Optically Active Triptycenes. VII.[1] Synthesis, Optical Resolution and Absolute Configuration of 3-Chloro and 4-Chloro-7-substituted Triptycenes.

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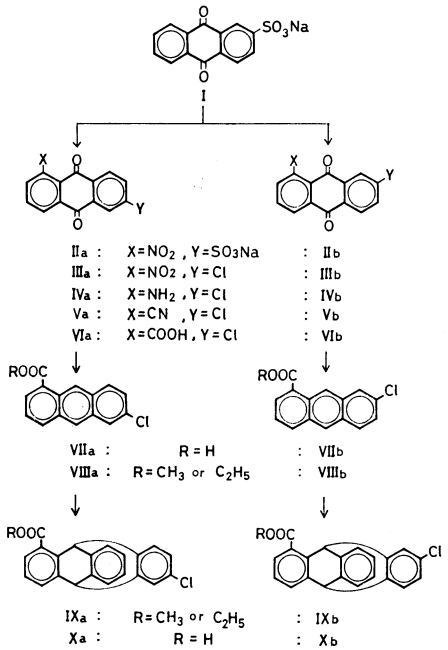
Isomeric 3- or 4-chlorotriptycene-7-carboxylic acid was synthesized from sodium anthraquinone-β-sulfonate and resolved with quinidine methohydroxide. The absolute configurations of (−)-3-chloro- and (−)-4-chlorotriptycene-7-carboxylic acids could be determined to be 1*S*,6*S* and 1*S*,6*R*, respectively, by the chemical correlation with (+)-2,5-dimethoxy-8-chlorotriptycene whose absolute configuration was proved to be 1*R*,6*S* by X-ray and chemical means.

The synthesis, optical resolution and absolute configuration of 2,5,7-[2] and 2,5,8-trisubstituted triptycenes[3] and 2,5- and 2,7-disubstituted triptycenes[4,5] as well as the analysis of CD spectra of these and related compounds[6] have been reported. The present paper deals with the synthesis, optical resolution of 3- or 4-chloro-7-substituted triptycenes and the determination of their absolute configuration by chemical correlation which were performed with the purpose of clarifying the effect of difference in the mode of coupling on chiroptical properties.

Synthesis and Optical Resolution. The route of synthesis is outlined in Scheme 1. Chloronitroanthraquinone (IIIa or IIIb) was prepared starting from sodium anthraquinone-β-sulfonate (I) *via* sodium nitroanthraquinonesulfonate (IIa or IIb) according to a modified method of Fierz-David.[7] Aminochloroanthraquinone (IVa or IVb) obtained by reduction of the nitro compound (IIIa or IIIb) with sodium sulfide was converted into nitrile (Va or Vb) by the Sandmeyer reaction. Acid hydrolysis of the nitrile (Va or Vb) afforded carboxychloroanthraquinone (VIa or VIb), which was reduced with zinc dust and aqueous ammonia to give 6- or 7-chloroanthracene-1-carboxylic acid (VIIa or VIIb). The acid (VIIa or VIIb) was converted into methyl or ethyl ester (VIIIa or VIIIb) by the usual method.

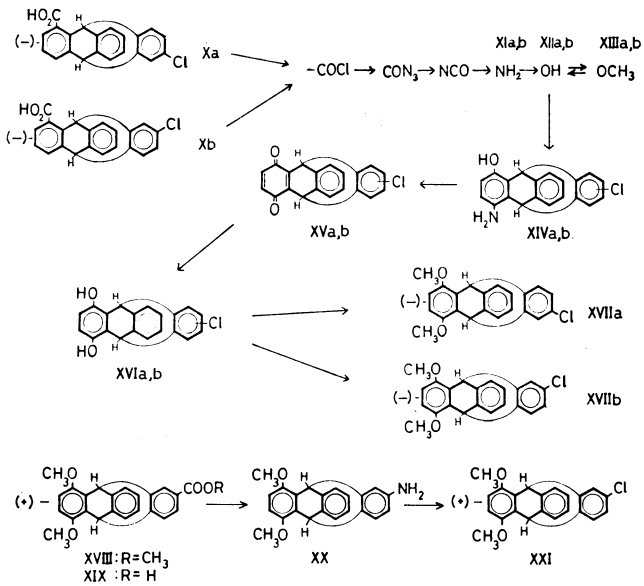


Scheme 1. Synthesis of 3,7- and 4,7-disubstituted triptycenes.

Reaction of benzyne generated by the decomposition of benzenediazonium carboxylate[8] with the ester (VIIIa or VIIIb) gave 3- or 4-chloro-7-methoxy(or ethoxy)carbonyltriptycene (IXa or IXb). Ethyl esters gave a less satisfactory result with respect to the yield and crystallinity. No significant increase in the yield of IX could be attained by varying the solvent from dichloromethane to 1,2-dimethoxyethane.[9]

The IR spectrum of IXa is almost superimposable with that of IXb, the difference in their NMR spectra being distinct in the region of aromatic protons. Racemate of 3- or 4-chlorotriptycene-7-carboxylic acid (Xa or Xb) was obtained hydrolyzing the ester (IXa or IXb) by the usual method. After several unsuccessful trials, optical resolution of Xa or Xb was accomplished with equimolar quinidine methohydroxide.[10] (−)-3-Chloro-7-carboxytriptycene (Xa) and (−)-4-chloro-7-carboxytriptycene (Xb) were isolated from the optically pure salts by decomposition with hydrochloric acid.

Absolute Configuration. Relative and absolute configurations of (−)-Xa and (−)-Xb were determined by chemical means as shown in Scheme 2. (−)-Xa



Scheme 2. Chemical correlation.

and (−)-Xb were converted into amine (XIa) and (XIb), respectively, by the Curtius reaction *via* acid chloride, acid azide, and isocyanate. In the case of XIb, a certain amount of urea derivative possibly resulting from the reaction of isocyanate with XIb was isolated. Phenols (XIIa and XIIb) were obtained by hydrolysis of diazonium salts of the amines (XIa and XIb) and purified as methyl ethers (XIIIa and XIIIb). Coupling of diazotized sulfanilic acid with the pure phenol (XIIa or XIIb) followed by reduction afforded *p*-aminophenol derivative (XIVa or XIVb) which was oxidized with ferric sulfate to yield *p*-benzoquinone derivative (XVa or XVb). Attempts to obtain the *p*-benzoquinone derivative (XVa or XVb) directly from the amine (XIa or XIb) by oxidation with sodium dichromate or chromium trioxide were unsuccessful, the only product isolated being 2-chloroanthraquinone. Oxidation of the phenol (XIIa or XIIb) with potassium nitrosodisulfonate or chromium trioxide gave the quinone (XVa or XVb) in a very poor yield, 2-chloroanthraquinone being isolated also in the case of chromium trioxide. Hydroquinone derivative (XVIa or XVIb) obtained from the quinone (XVa or XVb) by reduction with sodium hydrosulfite was converted into dimethyl ether (XVIIa or XVIIb) with dimethyl sulfate. The dimethyl ether derivatives thus prepared were found to be the same, including their chiroptical properties.

