337. *The Symmetrical Dianthryls. Part II.*

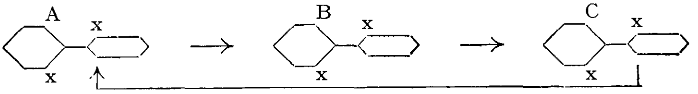
By F. Bell and D. H. Waring.

Optically active 1 : 1′-dianthryl-2 : 2′-dicarboxylic acid (improved preparation and resolution) can be converted into 2 : 2′-diamino-1 : 1′-dianthryl and this back into the initial material by two different routes without change either in magnitude or in sign of rotation.

(+)- and (−)-1 : 1′-Dianthryls are obtained from (+)- and (−)-2 : 2′-diamino-1 : 1′-dianthryls. This hydrocarbon is racemised in hot solvents.

An improved preparation of anthrapinacol allows the ready preparation of 9 : 9′-dianthryl.

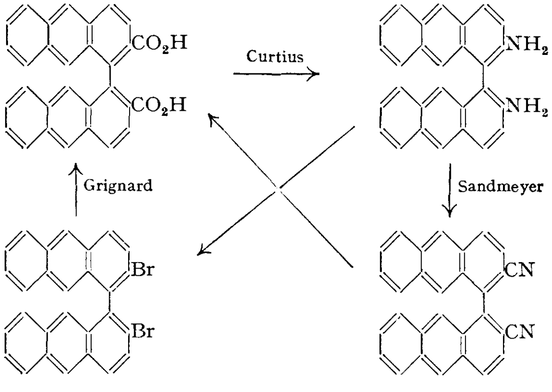
The object of the present investigation was to carry out a cycle of the type shown, commencing with one of the optically active forms of (I). The asymmetry of (I) is determined by restricted rotation about the single linkage connecting the nuclei. In the changes I ⟶ II, II ⟶ III, and III ⟶ I, one of the obstacle groups is removed completely and replaced by a different group. It appeared to the authors impossible, from existing knowledge, to state in advance whether, after such a process, compound (I) would be recovered with undiminished rotatory power and, indeed, even with the same sign of rotation. Two considerations must govern the choice of starting material : (*a*) that it possesses good optical stability, and (*b*) that it lends itself to a cycle in which the intermediates (II) and (III) are likely themselves to be optically stable. 1 : 1′-Dianthryl-2 : 2′-dicarboxylic acid (IV) appeared to fulfil these conditions, as it was known from the work of Lauer, Oda, and Miyawaki (*J. pr. Chem.*, 1937, [ii], **148**, 310) that the optically active acid could be converted by the Hofmann reaction into 2 : 2′-diamino-1 : 1′-dianthryl of high rotatory power.



(I.) (II.) (III.)

Scholl and Tanzer (*Annalen*, 1923, **433**, 163) obtained 1 : 1′-dianthryl-2 : 2′-dicarboxylic acid by the reduction of 1 : 1′-dianthraquinonyl-2 : 2′-dicarboxylic acid, and describe it as pale greenish-yellow needles or leaflets which char at about 183° and melt indefinitely at 273—275°. Lauer, Oda, and Miyawaki (*loc. cit.*), using the same method of preparation, obtained greenish-yellow needles, m. p. 201—203° (decomp.). Resolution of the acid into optically active forms was accomplished by a curious and empirical process involving the use of quinine. It was clearly necessary to re-examine both the preparation and the resolution of the acid.

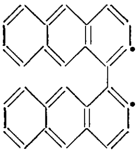
(IV.)

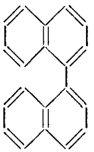


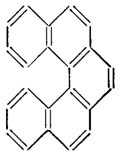
(V.) (VI.) (VII.)

