from methyl acetate–petroleum ether (bp 35—45°C) yielded pure X containing 1 mol of methyl acetate. The crystals melted once at 170°C and immediately crystallized again and re-melted with decomposition at 234—235°C [racemate, mp 167—169°C(decomp.)], IR (KBr-disk): 3380 (ν_{N-H}), 1690 ($\nu_{C=O}$, -CO_2CH_3) cm^{-1}.

Found: C, 74.30; H, 5.42; N, 3.62%. Calcd for $C_{21}H_{15}NO_2 \cdot C_3H_6O_2$: C, 74.40; H, 5.46; N, 3.59%.

The methyl acetate could be removed by heating the crystals *in vacuo*.

(+)-2-Amino-7-methoxycarbonyltriptycene (XI). A mixture of X (0.500 g), methanol (10 ml) and concentrated sulfuric acid (1 ml) was refluxed to yield (+)-XI in a quantitative yield, mp 161—162°C (from methyl acetate–petroleum ether and then from ligroin) [racemate, mp 194—195°C (decomp.)], UV: $\lambda_{\max}^{\text{MeOH}}$ (ε) 293.5 (5760), 269 (3380), 240* (19000), 217 (36700), 207.5 (45200); $\lambda_{\max}^{\text{MeOH-HCl}}$ (ε) 293 (3900), 276 (2980), 270* (2140), 240* (12600), 208.5 (52200) nm, CD: $\lambda_{\max}^{\text{MeOH}}$ ($\Delta\varepsilon$) 285 (+5.10), 265 (−3.23), 238 (+3.11); $\lambda_{\max}^{\text{MeOH-HCl}}$ ($\Delta\varepsilon$) 302 (+0.19), 290 (−0.12), 273 (+3.48), 269 (+3.33), 252 (+0.75), 238 (−5.60), 226 (+2.90) nm.

Found: C, 80.89; H, 5.20; N, 4.23%. Calcd for $C_{22}H_{17}O_2N$: C, 80.71; H, 5.23; N, 4.28%.

(+)-2-Hydroxy-7-carboxytriptycene (XII). (+)-XI (1.736 g) in acetic acid (20.5 ml) was added to an ice-cooled and stirred solution of sodium nitrite (0.421 g) in concentrated sulfuric acid (3 ml). After 2 hr, the resulting solution of diazonium

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[12] This procedure is essential for effective resolution. Initially formed salt seems to rearrange in boiling methyl acetate to a stable form which has larger difference in solubility between the diastereomers.

salt was added dropwise to boiling 3M sulfuric acid (300 ml), yielding crude (+)-XII (1.135 g, 65.2%). Recrystallization of the crude material from methyl acetate–petroleum ether and from methyl acetate–benzene afforded pure (+)-XII, mp 269—271°C (decomp.) [racemate, mp 263—264°C (decomp.)].

Found: C, 78.69; H, 4.45%. Calcd for $C_{21}H_{14}O_3$: C, 80.24; H, 4.49%.

(+)-2-Hydroxy-7-methoxycarbonyltriptycene (XIII). Treatment of (+)-XII with methanol and sulfuric acid afforded (+)-XIII, mp 217—225°C (from ligroin) [racemate, mp 231—234°C], IR (KBr-disk): 3400 ($\nu_{\mathrm{O-H}}$), 1697 ($\nu_{\mathrm{C=O}}$) $\mathrm{cm^{-1}}$.

Found: C, 80.29; H, 5.02%. Calcd for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91%.