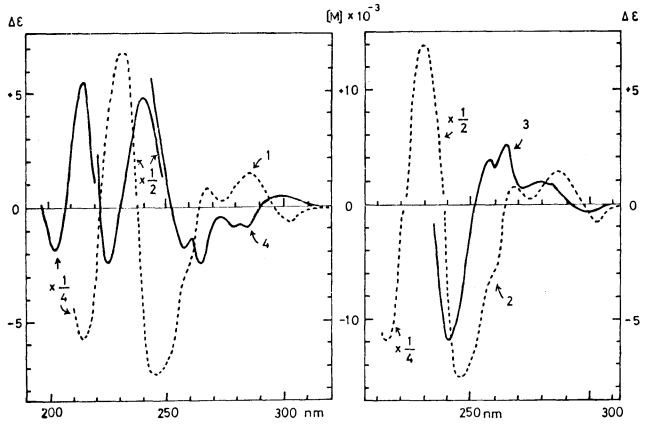


Fig. 1. CD (——) and ORD (----) spectra of (−)- and (+)-2,5-dimethoxy-8-chlorotriptycenes.
1: (−)-XVIIa, 2,3: (−)-XVIIb, 4: (+)-XXI

On the other hand, (+)-1*R*,6*S*-2,5-dimethoxy-8-methoxycarbonyltriptycene (XVIII)[3] was hydrolyzed to carboxylic acid (XIX) and then converted into amine (XX) by the Curtius reaction. (+)-2,5-Dimethoxy-8-chlorotriptycene (XXI) prepared from the amine (XX) by the Sandmeyer reaction was found to be the same as the above-mentioned chlorides (XVIIa and XVIIb) in melting point, IR, UV, and NMR spectra, but their chiroptical properties were antipodal (Fig. 1). The absolute configuration of (−)-2,5-dimethoxy-8-chlorotriptycene (XVII) was thus determined to be 1*S*,6*R*. Consequently the absolute configuration of (−)-3-chlorotriptycene-7-carboxylic acid (Xa) and (−)-4-chlorotriptycene-7-carboxylic acid (Xb) could be assigned to be 1*S*,6*S* and 1*S*,6*R*, respectively, on the combined evidence of X-ray[11] and chemical correlation.[3] Recently the X-ray crystal structure analysis was carried out on a single crystal of (+)-XXI. The absolute configuration was shown to be 1*R*,6*S* by the Bijvoet method[12] which is consistent with the results of chemical correlation.

Experimental

The melting points were measured on a Mettler FP2 apparatus and a Shimazu Kohfler micro hot stage, and are uncorrected. Purified and anhydrous solvents were used throughout the whole experiments, unless otherwise stated. The IR spectra were obtained on a Hitachi EPI-2 or a JASCO DS-301 spectrometer, electronic spectra on Hitachi EPS-3T and Zeiss PMQII4QIIId sopectrometers, NMR spectra in deuteriochloroform on a Varian A-60 spectrometer using TMS as an internal standard and given in τ-units. The optical rotations and CD spectra were obtained on Rudolf 200S-80, Yanagimoto ORD-185 spectropolarimeter, Roussel Jouan Dichrograph B, II-CD-185 and JASCO J-20 spectrometers, respectively. Shoulders and inflections are denoted by an asterisk.

6-Chloro-1-nitroanthraquinone (IIIa) and 7-Chloro-1-nitroanthraquinone (IIIb). The synthesis was performed by the reported method[7] with some modification. Sodium anthraquinone-β-sulfonate (310 g, 1 mol), dried thoroughly at 150 °C *in vacuo*, was added to 100% sulfuric acid (620 g) in small portions under stirring. To the dark brown solution was added dropwise at 90—95 °C a mixture of fuming nitric acid (d=1.52, 82 g) and 100% sulfuric acid (82 g). The reaction mixture containing yellow precipitates was heated to 100 °C for 30 min. The cooled reaction mixture was added to cold water (1.5 l). To the clear solution obtained on heating the mixture was added sodium chloride (82 g) to precipitate yellow crystals which were recrystallized from boiling water (1 l) to give sodium 1-nitroanthraquinone-6-sulfonate (IIa). 1-Nitro-7-sulfonate (IIb) in the mother liquor was not isolated as solid and subjected directly to further reaction.

1-Nitro-6-sulfonate (IIa) was dissolved in water (2.5 l) and mixed with concd. hydrochloric acid (460 g). To this solution was added at 100 °C dropwise an aqueous sodium chlorate (80 g in 800 ml) for 3 hr under stirring. After the mixture had been stirred for further 24 hr at 100 °C, light yellow precipitates were collected by filtration from the hot solution and recrystallized from benzene to give 6-chloro-1-nitroanthraquinone (IIIa 190 g, 22% based on I). 1-Nitro-7-chloro-isomer (IIIb) was prepared from 1-nitro-7-sulfonate (IIb) by essentially the same procedure and purified by recrystallization from benzene (180 g, 21% based on I).

1,6-Isomer: Mp 274—275 °C, light yellow rods (sublimed from *ca.* 220 °C), IR (KBr-disk): $\nu_{C=O}$ 1680 cm^{-1}.

Found: C, 58.34; H, 2.18%. Calcd for $C_{14}H_6O_4NCl$: C, 58.45; H, 2.11%.

1,7-Isomer: Mp 256—257 °C, yellow needles (sublimed from *ca.* 230 °C), IR (KBr-disk): $\nu_{C=O}$ 1682, 1670 cm^{-1} (doublet).

Found: C, 58.63; H, 2.22%. Calcd for $C_{14}H_6O_4NCl$: C, 58.45; H, 2.11%.