In the Experimental section details are given for the preparation of 1 : 1′-dianthraquinonyl-2 : 2′-dicarboxylic acid in considerable quantity and in much higher purity than is obtained by the oxidation of 2 : 2′-dimethyl-1 : 1′-dianthraquinonyl. This compound gave on reduction 1 : 1′-dianthryl-2 : 2′-dicarboxylic acid of m. p. 305°. The inactive acid was readily resolved by crystallisation of the quinidine salt. The optically active forms, which were noticeably more soluble than the inactive acid, had the following properties : *dextro*, $[\alpha]_D$ +382°, m. p. 251—253°; *lævo*, $[\alpha]_D$ −386°, m. p. 253—255°. Lauer, Oda, and Miyawaki give *dextro*, $[\alpha]_D$ +352°, m. p. 187—198°; *lævo*, $[\alpha]_D$ −358°, m. p. 190—200°. The *dextro*- and *lævo*-acids were converted by the Curtius reaction into *dextro*- and *lævo*-2 : 2′-diamino-1 : 1′-dianthryl (V). The *dextro*-diamine was converted by diazotisation into 2 : 2′-dibromo-1 : 1′-dianthryl (VI) and this by the Grignard reaction into the original acid, which had $[\alpha]^{20^\circ}_{5461}$ +422°. The *lævo*-diamine was converted by the Sandmeyer reaction into the dicyanide (VII) and this by hydrolysis with potassium hydroxide in ethylene glycol into the original acid which had $[\alpha]^{20^\circ}_{5461}$ −437°. In both cycles, therefore, the acid is recovered unchanged both in sign and, essentially, in magnitude of rotation.

This so conclusive result shows that, if the reactions involve the formation of an ion or radical of type (VIII), this is possessed of a high degree of optical stability. In consequence, 1 : 1′-dianthryl itself might be expected to exist in optically active forms of considerable stability. This was found to be the case. *dextro*- and *lævo*-1 : 1′-Dianthryl were prepared from *dextro*- and *lævo*-2 : 2′-diamino-1 : 1′-dianthryl (V). The optically active forms were completely stable in chloroform at room temperature, but were racemised in about 7 hours at the boiling point or more rapidly in boiling xylene solution. When a drawing of this hydrocarbon is made according to the method of Sidgwick (*Ann. Reports*, 1932, **29**, 70), it is found that the interference of the hydrogen atom in position 9 with that in position 2′ does not exceed 0·2 A.


(VIII.)


(IX.)


(X.)

It appears from this result that compounds such as 1 : 1′-dinaphthyl (IX) and 3 : 4 : 5 : 6-dibenzphenanthrene (X) might be expected to exist in optically active forms (cf. Cook, *Ann. Reports*, 1942, **39**, 173), and these and related matters are under active investigation.

In Part I (this vol., p. 267) methods for preparing 9 : 9′-dianthryl were summarised.* It is now found that the most efficient process is the reduction of anthrone to anthrapinacol and dehydration of the latter by the method of Bergmann and Schuchardt (*Annalen*, 1931, **487**, 225); the overall yield is 50% based on anthraquinone.

EXPERIMENTAL.

(Analyses are by Drs. Weiler and Strauss, Oxford. M. p.s are uncorrected.)

2 : *2′-Bisdibromomethyl*-1 : *1′-dianthraquinonyl*.—Crude 2 : 2′-dimethyl-1 : 1′-dianthraquinonyl was purified by crystallisation from *o*-dichlorobenzene. 175 G. of the purified material were stirred in 1 l. of dry nitrobenzene at 145—150° while a mixture of 85 c.c. of bromine in 200 c.c. of dry nitrobenzene was run in during 3 hours. The reaction mixture was stirred at 170° for a further two hours. The tetrabromo-compound separated as a bright yellow crystalline deposit which was washed on the filter with nitrobenzene and finally ether; m. p. >300° (decomp.); yield, 255 g. (84%).

1 : *1′-Dianthraquinonyl*-2 : *2′-dicarboxylic Acid*.—2 : 2′-Bisdibromomethyl-1 : 1′-dianthraquinonyl (100 g.) and anhydrous boric acid (100 g.) were stirred for 5 hours at 120—130° with 98% sulphuric acid (600 c.c.). The reaction mixture was then poured into 1500 c.c. of ice-water, and the pink precipitate filtered off, washed until acid-free, and dried in a steam-oven. The dry material was dissolved in glacial acetic acid (600 c.c.) and stirred at 60° while chromium trioxide (100 g.) was added gradually during 1 hour. The mixture was then heated under reflux for 5 hours and poured into 2 l. of water. The product was filtered, washed free from chromium salts, and extracted at the boil for 1 hour with water (3 l.) containing sodium hydroxide (20 g.). The solution was filtered at the boil, and the bright red filtrate boiled for 15 minutes with Norite (10 g.). 1 : 1′-Dianthraquinonyl-2 : 2′-dicarboxylic acid (33 g., 47%) was precipitated from the hot filtrate by hydrochloric acid.