(+)-2-Methoxy-7-methoxycarbonyltriptycene (XIV). A mixture of (+)-XIII (0.5188 g), dimethyl sulfate (0.66 g), anhydrous potassium carbonate (3 g) and acetone (70 ml) was refluxed for 8 hr under stirring to give crude (+)-XIII in a quantitative yield, mp 240—241°C (from methanol) [racemate, 219—222°C], IR (KBr-disk): 2850 ($\nu_{\mathrm{C-H}}$, -OCH_3), 1715 ($\nu_{\mathrm{C=O}}$) $\mathrm{cm^{-1}}$, NMR ($CDCl_3$): 2.33—3.17 (m, 11H, aromatic and C^6-H), 4.07 (s, 1H, C^1-H), 6.05 (s, 3H, $\text{-CO}_2\text{CH}_3$) 6.18 (s, 3H, -OCH_3), UV: $\lambda_{\max}^{\mathrm{dioxane}}$ (ε) 209.5 (53300), 215 (51100), 267 (3550), 283.5 (4130), 296 (3880); $\lambda_{\max}^{\mathrm{MeOH}}$ (ε) 208.5 (67700), 215* (54300), 240* (13900), 266.5 (3430), 283 (4030), 296 (3750) nm, CD: $\lambda_{\max}^{\mathrm{dioxane}}$ ($\Delta\varepsilon$) 220 (−55.8), 232 (+12.7), 242* (+9.23), 265 (−2.31), 280 (+2.65), 325—290 (very broad peak, +0.41); $\lambda_{\max}^{\mathrm{MeOH}}$ ($\Delta\varepsilon$) 232 (+12.6), 262 (−2.05), 276 (+2.51), 320—290 (very broad peak, +0.40) nm.

Found: C, 80.44; H, 5.24%. Calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30%.

The melting point showed no depression on admixture with an authentic specimen of (+)-XVI (mp 240—241°C).[9]

(+)-2-Methoxy-7-carboxytriptycene (XV). A mixture of (+)-XIV (0.200 g), acetic acid (20 ml) and 3M sulfuric acid (10 ml) was refluxed for 19 hr to yield (+)-XV, mp 267°C (decomp.) (from aqueous acetic acid) [racemate, mp 299—300°C (decomp.)], NMR (DMSO-d_6): 2.20—3.18 (m, 11H, aromatic and C^6-H), 3.93 (s, 1H, C^1-H), 6.13 (s, 3H, -OCH_3).

Found: C, 80.28; H, 4.91%. Calcd for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91%.

(+)-2,7-Diaminotriptycene (XIX). (+)-Dicarboxytriptycene (VII, 432.5 mg) in tetrahydrofuran was refluxed for 2 hr with excess thionyl chloride, crude acid chloride (450.8 mg) being obtained by evaporating volatile material under reduced pressure. To an ice-cooled solution of the acid chloride in tetrahydrofuran was added a solution of sodium azide (155 mg) in water (2 ml). After 3 hr, the reaction mixture was poured onto water to give acid azide [386.8 mg, IR (Nujol mull): 2120 ($\nu_{\mathrm{N=\overset{+}{N}=\overset{-}{N}}}$), 1685 ($\nu_{\mathrm{C=O}}$) $\mathrm{cm^{-1}}$]. A solution of thoroughly dried azide in benzene (100 ml) was refluxed for 4 hr. Isocyanate [388.2 mg, IR (Nujol mull): 2210 ($\nu_{\mathrm{C=O}}$) $\mathrm{cm^{-1}}$] obtained by evaporating the solvent *in vacuo* was mixed with water (10 ml), 99% ethanol (50 ml) and potassium hydroxide (4.0 g) and the mixture was refluxed for 6 hr. The reaction mixture was poured onto ice–water to yield crude (+)-XIX (319.6 mg) which was recrystallized from benzene and dried *in vacuo* at 110°C for 5 hr to give pure (+)-XIX, mp 266—267°C (sublimed at *ca.* 230°C) [racemate, mp 279—283°C (decomp.), sublimed at *ca.* 210°C], NMR ($CDCl_3$): 2.55—3.72 (m, 10H, aromatic), 4.62 (s, 2H, bridgehead), 6.45 (broad s, 4H, -NH_2), UV: $\lambda_{\max}^{\mathrm{MeOH}}$ (ε) 194 (56900), 219.5 (56500), 240* (20900), 269 (4040), 275 (3320), 295 (3660); $\lambda_{\max}^{\mathrm{MeOH\text{-}HCl}}$ (ε) 212.5 (64400), 262* (1330), 269 (2230), 276.5 (2910) nm, CD: $\lambda_{\max}^{\mathrm{EtOH}}$ ($\Delta\varepsilon$) 214 (−61.2), 227.5 (+55.3), 258* (−11.7), 268 (−17.1), 283* (+1.53), 297 (+6.37); $\lambda_{\max}^{\mathrm{EtOH\text{-}HCl}}$ ($\Delta\varepsilon$) 250.5 (+0.95), 262 (−2.22), 274 (−0.41), 277.5 (+0.31) nm.