1-Amino-6-chloroanthraquinone (IVa) and 1-Amino-7-chloroanthraquinone (IVb). A stirred suspension of IIIa (50 g) in water (1.4 l) containing sodium sulfide (130 g) was refluxed for 4.5 hr. After cooling, red precipitates were collected by filtration and crystallized from benzene to yield IVa as dark red needles (34 g, 79.1%), mp 214—216 °C (sublimed from *ca.* 150 °C), IR (KBr-disk): ν_{NH} 3440, 3320, $\nu_{C=O}$ 1665, 1645 cm^{-1}.

Found: C, 65.16; H, 2.96%. Calcd for $C_{14}H_8O_2NCl$: C, 65.26; H, 3.13%.

The product obtained on treatment of IIIb by essentially the same procedure was recrystallized from benzene to afford IVb (83.9%) as bright brick red needles, mp 234—235 °C, IR (KBr-disk): ν_{NH} 3445, 3340, $\nu_{C=O}$ 1670, 1635 cm^{-1}.

Found: C, 65.40; H, 3.20%. Calcd for $C_{14}H_8O_2NCl$: C, 65.26; H, 3.13%.

6-Chloro-1-cyanoanthraquinone (Va) and 7-Chloro-1-cyanoanthraquinone (Vb). To a vigorously stirred solution of IVa (35 g, 0.13 mol) in concd. sulfuric acid (175 ml) was added powdered sodium nitrite (12.2 g, 0.18 mol) in small portions over a 40 min-period. Cracked ice (115 g) was added to the dark brown mixture maintaining the temperature at 50—60 °C. After stirring for further 1 hr, the mixture was poured onto ice (530 g) to precipitate diazonium salt. A suspension of the diazonium salt in water (900 ml) was added dropwise to an aqueous solution (350 ml) of copper sulfate (63 g) and potassium cyanide (70 g) maintained at 70 °C. After the mixture was stirred for 40 min at 100 °C, precipitate was collected by filtration and digested with 3 M nitric acid to yield brown crystals. Recrystallization of the crystals from toluene afforded pure Va as brown needles (28.0 g, 79.4%), mp 299.5—300.5 °C (decomp.) in a sealed tube, IR (KBr-disk): ν_{CN} 2220, $\nu_{C=O}$ 1680 cm^{-1}.

Found: C, 67.31; H, 2.29%. Calcd for $C_{15}H_6O_2NCl$: C, 67.31; H, 2.26%.

Application of a similar procedure to 1-amino-6-chloro-isomer (IVb) afforded Vb (crude yield 90%). Prolonged reaction time of diazotization resulted in a better yield of Vb. Recrystallization of crude product from benzene gave pure Vb as yellowish green needles, mp 299—300 °C (decomp.), IR (KBr-disk): ν_{CN} 2235, $\nu_{C=O}$ 1680 cm^{-1}.

Found: C, 67.31; H, 2.21%. Calcd for $C_{15}H_6O_2NCl$: C, 67.31; H, 2.26%.

6-Chloroanthracene-1-carboxylic Acid (VIIa) and 7-Chloroanthracene-1-carboxylic Acid (VIIb). Water (223 ml) was added dropwise under stirring to an ice-cooled solution of Va (55.7 g, 0.20 mol) in concd. sulfuric acid (668 ml). The mixture was heated to 160—170 °C for 4 hr and then poured into cold water (1 l) to give a black purple precipitate of VIa. To a stirred purple red solution of crude VIa in 15% aqueous ammonia was added zinc dust at 80—90 °C. Occasional addition of aqueous ammonia and zinc dust gave a greyish green suspension in *ca.* 7 hr. Brown filtrate, after treatment with active charcoal, was acidified with concd. hydrochloric acid to precipitate yellowish green VIIa (52.0 g, 97.1%). The precipitate could be used for esterification without further purification. Pure VIIa was obtained by recrystallization from toluene as greenish yellow needles, mp 258—266 °C (decomp.), IR (Nujol mull): $\nu_{C=O}$ 1685 cm^{-1}.

A similar reaction applied to Vb afforded VIIb (95.6%), which could be used directly for further reactions. Pure VIIb was obtained by recrystallization from benzene as yellow needles, mp 262—264 °C (decomp.), IR (Nujol mull): $\nu_{C=O}$ 1680 cm^{-1}.

6-Chloro-1-ethoxy(or methoxy)carbonylanthracene (VIIIa) and 7-Chloro-1-ethoxy(or methoxy)carbonylanthracene (VIIIb).

VIIIa (ethyl ester): To a solution of VIIa (17.8 g, 0.0690 mol) in ethanol (1500 ml) was added dropwise concd. sulfuric acid (150 ml) and the mixture was refluxed for 13 hr. After removal of a major portion of ethanol under reduced pressure, the reaction mixture was poured into water (1 l) and extracted with benzene. The extract, after being washed and dried, was concentrated under reduced pressure to yield brown crystals, which were dissolved in benzene and passed through a short column of alumina. Yellow crystals obtained by drying up benzene eluate under reduced pressure were recrystallized from ligroin to give pure VIIIa as yellow needles (14.1 g, 71.4%), mp 113—114 °C, IR (KBr-disk): $\nu_{C=O}$ 1718 cm^{-1}.

Found: C, 71.69; H, 4.58%. Calcd for $C_{17}H_{13}O_2Cl$: C, 71.71; H, 4.60%.

VIIIa (methyl ester): A mixture of VIIa (35 g), methanol (3 l) and concd. sulfuric acid (300 ml) was refluxed for 15 hr. Yellowish brown crystals deposited on cooling the mixture were collected by filtration. The filtrate neutralized by sodium hydrogen carbonate and concentrated under reduced pressure was poured into water and extracted with benzene. The extract was worked up in the usual way to give an additional amount of VIIIa (6 g). Benzene solutions of both crops of crystals were passed through short columns of alumina and the crystals obtained from the filtrates were recrystallized from benzene to afford pure material, yellow needles (total 28.1 g, 76.8%), mp 130—131 °C, IR (KBr-disk): $\nu_{C=O}$ 1710 cm^{-1}.

Found: C, 71.12; H, 4.10%. Calcd for $C_{16}H_{11}O_2Cl$: C, 70.98; H, 4.10%.