Inactive 1 : *1′-Dianthryl*-2 : *2′-dicarboxylic Acid*.—A boiling solution of 1 : 1′-dianthraquinonyl-2 : 2′-dicarboxylic acid (20 g.) in 0·5% w/v sodium hydroxide (700 c.c.) was treated with 25% sodium hydroxide solution until there was a slight permanent crystalline precipitate (*ca.* 150 c.c. required). The solution was then set aside overnight, and the orange-coloured plates of the sodium salt were washed on the filter with 10% sodium hydroxide solution. This salt was suspended in ammonium hydroxide (sp. gr. 0·88; 600 c.c.) contained in a 3-necked flask fitted with a mechanical stirrer. The mixture was warmed gently while stirred, and the air displaced from the flask by a stream of nitrogen. Zinc dust (50 g.) was added gradually during the first ½ hour, and the mixture then gently boiled under reflux for a further 2 hours. The reduction is complete when the colour of the solution (initially bright red) changes to a yellow colour. The mixture was poured into water (3 l.), boiled for ½ hour, and filtered.

1 : 1′-Dianthryl-2 : 2′-dicarboxylic acid, obtained from the filtrate by hydrochloric acid as a gelatinous yellow precipitate (16 g., 90%), was washed free from mineral acid and dried in the steam-oven. The acid (50 g.) from three such experiments was pulverised in a mortar, heated under reflux for ½ hour with glacial acetic acid (600 c.c.), cooled, filtered, and washed with glacial acetic acid. The filter-cake was

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* Dr. E. de Barry Barnett asks us to state that the substance, m. p. above 360°, described by him as 9 : 9-dianthryl (Barnett and Matthews, *J.*, 1923, **123**, 380) has not this constitution. It was produced from some unsuspected impurity in the anthrone used in these experiments and cannot be obtained by reduction of pure anthrone.

crystallised from glacial acetic acid (1400 c.c.), which on cooling deposited the dicarboxylic acid as a yellow, fine, hair-like mass. A further crystallisation from acetic acid gave a product (42 g.), m. p. 298—303°. The pure acid, m. p. 305°, can be obtained as yellow plates or prisms from *o*-dichlorobenzene or methyl ethyl ketone.

Resolution.—Results with brucine, morphine, quinine, cinchonine, or cinchonidine were negative or unsatisfactory.