Found: C, 84.45; H, 5.69; N, 9.90%. Calcd for $C_{20}H_{16}N_2$: C, 84.48; H, 5.67; N, 9.85%.

(+)-2,7-Bis(dimethylamino)triptycene (XX). After a mixture of (+)-XIX (197 mg) and trimethyl phosphate (200 mg) had been refluxed for 3 hr, a solution of sodium hydroxide (1.7 g) in water (2 ml) was added and the mixture was refluxed for 30 min. Water (30 ml) was added to the reaction mixture. Crude (+)-XX (0.226 g) deposited after being left to stand overnight was recrystallized from 99% ethanol and then sublimed *in vacuo* to give pure (+)-XX, mp 215—215.5°C (sublimed at 170°C) [racemate, mp 209—210°C, (sublimed at 160°C)], NMR ($CDCl_3$): 2.45—3.33 (m, 10H, aromatic), 4.07 (s, 2H, bridgehead), 7.22 (s, 12H, N-CH_3), UV: $\lambda_{\max}^{\mathrm{MeOH}}$ (ε) 225 (42000), 240* (25200), 260* (15400), 275* (5000), 295* (1500) nm, CD: $\lambda_{\max}^{\mathrm{MeOH}}$ ($\Delta\varepsilon$) 220 (−37.72), 236 (+24.33), 271 (−7.06), 292 (+1.11) nm.

Found: C, 84.86; H, 6.96; N, 8.26%. Calcd for $C_{24}H_{24}N_2$: C, 84.66; H, 7.11; N, 8.23%.

(−)-2,7-Dinitrotriptycene (XXI). To an ice-cooled and stirred mixture of dichloromethane (4.5 ml) and 90% hydrogen peroxide (0.24 ml) was added trifluoroacetic anhydride (1.5 ml). After 5 min, a solution of (−)-diamine (XIX, 297 mg) in the same solvent (10 ml) was added and the mixture was refluxed for 1 hr. After washing (aqueous sodium carbonate and water) and drying, the solvent was removed to yield yellow solid which was recrystallized from benzene–ligroin to afford pure (−)-XXI, mp 320—326°C (sublimed at 160°C) [racemate, mp 325—331°C (decomp.), (sublimed at 200°C)], UV: $\lambda_{\max}^{\mathrm{MeOH}}$ (ε) 207* (61500), 254 (11200), 315 (4350) nm, CD: $\lambda_{\max}^{\mathrm{MeOH}}$ ($\Delta\varepsilon$) 242 (+12.12), 282 (−2.15), 306 (+1.21), 328 (−0.91) nm.

Found: C, 69.31; H, 4.22; N, 7.08%. Calcd for $C_{20}H_{12}O_4N_2$: C, 69.76; H, 3.51; N, 8.14%.

(−)-2,7-Bis(phenylazo)triptycene (XXII). A mixture of (−)-diamine (XIX, 489.1 mg), nitrosobenzene (400 mg) and acetic acid (6 ml) was heated in a sealed tube at 200°C for 2 hr. The solvent was removed *in vacuo* and the residue dissolved in benzene was passed through a column of alumina (50 g). Crude crystals (600 mg) obtained from benzene eluate was recrystallized from benzene–ethanol to give pure (−)-XXII, mp 216—217°C [racemate, mp 272—273.1°C], NMR (CS_2): 1.82—3.02 (m, 20H, aromatic), 3.30 (s, 2H, bridgehead), UV: $\lambda_{\max}^{\mathrm{MeOH}}$ (ε) 212 (53300), 232 (28000), 240* (23800), 242* (19000), 253* (12600), 258* (10800), 325 (33500), 440 (1600) nm, CD: $\lambda_{\max}^{\mathrm{MeOH}}$ ($\Delta\varepsilon$) 216 (+11.3), 236 (+15.1), 248 (−6.40), 272 (−1.8), 320 (+9.56), 355 (−10.82), 438—432 (−1.38) nm.