VIIIb (ethyl ester): By a similar procedure to that used for VIIIa, VIIb was converted into ethyl ester which was recrystallized from ligroin to give pure substance, yellow needles, mp 91—92 °C, IR (KBr-disk): $\nu_{C=O}$ 1718 cm^{-1}.

Found: C, 71.75; H, 4.61%. Calcd for $C_{17}H_{13}O_2Cl$: C, 71.71; H, 4.60%.

VIIIb (methyl ester): Treatment of VIIb by a similar procedure to that used for VIIIa afforded methyl ester, yellow needles, mp 128—129 °C (from methanol), IR (KBr-disk): $\nu_{C=O}$ 1710 cm^{-1}.

Found: C, 70.71; H, 4.13%. Calcd for $C_{16}H_{11}O_2Cl$: C, 70.98; H, 4.10%.

3-Chloro-7-ethoxy(or methoxy)carbonyltriptycene (IXa) and 4-Chloro-7-ethoxy(or methoxy)carbonyltriptycene (IXb). IXa (ethyl ester): To a gently refluxing mixture of VIIIa (ethyl ester, 12.3 g, 0.0432 mol), isoamyl nitrite (7.2 g, 0.0615 mol) and dichloromethane (200 ml) was added dropwise a solution of anthranilic acid (7.8 g, 0.0569 mol) in acetone (40 ml) under stirring over a period of 9.25 hr. After removal of volatile components under reduced pressure, xylene (123 ml) and maleic anhydride (6 g, 0.06 mol) were added. The mixture was refluxed for 1 hr and poured into cold water (360 ml). This was extracted with dichloromethane and the extract was worked up in the usual way to give a red brown oil. A benzene solution of the crude material was chromatographed on alumina to remove unreacted anthracene ester (VIIIa). The desired product (IXa) was obtained as colorless liquid (10.0 g, 63.5%), which was identified by NMR spectroscopy [NMR (CCl_4): 8.65 (t, CH_3), 5.65 (q, CH_2), 4.72 (s, bridgehead C^6), 2.29—3.34 (m, aromatic and bridgehead C^1)]. The reaction carried out in 1,2-dimethoxyethane reduced the yield of adduct to 52.5%. The compound showed an almost identical IR spectrum (Nujol mull) with that of IXb (ethyl ester).

IXa (methyl ester): By essentially the same procedure, VIIIa (methyl ester) could be converted into IXa (methyl ester), colorless rods, mp 153—155 °C (from methanol), IR (KBr-disk): $\nu_{C=O}$ 1718 cm^{-1}.

Found: C, 75.76; H, 4.34; Cl, 10.64%. Calcd for $C_{22}H_{15}O_2Cl$: C, 76.19; H, 4.36; Cl, 10.22%.

IXb (ethyl ester): This was prepared according to the method used for IXa (ethyl ester) in yields of 58.9% (in dichloromethane) and 38.1% (in dimethoxyethane), colorless needles, mp 178—180 °C (from methanol), NMR (CCl_4): 8.65 (t, CH_3), 5.66 (q, CH_2), 4.76 (s, bridgehead C^6), 2.29—3.34 (m, aromatic and bridgehead C^1).

Found: C, 76.48; H, 4.70%. Calcd for $C_{23}H_{17}O_2Cl$: C, 76.55; H, 4.75%.

IXb (methyl ester): The ester was prepared from VIIIb (methyl ester) by essentially the same procedure in 63% yield, colorless leaflets, mp 192.5—193.5 °C (from methanol), IR (KBr-disk): $\nu_{C=O}$ 1720 cm^{-1}.

Found: C, 75.81; H, 4.43; Cl, 10.02%. Calcd for $C_{22}H_{15}O_2Cl$: C, 76.19; H, 4.36; Cl, 10.22%.

3-Chlorotriptycene-7-carboxylic Acid (Xa). From Ethyl Ester (IXa): IXa (ethyl ester, 10.0 g, 0.0277 mol) dissolved in 99% ethanol (1400 ml) was mixed with powdered potassium hydroxide (7.8 g) and water (800 ml). The mixture was refluxed for 24 hr and then concentrated *in vacuo* to remove the solvent. A small amount of water was added to the hot residue until a faint turbidity was produced and the mixture was allowed to stand to precipitate colorless leaflets. The potassium salt collected by filtration was washed with ether and dissolved in a small amount of 99% ethanol. The ethanol solution was mixed with concd. hydrochloric acid and extracted with ether. The extract was worked up in the usual way to give Xa (5.0 g). An additional amount of Xa was obtained from the filtrate of the potassium salt (total yield 6.7 g, 72.7%). Combined crystals were recrystallized from ligroin to give pure Xa, colorless needles, mp 227—228 °C (sublimed from *ca.* 195 °C), IR (KBr-disk): $\nu_{C=O}$ 1685 cm^{-1} (the IR spectrum was found to be similar to that of Xb over the entire region), UV: $\lambda_{max}^{95\%EtOH}$ (ε) 292.5 (4190), 279.5 (4000), 270* (2240), 240* (12700), 217.5 (50400), 207.5 (61700) nm.

Xa could be obtained also by hydrolysis in acetic acid with 3 M sulfuric acid in 81% yield, but above-stated alkaline hydrolysis was superior as regards the purity of product.

Found: C, 75.92; H, 4.09%. Calcd for $C_{21}H_{13}O_2Cl$: C, 75.79; H, 3.94%.

From Methyl Fster (IXa): An alkaline hydrolysis of IXa (methyl ester) under the above-mentioned conditions afforded Xa in 96.3% yield.

4-Chlorotriptycene-7-carboxylic Acid (Xb). Hydrolysis of IXb (ethyl or methyl ester) according to the method used in the preparation of Xa gave Xb in 90 or 99% yield, respectively, mp 243—245 °C (from ligroin), IR (KBr-disk): $\nu_{C=O}$ 1685 cm^{-1}, UV: $\lambda_{max}^{99\%EtOH}$ (ε) 293 (4170), 278.5 (4070), 270* (2320), 240* (12200), 216.5* (53500), 209 (60800), 203* (53000) nm.

Found: C, 75.81; H, 3.83%. Calcd for $C_{21}H_{13}O_2Cl$: C, 75.79; H, 3.94%.