A suspension of the acid (25 g.) in alcohol (1 l.) was heated under reflux on a water-bath. Finely powdered quinidine ($C_{20}H_{24}O_2N_2,2H_2O$; 41 g.) was added slowly. After addition of about 15 g. of the alkaloid the acid was in solution. Addition of the remainder of the alkaloid caused immediate precipitation of a highly crystalline alkaloidal salt. The mixture was kept warm on the water-bath for a further 10 minutes, cooled, and filtered, and the salt well washed with alcohol. Yield, 30·5 g.; $[\alpha]_{5461}^{20^\circ}$ −509° (*c*, 0·51 in chloroform). The combined mother-liquor and washings were distilled on the water-bath until 800 c.c. of alcohol had been removed, and the residual solution set aside overnight. The small quantity (1·73 g.) of amorphous material which separated was filtered off and discarded. The alcohol was then completely removed from the filtrate, and the residual brown honey-like mass decomposed by warming on the water-bath for ½ hour with 1% sodium hydroxide solution (500 c.c.). After filtration from the precipitated alkaloid, the warm yellow solution was poured into 3·5% hydrochloric acid (200 c.c.). The gelatinous precipitate of *dextro*-1 : 1′-dianthryl-2 : 2′-dicarboxylic acid (12·5 g.) was filtered off, washed, and dried in the steam oven at 90—95°. The crude acid was pulverised in a mortar, added to boiling glacial acetic acid (250 c.c.), and freed from a little undissolved material. The solution on cooling deposited the acid as a bright canary-yellow crystalline powder, m. p. 251—253°, $[\alpha]_{5461}^{21^\circ}$ +362° (*c*, 0·7265 in acetone). Two further crystallisations from glacial acetic acid gave the optically pure acid (8·25 g.), m. p. 251—253°, $[\alpha]_{5461}^{20^\circ}$ +439°, $[\alpha]_{5790}^{20^\circ}$ +392°, $[\alpha]_{D}^{21^\circ}$ +382° (*c*, 0·795 in acetone). The crystalline salt of the *lævo*-acid was extracted with boiling alcohol (500 c.c.); the residual salt (27 g.) had $[\alpha]_{5461}^{20^\circ}$ −522° (*c*, 1·03 in chloroform). Decomposition of this by the above method yielded 12·0 g. of acid which, on crystallisation from boiling glacial acetic acid (120 c.c.), yielded 11·1 g. of bright yellow crystalline powder, m. p. 253—255°, $[\alpha]_{5461}^{20^\circ}$ −429° (*c*, 0·80). A further crystallisation from glacial acetic acid yielded 10·4 g. of optically pure acid, m. p. 253—255°, $[\alpha]_{5461}^{20^\circ}$ −440°, $[\alpha]_{5790}^{20^\circ}$ −395°, $[\alpha]_{D}^{21^\circ}$ −386° (*c*, 0·80 in acetone).

Inactive 2 : 2′-*Diamino*-1 : 1′-*dianthryl.*—1 : 1′-Dianthryl-2 : 2′-dicarboxyl chloride, prepared in the usual way from the acid (5 g.) and thionyl chloride (10 c.c.), was dissolved in 50 c.c. of dry sulphur-free benzene. Finely ground sodium azide (4·0 g.) was added and the red solution heated under reflux for 7½ hours. 3N-Sodium hydroxide (25 c.c.) was added to the cooled solution, and boiling continued for a further 2 hours. The solvent was completely removed by steam, and the solid material extracted with 50% v/v hydrochloric acid. The acid filtrate was neutralised with ammonium hydroxide, and the resulting red solid crystallised from a benzene–ethyl alcohol solution (Norite). Several recrystallisations were necessary to free the amine from a red resinous by-product. The 2 : 2′-diamino-1 : 1′-dianthryl crystallises in small colourless plates, m. p. 233°. Yield, 2·9 g. (68%).

lævo-2 : 2′-*Diamino*-1 : 1′-*dianthryl.*—The procedure was as above, except that the thionyl chloride solution of the acid was not warmed, ½ hour at room temperature being sufficient to complete the reaction. There was less formation of resinous by-products, and two crystallisations (Norite with the first) from benzene–ethyl alcohol yielded 3·1 g. of the *lævo*-diamine (72%), m. p. 182—184°, $[\alpha]_{5461}^{20^\circ}$ −415°, $[\alpha]_{D}^{20^\circ}$ −384° (*c*, 0·40 in chloroform).

dextro-2 : 2′-*Diamino*-1 : 1′-*dianthryl.*—By use of the following quantities, the*dextro*-diamine was obtained by the same procedure: Acid (8·0 g.), thionyl chloride (10 c.c.), benzene (50 c.c.), and sodium azide (5 g.). Yield, 5·6 g. (80%); m. p. 185°; $[\alpha]_{5461}^{20^\circ}$ +417°, $[\alpha]_{D}^{20^\circ}$ +387 (*c*, 0·40 in chloroform).

Inactive 2 : 2′-*Dicyano*-1 : 1′-*dianthryl.*—A solution of the inactive diamine (1·5 g.) in 27% hydrochloric acid (10 c.c.) was diazotised by addition of solid sodium nitrite (0·7 g.). The filtered diazo-solution was added to potassium cuprocyanide (0·8 g. of cuprous cyanide in 20 c.c. of 5% potassium cyanide solution). The mixture was warmed on the water-bath for 15 minutes, and the solid filtered off and washed with dilute hydrochloric acid and water. After drying, the product was crystallised twice from alcohol (Norite). Inactive 2 : 2′-*dicyano*-1 : 1′-*dianthryl* crystallises in yellow needles, m. p. 238°. The solution in alcohol has a strong blue fluorescence. Yield, 0·66 g. (42%) (Found: C, 88·6; H, 4·28. $C_{30}H_{16}N_2$ requires C, 88·8; H, 3·9%).