Found: C, 82.69; H, 4.84; N, 11.88%. Calcd for $C_{32}H_{22}N_4$: C, 83.09; H, 4.79; N, 12.11%.

(+)-2,7-Difluorotriptycene (XXIII). A solution of (+)-XIX (500 mg) in hot concentrated hydrochloric acid (6 ml) was chilled to −15——20°C and a solution of sodium nitrite (270 mg) in water (2 ml) was added under stirring. Sodium fluoroborate (500 mg) in a small amount of water was added to the mixture. After being stirred for 1 hr at the same temperature, diazonium fluoroborate deposited was filtered and washed successively with cold water, methanol and ether. Diazonium salt (550 mg) thus obtained was gradually heated to 150°C and maintained at the same temperature for 3 hr, resulting in a purple solid. The product dissolved in benzene was treated with active charcoal and recrystallized from aqueous ethanol to afford pure (+)-XXIII, mp 224—226°C [racemate, mp 236—139°C (decomp.)], NMR ($CDCl_3$): 2.30—3.20 (m, 10H, aromatic), 3.99 (s, 2H, bridgehead), UV: $\lambda_{\max}^{\mathrm{MeOH}}$ (ε) 212.5 (60300), 235* (7920), 255* (2140), 260*

(2070), 268 (1700), 276 (1320) nm, CD: $\lambda_{\max}^{\mathrm{MeOH}}$ ($\Delta\varepsilon$) 225 (+1.18), 255 (−2.40), 268 (+1.48), 278 (+2.83) nm.

Found: C, 82.68; H, 4.19%. Calcd for $C_{20}H_{12}F_2$: C, 82.74; H, 4.17%.

(+)-2,7-Dihydroxytriptycene (XXIV). To a solution of (+)-XIX (3.90 g) in acetic acid (80 ml) was added a solution of sodium nitrite (1.485 g) in water (4 ml) at 14—17°C. After being stirred for 3 hr at the same temperature, the mixture was added to boiling 3M sulfuric acid (240 ml) over a 30 min-period and boiling was continued for 1 hr. Brown solid (2.60 g) isolated from the reaction mixture was converted into acetate (XXV) and the purified (+)-XXV was reduced by lithium aluminum hydride to give pure (+)-XXIV, mp 280°C (from ethanol), UV: $\lambda_{\max}^{\mathrm{MeOH}}$ (ε) 216.5 (51,800), 234 (12900), 240* (10000), 262* (3150), 267.5 (4070), 276.5 (3780), 286 (3510); $\lambda_{\max}^{\mathrm{MeOH\text{-}NaOH}}$ (ε) 217 (49,400), 245* (22500), 270 (4590), 277.5 (4530), 330 (5590) nm, CD: $\lambda_{\max}^{\mathrm{MeOH}}$ ($\Delta\varepsilon$) 219 (+31.33), 232 (−5.53), 250 (−6.70), 264* (−4.75), 280 (+4.29), 285 (+4.58); $\lambda_{\max}^{\mathrm{MeOH\text{-}NaOH}}$ ($\Delta\varepsilon$) 215 (−38.8), 232 (+36.5), 268 (−11.6), 300 (+3.22), 303 (+3.24) nm.

Found: C, 83.59; H, 4.97%. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93%.

(+)-2,7-Diacetoxytriptycene (XXV). Crude crystals of (+)-XXV (1.05 g) obtained by heating a mixture of (+)-XXIV (800 mg), acetic anhydride (50 ml) and sodium acetate (2.0 g) at 100°C for 20 hr were dissolved in benzene and passed through a column of silica gel (30 g). Concentration of the filtrate afforded (+)-XXV, mp 209.8—213.7°C (from benzene–ligroin and from ethanol), NMR ($CDCl_3$): 2.45—3.23 (m, 10H, aromatic), 4.42 (s, 2H, bridgehead), 7.50 (s, 6H, CH_3CO_2-), UV: $\lambda_{\max}^{\mathrm{MeOH}}$ (ε) 214 (59800), 240* (4200), 255* (1290), 262 (1220), 269 (1710), 276.5 (1990) nm, CD: $\lambda_{\max}^{\mathrm{MeOH}}$ ($\Delta\varepsilon$) 235 (−0.38), 257 (−1.69), 269 (+0.75), 276 (+1.38) nm.