Optical Resolution of (±)-3-Chlorotriptycene-7-carboxylic Acid (Xa). Xa (2.157 g, 0.00648 mol) dissolved in 99% ethanol (40 ml) was mixed with aqueous quinidine methohydroxide (0.592 M, 10.9 ml, 0.0065 mol). After being left to stand overnight, the solvent was removed under reduced pressure and partly crystalline residue was recrystallized from dioxane. Repeated fractional recrystallization (7 times) afforded colorless crystals of optically pure salt, 0.389 g, mp 177—179 °C, $[\alpha]_{600}^{17.5}$ +95.10°, $[\alpha]_{589}^{17.5}$ +97.96°, $[\alpha]_{500}^{17.5}$ +154.7°, $[\alpha]_{400}^{17.5}$ +326.1° (*c* 0.490, EtOH). The crystals contained two molecules of dioxane as a solvent of crystallization and were slightly hygroscopic.

Found: C, 70.66; H, 6.47; N, 3.53%. Calcd for $C_{42}H_{39}N_2O_4 \cdot 2C_4H_8O_2$: C, 70.86; H, 6.54; N, 3.31%.

An effective resolution could not be attained by the use of ethanol or ethanol–ether.

The optically pure salt was decomposed by 5% aqueous hydrochloric acid to obtain (−)-Xa (0.13 g), which was recrystallized from ligroin, mp 236—238 °C, IR (KBr-disk): $\nu_{C=O}$ 1685 cm^{-1} (almost identical over entire region with (−)-Xb, (±)-Xa, and (±)-Xb), $[\alpha]_{600}^{16}$ −15.2°, $[\alpha]_{589}^{16}$ −16.3°, $[\alpha]_{500}^{16}$ −27.7°, $[\alpha]_{400}^{16}$ −70.8°, $[\alpha]_{350}^{16}$ −168° (*c* 0.516, 99% EtOH), CD: $\lambda_{max}^{99\%EtOH}$ ($\Delta\varepsilon$) 292 (−2.1), 278* (−0.89), 260* (+1.2), 254 (+2.1), 247 (−0.816), 240 (−1.14), 232 (−0.245), 220 (+11.4), 210 (−18.9) nm.

Found: C, 75.77; H, 4.18%. Calcd for $C_{21}H_{13}O_2Cl$: C, 75.79; H, 3.94%.

Optical Resolution of 4-Chlorotriptycene-7-carboxylic Acid (Xb). A solution of Xb (2.27 g, 0.00683 mol) in 99% ethanol (80 ml) was mixed with aqueous quinidine methohydroxide (0.614 M, 11.1 ml, 0.0068 mol) and left to stand overnight. The solid obtained by evaporating the solvent under reduced pressure was recrystallized from ethanol–ether. Repeated fractional recrystallization (16 times) from ethanol–ether or ethanol afforded colorless crystals of optically pure salt containing one molecule of ethanol as a solvent of crystallization, 1.134 g, mp 175—177 °C, $[\alpha]_{600}^{16}$ +133.9°, $[\alpha]_{589}^{16}$ +137.1°, $[\alpha]_{500}^{16}$ +213.4°, $[\alpha]_{400}^{16}$ +461.7° (*c* 0.440, EtOH).

Found: C, 73.76; H, 6.47; N, 3.91%. Calcd for $C_{42}H_{39}N_2O_4Cl \cdot C_2H_6O$: C, 73.67; H, 6.32; N, 3.91%.

The salt was decomposed with 5% aqueous hydrochloric acid to obtain (−)-Xb. Recrystallization of (−)-Xb from ligroin yielded colorless crystals of mp 90 °C containing some unidentified hydrocarbon as a solvent of crystallization. Upon heating *in vacuo* they gradually lost the solvent and showed a gradual rise in the melting point. After heating to 120 °C for 6 hr under reduced pressure, crystals free from the solvent were obtained, mp 204—205 °C, IR (KBr-disk): $\nu_{C=O}$ 1685 cm^{-1}, $[\alpha]_{436}^{21}$ −4.74°, $[\alpha]_{405}^{21}$ −9.95°, $[\alpha]_{365}^{21}$ −33.1° (*c* 0.980, 99% EtOH), CD: $\lambda_{max}^{99\%EtOH}$ ($\Delta\varepsilon$) 290 (−2.7), 274 (+2.0), 264* (+0.79), 250 (+2.0), 240 (−3.5), 225 (+33) nm.

Found: C, 75.86; H, 3.91; Cl, 10.42%. Calcd for $C_{21}H_{13}O_2Cl$: C, 75.79; H, 3.94; Cl, 10.66%.

7-Amino-3-chlorotriptycene (XIa). (−)-Xa (5.0 g, 0.015 mol) dissolved in ether (250 ml) was mixed with thionyl chloride (21.4 g) and refluxed for 7 hr. The mixture was concentrated under reduced pressure to yield colorless crystals of acid chloride, 5.3 g, mp 159—161 °C, IR (Nujol mull): $\nu_{C=O}$ 1755 cm^{-1}. To an ice-cooled solution of the chloride in acetone (200 ml), sodium azide (1.06 g) in water (10 ml) was added dropwise under stirring. The mixture was stirred for further 1.5 hr at the same temperature and then a major portion of the solvent was removed under reduced pressure. The residue was mixed with cold water (300 ml) and extracted with ether. The extract was worked up as usual, giving colorless crystals of acid azide, 5.45 g, mp 105—107 °C (decomposed with frothing), IR (Nujol mull): ν_{N_3} 2150, $\nu_{C=O}$ 1685 cm^{-1}. Thoroughly dried azide spread over the bottom of 1 l Erlenmeyer flask was heated gradually to 105 °C and kept at the temperature for 1 hr to yield light yellow crystals of isocyanate, mp 124—132 °C, IR (Nujol mull): $\nu_{N=C=O}$ 2250 cm^{-1}.