Hydrolysis.—A solution of the dicyanide (0·4 g.) in ethylene glycol–potassium hydroxide solution (10%; 10 c.c.) was heated in an oil-bath at 160° for 2 hours. The yellow solution on pouring into dilute hydrochloric acid yielded quantitatively 1 : 1′-dianthryl-2 : 2′-dicarboxylic acid.

lævo-2 : 2′-*Dicyano*-1 : 1′-*dianthryl.*—Procedure was as above using *lævo*-diamine (2·6 g.), hydrochloric acid (15 c.c.), and sodium nitrite (AnalaR, 1·0 g.); the potassium cuprocyanide solution was prepared from cuprous cyanide (1 g.) in 5% potassium cyanide solution (25 c.c.). Yield, 1·12 g. (41%). lævo-2 : 2′-*Dicyano*-1 : 1′-*dianthryl* crystallises from alcohol in yellow needles, m. p. 162—165°, $[\alpha]_{5461}^{19^\circ}$ −382° (*c*, 0·5 in alcohol).

Hydrolysis.—The hydrolytic procedure described above, at 110—120° for 2 hours, yielded *lævo*-1 : 1′-dianthryl-2 : 2′-dicarboxylic acid, m. p. 254—255°, after one crystallisation from boiling glacial acetic acid; $[\alpha]_{5461}^{20^\circ}$ −437° (*c*, 0·80 in acetone).

Inactive 2 : 2′-*Dibromo*-1 : 1′-*dianthryl.*—The inactive diamine (3·0 g.) was diazotised as described above and added to a solution of cuprous bromide (0·8 g.) in 48% hydrobromic acid (5 c.c.). After the mixture had been heated on the water-bath for 1 hour, the solid was filtered off, washed, dried, and extracted with boiling alcohol in which it is moderately soluble. Recrystallisation from alcohol yielded inactive 2 : 2′-*dibromo*-1 : 1′-*dianthryl* as fine lemon-yellow needles, m. p. 212° (3·2 g., 80%) (Found: C, 65·8; H, 3·26. $C_{28}H_{16}Br_2$ requires C, 65·6; H, 3·0%).

Preparation of 1 : 1′-*Dianthryl*-2 : 2′-*dicarboxylic Acid by the Grignard Reaction.*—The Grignard solution was prepared by treating the above dibromo-compound (3 g.) in anhydrous ether (150 c.c.) with dry pulverised magnesium (1·0 g.). Five drops of freshly distilled ethyl bromide were added, and the mixture was heated under reflux on the steam-bath for 12 hours (procedure of Bachmann and Kloetzel, *J. Org. Chem.*, 1938, **3**, 59). The separated magnesium complex was dissolved by adding 50 c.c. of dry benzene, and a stream of dry carbon dioxide was passed into the boiling mixture for 2 hours. The cooled solution was warmed with 50 c.c. of water, and the yellowish organic layer extracted three times with dilute ammonium hydroxide solution. The aqueous extracts yielded a gelatinous yellow precipitate (1·3 g., 51%) on acidification. After crystallisation from glacial acetic acid, it had m. p. 298—301° and gave no depression with 1 : 1′-dianthryl-2 : 2′-dicarboxylic acid.

dextro-2 : *2′-Dibromo-*1 : *1′-dianthryl.*—By a similar treatment to the above, the *dextro*-diamine (3·5 g.) was converted into *dextro*-2 : 2′-dibromo-1 : 1′-dianthryl, fine yellow needles, m. p. 168—170° (3·0 g.), $[\alpha]_{5461}^{20^\circ}$ +299° (*c*, 0·5 in alcohol).