Found: C, 77.62; H, 4.90%. Calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90%.

(+)-2,7-Dimethoxytriptycene (XXVI). A mixture of (+)-2,7-dihydroxytriptycene (XXIV, 200 mg), dimethyl sulfate (300 mg) and acetone (50 ml) was refluxed for 19 hr in the presence of anhydrous potassium carbonate (3.0 g) to afford crude crystals of (+)-XXVI (200 mg). The crude material was recrystallized from ethanol–benzene to yield pure (+)-XXVI, mp 277.8°C, NMR ($CDCl_3$): 2.20—3.38 (m, 10H, aromatic), 4.00 (s, 2H, bridgehead), 6.08 (s, 6H, CH_3O-), UV: $\lambda_{\max}^{\mathrm{dioxane}}$ (ε) 218.5 (46800), 240* (9300), 263* (3380), 268 (4110), 276.5 (3560), 285 (3100) nm, CD: $\lambda_{\max}^{\mathrm{dioxane}}$ ($\Delta\varepsilon$) 225 (+44.16), 250 (−12.39), 271* (+2.09), 278 (+3.09), 284 (+2.93) nm.

Found: C, 84.33; H, 5.80%. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77%.

(+)-2,7-Dicyanotriptycene (XXVII). Thionyl chloride (1.27 g) was added to a solution of (+)-VII (300 mg) in tetrahydrofuran (30 ml) and the mixture was refluxed for 2 hr. Crude acid chloride (326.2 mg) was obtained by removing volatile material under reduced pressure. The reaction of 28% aqueous ammonia (7.5 ml) with acid chloride (288.9 mg) in tetrahydrofuran (15 ml) at room temperature afforded acid amide [292.7 mg, IR (Nujol mull): 3100 ($\nu_{\mathrm{N-H}}$), 1660 ($\nu_{\mathrm{C=O}}$) cm^{-1}]. A mixture of acid amide (282.8 mg), dimethylformamide (40 ml) and thionyl chloride (4 ml) was heated to 70—80°C for 8 hr. The reaction mixture was filtered to remove sulfur deposited and the filtrate was passed through a short column of alumina (10 g). Colorless solid (108 mg) obtained from the eluate was recrystallized from methanol to yield pure (+)-XXVII, mp 261—262°C (sublimed at 210°C) [racemate, mp 247—250.5°C], IR (KBr-disk): 2230 ($\nu_{\mathrm{C\equiv N}}$) cm^{-1}, NMR ($CDCl_3$): 2.18—2.92 (m, 10H, aromatic), 4.03 (s, 2H, bridgehead), UV: $\lambda_{\max}^{\mathrm{EtOH}}$ (ε) 212* (37900), 222* (38600), 235* (20500), 280* (4750), 288.5 (6330), 298 (8090) nm, CD: $\lambda_{\max}^{\mathrm{EtOH}}$ ($\Delta\varepsilon$) 220 (−28.6), 231 (+10.8), 240 (−2.86), 251 (+1.91), 280 (+6.34), 303 (+1.04) nm.

Found: C, 86.45; H, 4.12; N, 9.18%. Calcd for $C_{22}H_{12}N_2$: C, 86.82; H, 3.97; N, 9.21%.

(+)-2,7-Dimethoxycarbonyltriptycene (VI). (+)-Dicarboxylic acid (VII) was treated with methanol containing concentrated sulfuric acid to give (+)-VI, mp 170—171°C (from methanol), CD: $\lambda_{\max}^{\mathrm{dioxane}}$ ($\Delta\varepsilon$) 222 (−37.6), 235 (+6.71), 244 (−2.58), 257 (−0.97), 282 (+5.90), 305 (+1.83) nm.