The isocyanate mixed with powdered potassium hydroxide (40 g) and 99% ethanol (500 ml) was refluxed for 6 hr and then a major portion of the solvent was removed *in vacuo*. The residue was mixed with water and extracted with ether. The extract was worked up in the usual way to yield light yellow crystals which gave, after sublimation *in vacuo* followed by recrystallization from ligroin, pure XIa, 3.542 g (77.6%), colorless needles, mp 201.2—203.2 °C, IR (KBr-disk): ν_{NH} 3470, 3380, δ_{NH} 1620 cm^{-1}, UV: $\lambda_{max}^{99\%EtOH}$ (ε) 295 (2140), 284.5 (4360), 278.8 (4120), 265.5 (4400), 255* (5910), 249* (8200), 245* (9890), 217 (50400), 207.5* (15900), 202 (11800) nm, $\lambda_{max}^{99\%EtOH\text{-}HCl}$ (ε) 283.4 (2710), 277.3 (3520), 270 (2740), 214 (64000), 203.5 (58200) nm, CD: $\lambda_{max}^{99\%EtOH}$ ($\Delta\varepsilon$) 302 (−0.65), 282 (−3.21), 278* (−2.38), 266 (+0.69), 250 (−4.0), 234 (+6.50), 226 (−7.58), 214 (−8.67), 206 (−3.03)

nm, $\lambda_{max}^{99\%EtOH\text{-}HCl}$ ($\Delta\varepsilon$) 282 (+0.78), 274* (−0.84), 270 (−1.31), 255 (+4.91), 236 (−13.7), 218 (+14.3) nm.

Found: C, 79.08; H, 4.58; N, 4.71; Cl, 11.75%. Calcd for $C_{20}H_{14}NCl$: C, 79.07; H, 4.64; N, 4.61; Cl, 11.67%.

By a similar sequence of reactions (±)-Xb afforded racemate, faintly brown crystals, 87.2%, mp 198—201 °C (from ligroin), IR (KBr-disk): ν_{NH} 3470, 3380 cm^{-1}. In the case of racemate, a small amount of urea derivative was obtained in the last stage of the reactions.

7-Amino-4-chlorotriptycene (XIb). The Curtius reaction of (−)-Xb under similar reaction conditions described above afforded optically active XIb (81.9%) which was recrystallized from ligroin to give pure XIb, mp 169—172 °C. IR (KBr-disk): ν_{NH} 3380, 3460 cm^{-1}, δ_{NH} 1620 cm^{-1}, UV: $\lambda_{max}^{99\%EtOH}$ (ε) 295 (2070), 284 (4290), 278.7 (3960), 266 (4040), 217 (50000), 202 (47100) nm, $\lambda_{max}^{99\%EtOH\text{-}HCl}$ (ε) 283.8 (2480), 277.5 (3260), 270.5 (2510), 214 (59600), 203 (53300) nm, CD: $\lambda_{max}^{99\%EtOH}$ ($\Delta\varepsilon$) 302 (+0.58), 283 (+4.93), 268 (+0.56), 248 (−6.91), 228 (+12.2), 216 (−23.3) nm, $\lambda_{max}^{99\%EtOH\text{-}HCl}$ ($\Delta\varepsilon$) 283 (−2.36), 274 (+0.49), 269 (+2.26), 254 (+5.45), 237 (−12.7), 220 (+16.6) nm.

Found: C, 78.61; H, 4.70; N, 4.64; Cl, 11.60%. Calcd for $C_{20}H_{14}NCl$: C, 79.07; H, 4.64; N, 4.61; Cl, 11.67%.

Racemate was prepared similarly from (±)-Xb, mp 181—184 °C (from ligroin), IR (KBr-disk): ν_{NH} 3480, 3380 cm^{-1}.

Formation of a small amount of urea derivative was observed in the reaction both of (±)- and (−)-Xb. In the case of optical isomer, the urea derivative was purified by recrystallization from ligroin, mp 301—302 °C, IR (KBr-disk): ν_{NH} 3320, δ_{NH} 1550, $\nu_{C=O}$ 1650 cm^{-1}, UV: $\lambda_{max}^{99\%EtOH}$ (ε) 284.5 (6910), 274* (12300), 261* (24700), 249* (28000), 214 (99500), 207.4 (77500), 203.5 (44400) nm, CD: $\lambda_{max}^{99\%EtOH}$ ($\Delta\varepsilon$) 290 (−0.71), 280* (+7.6), 276 (+8.5), 264 (+4.0), 256* (+2.8), 242 (−1.6), 238 (+2.4) nm

Found: C, 77.36; H, 4.05; N, 4.36; Cl, 11.04%. Calcd for $C_{41}H_{26}N_2OCl_2$: C, 77.72; H, 4.14; N, 4.42; Cl, 11.19%.

4-Chloro-7-hydroxytriptycene (XIIb). Optically active XIb (0.86 g, 2.8 mmol) dissolved in acetic acid (12 ml) was added over a period of 35 min to a stirred solution of nitrosyl sulfate at 10—15 °C prepared from sodium nitrite (0.220 g) and concd. sulfuric acid (2 ml). The mixture was stirred for further 55 min and mixed with water (3 ml) to give a reddish green solution. The cooled solution of diazonium salt was added dropwise to a refluxing 3 M sulfuric acid (60 ml) under stirring. After being refluxed for further 1 hr, the mixture was extracted with benzene. Red amorphous solid obtained by working up the extract by the usual way was difficult to purify. Pure phenol (XIIb) could be prepared *via* methyl ether (XIIIb, see below). Purified ether (XIIIb, 0.60 g) dissolved in a mixture of acetic acid (35 ml) and 47% hydrobromic acid (20 ml) was refluxed for 8 hr. The mixture was poured into water and extracted with ether. Light yellow crystals (0.551 g) obtained by working up the extract were recrystallized from ligroin to give pure optically active XIIb, colorless crystals, mp 242—246 °C, IR (KBr-disk): ν_{OH} 3520—3400 cm^{-1}, UV: $\lambda_{max}^{99\%EtOH}$ (ε) 284 (4370), 278 (4340), 265.4 (3470), 216 (58700), 195 (56600) nm, CD: $\lambda_{max}^{99\%EtOH}$ ($\Delta\varepsilon$) 278 (+3.27), 273 (+3.22), 266 (+3.09), 252 (−6.27), 240* (−3.13), 224 (+19.0), 215 (−28.2) nm.

Found: C, 78.90; H, 4.15; Cl, 11.76%. Calcd for $C_{20}H_{13}OCl$: C, 78.82; H, 4.30; Cl, 11.63%.

3-Chloro-7-hydroxytriptycene (XIIa). By the procedure used for the preparation of XIIb, optically active XIa was converted into optically active XIIa. Though analytically pure XIIa could not be obtained by the hydrolysis of pure XIIIa, it could be used for subsequent reaction.