Preparation of dextro-1 : *1′-Dianthryl-*2 : *2′-dicarboxylic Acid by the Grignard Reaction.*—The procedure was as above, except that less solvent was required owing to the higher solubility of the *dextro*-dibromodianthryl. Anhydrous ether (80 c.c.) and anhydrous benzene (30 c.c.) were used. The crude acid (1·7 g.), after crystallisation from glacial acetic acid, had m. p. 252—253°, $[\alpha]_{5461}^{20^\circ}$ +422° (*c*, 0·80 in acetone).

Deamination of Inactive 2 : *2′-Diamino-*1 : *1′-dianthryl.*—A solution of the inactive diamine (3·5 g.) in a mixture of dry benzene (5 c.c.), and ethyl alcohol (20 c.c.) was treated with concentrated sulphuric acid (2 c.c.). To the fine resultant suspension was added, at room temperature, sodium nitrite (1 g.) in water (5 c.c.). To the clear diazo-solution was added copper-bronze (0·5 g.) in small portions. There was a vigorous reaction, and a highly crystalline deposit immediately separated; this was filtered off after the mixture had been heated on the water-bath for ½ hour. The residue after drying was warmed with toluene (10 c.c.) in which only part was soluble. The filtrate on cooling deposited 0·63 g. of small colourless plates, m. p. 318—319° alone or mixed with authentic 1 : 1′-dianthryl. The residue from the toluene extraction was crystallised from a large volume of glacial acetic acid and gave 2 : *2′-dihydroxy-*1 : *1′-dianthryl* as beautiful prismatic needles, m. p. 260° (decomp.) (0·93 g.) (Found : C, 86·7; H, 4·7. $C_{28}H_{18}O_2$ requires C, 87·0; H, 4·6%).

Deamination of Active 2 : *2′-Diamino-*1 : *1′-dianthryl.*—The procedure was as above, except that the quantity of water was reduced considerably. The following quantities were used : *dextro*-diamine (2·5 g.), concentrated sulphuric acid (1 c.c.), sodium nitrite (0·8 g.), distilled water (5 drops). The separated crystalline material was completely soluble in boiling toluene (rapid crystallisation), yielding 0·83 g. of *dextro*-1 : 1′-dianthryl, m. p. 283—285°, $[\alpha]_{5461}^{20^\circ}$ +221° (*c*, 1·0 in chloroform).

Similar treatment of the *lævo*-diamine (1·5 g.) yielded 0·52 g. of *lævo*-1 : 1′-dianthryl as small colourless plates, m. p. 280—283°, $[\alpha]_{5461}^{19^\circ}$ −212° (*c*, 0·98 in chloroform). Slight racemisation had occurred in the crystallisation.

Racemisation Experiments.—A solution of *dextro*-1 : 1′-dianthryl ($[\alpha]_{5461}^{20^\circ}$ +260°; *c*, 0·10) in xylene was boiled under reflux for 2 hours. The resulting solution was completely inactive; the recovered material had m. p. 319—320° and gave no depression with inactive 1 : 1′-dianthryl.

A solution of *dextro*-1 : 1′-dianthryl in chloroform was heated under reflux (temperature of the solution, 63°). The solution was rapidly chilled periodically and the rotation observed. $[\alpha]_{5461}^{19-21^\circ}$ were : initial, 4·40°; ½ hour, 3·52°; 1 hour, 2·48°; 3 hours, 1·36°; 5 hours, 0·42°.

Anthrapinacol.—Anthrone (50 g.) was reduced by the procedure of Newman (*J. Amer. Chem. Soc.*, 1940, **62**, 1683), and the product worked up by steam-distillation of the solvent. The residual white crystalline powder (48 g., 98%) was almost pure anthrapinacol. Crystallisation from benzene gives fine white needles, m. p. 185°.

9 : *9′-Dianthryl.*—The above pinacol can be converted into 9 : 9′-dianthryl in 73% yield by the method of Bergmann and Schuchardt (*loc. cit.*). On dissolution in warm thionyl chloride, the pinacol yields α-anthrapinacolin, m. p. 219° (Barnett and Matthews, *J.*, 1923, **123**, 380); with boiling acetic anhydride it gives anthracene (cf. the corresponding reaction with 10 : 10′-dihydroxy-9 : 10 : 9′ : 10′-tetrahydro-9 : 9′-dianthryl).

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