Found: C, 77.56; H, 5.02%. Calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90%.

(+)-2,7-Bis(hydroxymethyl)triptycene (XXVIII). Reduction of (+)-VI with lithium aluminum hydride afforded (+)-XXVIII in a quantitative yield, mp 220—221°C (from carbon tetrachloride followed by vacuum sublimation) (sublimed at 190°C) [racemate, 203.5—205°C (sublimed at 170°C)], IR (KBr-disk): 3390 ($\nu_{\mathrm{O-H}}$) cm^{-1}, NMR ($CDCl_3$): 2.50—3.01 (m, 10H, aromatic), 4.01 (s, 2H, bridgehead), 5.17 (s, 4H, methylene), 8.03 (s, 2H, OH), UV: $\lambda_{\max}^{\mathrm{MeOH}}$ (ε) 215 (60700), 240* (4800), 264* (1570), 272.5 (2640), 276.5* (2820), 280.5 (3720) nm, CD: $\lambda_{\max}^{\mathrm{MeOH}}$ ($\Delta\varepsilon$) 238 (−1.54), 250(+0.62), 258 (−0.89), 270 (+2.16), 277 (+1.33), 282 (−0.89) nm.

Found: C, 84.02; H, 5.74%. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77%.

(+)-2,7-Diformyltriptycene (XXIX). A solution of (+)-XXVIII (180.4 mg) in pyridine (2 ml) was added to an ice-cooled and stirred suspension of chromium trioxide-pyridine complex (from the trioxide, 150 mg and pyridine, 2 ml) and the mixture was kept in a refrigerator overnight. Crude crystals (123.9 mg) were sublimed twice under reduced pressure to give pure (+)-XXIX, mp 244—247°C (decomp.) (sublimed at 175°C) [racemate, mp 249—253°C (decomp.) (sublimed at 195°C)], IR (KBr-disk): 1690 ($\nu_{\mathrm{C=O}}$) cm^{-1}, NMR ($CDCl_3$): −0.18 (s, 2H, CHO), 2.30—3.05 (m, 12H, aromatic and bridgehead), UV: $\lambda_{\max}^{\mathrm{MeOH}}$ (ε) 209 (54800), 215* (47300), 238* (18700), 251 (20500), 260* (16000), 278 (2290), 305* (4810), 318 (5470) nm, CD: $\lambda_{\max}^{\mathrm{MeOH}}$ ($\Delta\varepsilon$) 228 (−23.3), 246 (+2.8), 260 (−4.7), 276 (+2.6), 296 (+3.2), 324 (+1.5) nm.

Found: C, 84.92; H, 4.57%. Calcd for $C_{22}H_{14}O_2$: C, 85.14; H, 4.55%.

(+)-2,7-Dimethyltriptycene (XXX). A solution of (+)-XVIII (239 mg) in benzene (25 ml) was refluxed with thionyl chloride (5 ml). Crude bis-chloromethyl derivative dissolved in tetrahydrofuran (15 ml) was added to a mixture of lithium aluminum hydride (772 mg) and the same solvent (75 ml). After being refluxed for 16 hr, a benzene solution of the product was passed through a column of alumina (20 g). The crystals obtained from the filtrate were recrystallized from aqueous methanol to give pure (+)-XXX, mp 133—137°C (decomp.) [racemate, mp 154.5—157°C (sublimed at 130°C)], NMR ($CDCl_3$): 2.53—3.18 (m, 10H, aromatic), 4.36 (s, 2H, bridgehead), 7.50 (s, 6H, CH_3), UV: $\lambda_{\max}^{\mathrm{MeOH}}$ (ε) 198 (63900), 214* (70500), 217.5 (72300), 240* (5980), 257* (1400), 263 (1370), 270.5 (1910), 274.5* (1460), 278.5 (2340) nm, CD: $\lambda_{\max}^{\mathrm{MeOH}}$ ($\Delta\varepsilon$) 259 (−3.5), 270.5 (+1.3), 278 (+1.8) nm.

Found: C, 93.06; H, 6.51%. Calcd for $C_{22}H_{18}$: C, 93.57; H, 6.43%.