3-Chloro-7-methoxytriptycene (XIIIa). A mixture of crude XIIa (1.036 g), potassium carbonate (6 g), dimethyl sulfate (1.1 g) and acetone (60 ml) was refluxed for 6 hr under stirring. The residue obtained by evaporating the solvent *in vacuo* was mixed with water and extracted with ether. Crude XIIIa obtained by working up the extract was dissolved in benzene and the solution was passed through a short column of alumina (30 g). Colorless crystals (0.885 g, 85.4%) obtained from the filtrate were recrystallized from ligroin to give pure XIIIa, mp 211—214 °C, IR (KBr-disk): $\nu_{CH(OCH_3)}$ 2850 cm^{-1}, UV: $\lambda_{max}^{99\%EtOH}$ (ε) 284.1 (3710), 277.5 (3870), 265 (3470), 261* (3000), 252* (3170), 215.8 (58500), 207 (25300), 202.5 (17800) nm, $\lambda_{max}^{isooctane}$ (ε) 284.5 (3740), 278 (3810), 265 (3460), 261.4 (3140), 254* (3100), 216.5 (63800), 199.3 (52900), 196 (47900), 194.5 (44000) nm, CD: $\lambda_{max}^{99\%EtOH}$ ($\Delta\varepsilon$) 284 (+1.8), 280* (+0.60), 270 (−1.4), 250 (−3.6), 232 (−5.2), 226 (−2.4) nm, $\lambda_{max}^{isooctane}$ ($\Delta\varepsilon$) 290 (+0.14), 284 (+1.9), 280* (+0.94), 272 (−0.85), 268* (−0.70), 252 (−3.7), 232 (−5.9), 228 (−1.9) nm.

Found: C, 79.31; H, 4.84; Cl, 10.99%. Calcd for $C_{21}H_{15}OCl$: C, 79.11; H, 4.74; Cl, 11.12%.

Racemate: Mp 196.5—198 °C (sublimed from *ca.* 150 °C), IR (KBr-disk): $\nu_{CH(OCH_3)}$ 2850 cm^{-1}.

4-Chloro-7-methoxytriptycene (XIIIb). Methylation of optically active XIIb by the above-mentioned procedure afforded XIIIb (79.7%) which was sublimed *in vacuo* and recrystallized from ligroin to give pure material, colorless crystals, mp 243—243.5 °C, IR (KBr-disk): $\nu_{CH(OCH_3)}$ 2850 cm^{-1}, UV: $\lambda_{max}^{99\%EtOH}$ (ε) 284.3 (3980), 277.6 (3900), 265.5 (3440), 215.5 (61000), 202 (51300) nm, $\lambda_{max}^{isooctane}$ (ε) 284.5 (3940), 278 (3820), 265.5 (3410), 262* (3000), 216.6 (64700), 199 (54800), 196.5* (50500), 194.5* (45100), 192* (27700) nm, CD: $\lambda_{max}^{99\%EtOH}$ ($\Delta\varepsilon$) 290 (+0.14), 270* (+2.7), 265 (+3.7), 250* (−5.4), 240 (−13), 226 (+20) nm, $\lambda_{max}^{isooctane}$ ($\Delta\varepsilon$) 290 (+0.10), 270* (+2.5), 264 (+3.6), 250 (−5.4), 240 (−12), 226 (+23) nm.

Found: C, 79.52; H, 4.80; Cl, 11.14%. Calcd for $C_{21}H_{15}OCl$: C, 79.11; H, 4.74; Cl, 11.12%.

Racemate: Mp 244—246 °C, IR (KBr-disk): $\nu_{CH(OCH_3)}$ 2850 cm^{-1}.

(−)-2,5-Dimethoxy-8-chlorotriptycene (XVIIa and XVIIb).

XVIIa from XIIa: To an ice-cooled and stirred solution of sulfanilic acid (0.150 g, 0.720 mmol) in aqueous sodium carbonate (0.032 g in 12 ml of water) was added a mixture of sodium nitrite (0.050 g, 0.720 mmol), ice (1 g) and concd. hydrochloric acid (0.12 ml). After 30 min, diazonium salt deposited as colorless crystals. To this mixture was added under stirring a solution of pure XIIa (0.210 g, 0.689 mmol) in methanol (3 ml) containing sodium hydroxide (0.56 g) and water (0.4 ml). After being left to stand overnight, the scarlet mixture was slightly warmed with sodium hydrosulfite (10 g) and concd. hydrochloric acid. The reaction mixture was poured into water and extracted with ethyl acetate. The extract was worked up in the usual way to give crude aminophenol (XIVa, 0.204 g, light yellow crystals). Ferric sulfate (4 g) was added to a solution of the crude XIVa in ethanol (25 ml), concd. sulfuric acid (4 ml) and water (50 ml) and the mixture was refluxed for 2 hr. The reaction mixture was concentrated under reduced pressure and extracted with ether. Evaporation of the extract, after washing and drying, afforded brown yellow crystals (0.198 g), which were dissolved in benzene and passed through a short column of alumina (7 g) to give pure quinone (XVa) as yellow crystals (0.105 g, 45.5% based on XIIa), IR (Nujol mull): $\nu_{C=O}$ 1655 cm^{-1} (racemate 1650 cm^{-1}). XIIa was recovered in a yield of 35%. Pure XVa (0.105 g, 0.33 mmol) dissolved in ether (8 ml) was mixed with aqueous

sodium hydrosulfite (0.2 g in 0.5 ml of water) and the mixture was stirred vigorously for 20 min. The colorless reaction mixture was poured into water and extracted with ether. Hydroquinone derivative (XVIa, 0.116 g, colorless crystals) obtained by working up the extract was methylated in the usual manner with potassium carbonate (1 g) and dimethyl sulfate (0.2 g) in acetone (10 ml). Crude XVIIa (light yellow crystals) was chromatographed on alumina and then recrystallized from methanol to give pure XVIIa, mp 209.0—210.5 °C, IR (KBr-disk): $\nu_{CH(OCH_3)}$ 2840 cm^{-1}, UV $\lambda_{max}^{99\%EtOH}$ (ε) 301* (3930), 295 (4090), 284.4 (5280), 278.8 (4270), 266 (2980), 256.8 (2500), 214.2 (58000), 202.3 (48200) nm, ORD: $[M]_{302}$ −1710°, $[M]_{286}$ +3230°, $[M]_{280}$* +1750°, $[M]_{266}$ +1770°, $[M]_{260}$* −5440°, $[M]_{246}$ −14600°, $[M]_{230}$ +26400°, $[M]_{215}$ −48100° (*c* 0.00898, EtOH).

Found: C, 75.40; H, 4.96; Cl, 9.87%. Calcd for $C_{22}H_{17}O_2Cl$: C, 75.75; H, 4.91; Cl, 10.17%.

Racemate: Mp 205.5—207 °C.

XVIIb from XIIb: According to an analogous sequence of reactions used for the preparation of XVIIa, pure XIIb was converted into(−)-2,5-dimethoxy-8-chlorotripycene (XVIIb), mp 209.0—210.5 °C. IR (KBr-disk): $\nu_{CH(OCH_3)}$ 2840 cm^{-1}, CD: $\lambda_{max}^{99\%EtOH}$ ($\Delta\varepsilon$) 298 (−0.22), 284 (+0.93), 280 (+1.0), 265 (+2.8), 258 (+2.0), 241 (−6.0) nm, ORD: $[M]_{302}$ −1720°, $[M]_{286}$ +3250°, $[M]_{280}$* +1580°, $[M]_{266}$ +1100°, $[M]_{260}$* −5420°, $[M]_{246}$ −15000°, $[M]_{230}$ +25600°, $[M]_{215}$ −48100° (*c* 0.00885, EtOH).

Found: C, 75.33; H, 4.83; Cl, 10.03%. Calcd for $C_{22}H_{17}O_2Cl$: C, 75.75; H, 4.91; Cl, 10.17%.

UV and IR spectra of XVIIb thus obtained were found to be completely superimposable with those of XVIIa.

Racemate: Mp 204.5—206.0 °C.

(+)-2,5-Dimethoxy-8-carboxytriptycene (XIX). To a refluxing solution of (+)-2,5-dimethoxy-8-methoxycarbonyltriptycene[3] (XVIII, 500 mg, 1.34 mmol) in acetic acid (25 ml) was added dropwise 3 M sulfuric acid (7 ml) and the mixture was refluxed for 12 hr. Colorless crystals deposited on cooling the reaction mixture were recrystallized from methanol to give pure (+)-XIX, mp 147.9—148.9 °C $[\alpha]_D$ +15° (*c* 0.2673, dioxane).

Found: C, 76.52; H, 5.04%. Calcd for $C_{23}H_{18}O_4$: C, 77.08; H, 5.06%.

(+)-2,5-Dimethoxy-8-aminotriptycene (XX). A mixture of (+)-XIX (533 mg, 1.34 mmol), thionyl chloride (1.5 ml) and tetrahydrofuran (11 ml) was refluxed for 3 hr to afford acid chloride [IR (Nujol mull): $\nu_{C=O}$ 1765 cm^{-1}] quantitatively. Sodium azide (252 mg) dissolved in water (3 ml) was added to a stirred and ice-cooled solution of the acid chloride in tetrahydrofuran (30 ml). After the mixture had been stirred for further 3 hr at the same temperature, water was added to precipitate acid azide [IR (Nujol mull): ν_{N_3} 2150, $\nu_{C=O}$ 1690 cm^{-1}]. Thoroughly dried acid azide (552 mg) dissolved in benzene (80 ml) was refluxed for 4 hr to yield isocyanate [553 mg, IR (Nujol mull): ν_{NCO} 2280 cm^{-1}]. A mixture of the isocyanate, 99% ethanol (50 ml), water (8 ml) and potassium hydroxide (5.0 g) was refluxed to afford (+)-XX (384 mg). Vacuum sublimation of the crude product (bath temp. 210—240 °C/800 Pa) afforded pure (+)-XX, colorless crystals, mp 287—289 °C (racemate, mp 243.5—245 °C), IR (KBr-disk): ν_{NH} 3420, 3350, δ_{NH} 1630 cm^{-1}, UV: $\lambda_{max}^{99\%EtOH}$ (ε) 300* (5900), 292.5 (6730), 269* (7260), 262 (7760), 220.5* (45300), 207.5* (56300), 203 (58300), 198 (58300) nm, CD: $\lambda_{max}^{99\%EtOH}$ ($\Delta\varepsilon$) 304.5 (+1.45), 274 (−13.6), 250* (+16.2), 242.5 (+16.9), 225.8 (−21.7), 218* (−4.77), 207.5 (−17.7) nm.

Found: C, 79.88; H, 5.96; N, 4.18%. Calcd for $C_{22}H_{19}O_2N$: C, 80.22; H, 5.81; N, 4.25%.

(+)-2,5-Dimethoxy-8-chlorotriptycene (XXI). To a stirred suspension of (+)-XX (60.6 mg, 0.184 mmol) in 6 M hydrochloric acid was added sodium nitrite (13.4 mg, 0.194 mmol) in water (3 ml) over a 15 min-period at 11—15 °C. The mixture, after being stirred for further 50 min, was added dropwise to a solution of cuprous chloride (36 mg) in 6 M hydrochloric acid (6 ml). Stirring was continued for 30 min at 20 °C and then for 1 hr at 100 °C. The reaction mixture was poured into water and extracted with ether. Crude product obtained by working up the extract was chromatographed on alumina and eluted with carbon tetrachloride. The crystals thus prepared were recrystallized from ligroin to give pure (+)-XXI, mp 209.6—210.4 °C (racemate, mp 206.1—207.1 °C), UV: $\lambda_{max}^{99\%EtOH}$ (ε) 301* (4020), 294.5 (4230), 284.5 (5510), 278.9 (4400), 266 (3320), 257 (2750), 240* (8290), 214.5* (61400), 212* (60600), 202* (57900), 198.5 (59600) nm, CD: $\lambda_{max}^{99\%EtOH}$ ($\Delta\varepsilon$) 300 (+0.52), 285 (−0.98), 278.5 (−0.88), 265.5 (−2.82), 258 (−1.98), 240 (+9.49), 225.5 (−5.08), 214 (+21.8), 202.5 (−17.9) nm, $[M]_{247}^{20}$ +14000° (*c* 1.417×10^{-4} mol/l, 99%EtOH).

Found: C, 75.61; H, 4.92; Cl, 10.15%. Calcd for $C_{22}H_{17}O_2Cl$: C, 75.75; H, 4.91; Cl, 10.16%.

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