9 : 10-*Dihydrophenanthrenes. Part III.** *Optically Active* 9 : 10-*Dihydro*-3 : 4-5 : 6-*dibenzophenanthrene.*

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(*With an Appendix on Theoretical Considerations of the Optical Stability of* 9 : 10-*Dihydrophenanthrene.* By K. E. HOWLETT.)

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The (+)- and the (−)-form of 9 : 10-dihydro-3 : 4-5 : 6-dibenzophenanthrene with $[\alpha]^{22}_{5461}$ +1496° and −1500° in benzene have respectively been prepared from the (−)- and the (+)-form of 1 : 1′-dinaphthyl-2 : 2′-dicarboxylic acid *via* 2 : 2′-bishydroxymethyl-1 : 1′-dinaphthyl and 2 : 2′-bisbromomethyl-1 : 1′-dinaphthyl. The hydrocarbon is optically stable in benzene at 60° but racemises in boiling toluene with a half-life of 218 min. and in boiling ethylbenzene with a half-life of 13 min.

Optically active azepinium salts have also been prepared from the active 2 : 2′-bisbromomethyl-1 : 1′-dinaphthyl.

The optical stabilities of 2 : 2′-bridged dinaphthyls and diphenyls are discussed.

THE method of preparation of 9 : 10-dihydrophenanthrene by the action of phenyl-lithium on 2 : 2′-bisbromomethyldiphenyl (Hall, Lesslie, and Turner, *J.*, 1950, 711) has been shown to be generally applicable to the synthesis of substituted 9 : 10-dihydrophenanthrenes (Hall and Turner, *J.*, 1951, **3072**; Beaven, Hall, Lesslie, and Turner, *J.*, 1954, **131**; Bergmann and Szmuszkovicz, *J. Amer. Chem. Soc.*, 1951, **73**, 5153; Wittig and Zimmermann, *Chem. Ber.*, 1953, **86**, 629; Bergmann and Pelchowicz, *J. Amer. Chem. Soc.*, 1953, **75**, 2663). The molecule of 9 : 10-dihydrophenanthrene can be regarded as having a collinear diphenyl skeleton, with the two benzene rings twisted at an angle of about 20° in order to accommodate the two methylene groups without appreciable distortion (Beaven, Hall, Lesslie, and Turner, *J.*, 1952, 854). A substance having such a molecule should be capable of exhibiting enantiomorphism, although it is possible that the energy required to distort this simple molecule into a (temporary) planar configuration might be low enough to make the demonstration of optical activity experimentally difficult. We and our colleagues (Dr. M. S. Lesslie and Dr. M. M. Harris) have so far failed to resolve a 2-substituted 9 : 10-dihydrophenanthrene; and a calculation by Dr. K. E. Howlett (see Appendix) of the energy required for the racemisation of such a compound indicates that its optical activity is likely to be detectable only at very low temperatures.

An alternative approach is to carry out the synthesis on an optically active 6 : 6′-disubstituted diphenic acid; in this case the steric requirements for optical activity in the diphenic acid ensure that the 9 : 10-dihydrophenanthrene will have 4 : 5-substituents leading to " intramolecular overcrowding." This phenomenon and the optical activity resulting from it are now well established in a number of compounds in which a normally planar molecule, *e.g.*, phenanthrene, becomes non-planar when 4 : 5-substituents are present (Newman and Hussey, *J. Amer. Chem. Soc.*, 1947, **69**, 978, 3023; Newman and Wheatley, *ibid.*, 1948, **70**, 1913; Bell and Waring, *Chem. and Ind.*, 1949, 321; *J.*, 1949, 2689; Theilacker and Baxmann, *Naturwiss.*, 1951, **38**, 156; *Annalen*, 1953, **581**, 117). These compounds all racemise readily, either at room temperature or, in the case of 1 : 8-diamino-4 : 5-dimethyl-9 : 10-diazaphenanthrene (Theilacker and Baxmann, *loc. cit.*), when kept in methanolic solution for 1 hr. at 60°.

A 9 : 10-dihydrophenanthrene with 4 : 5-substituents would be expected to be more stable optically than a similar phenanthrene, since racemisation would require the simultaneous passing of the 4- and the 5-substituent and of the two methylene groups.

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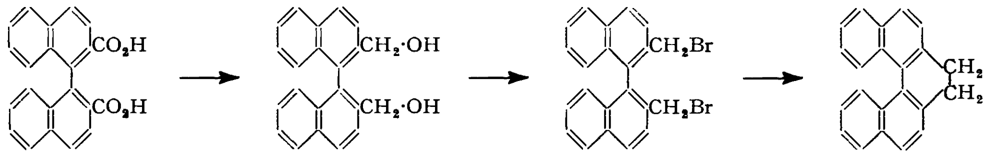
* Part II, *J.*, 1951, 3072.

Nevertheless, racemisation might occur during any of the three stages in the synthesis from the optically active diphenic acid or in the final product before its isolation.

1 : 1′-Dinaphthyl-2 : 2′-dicarboxylic acid (I), which had been resolved by Kuhn and Albrecht (*Annalen*, 1928, **465**, 282), seemed suitable for our purpose and was accordingly made and resolved through the quinine salt. Decomposition of the less soluble salt gave the acid with $[\alpha]^{22}_{5461}$ −125·2° (in 0·1N-sodium hydroxide), and this was reduced with lithium aluminium hydride in ethereal solution to (−)-2 : 2′-bishydroxymethyl-1 : 1′-dinaphthyl (II), $[\alpha]^{23}_{5461}$ −83·0° in acetone. Treatment of this compound with hydrobromic acid in boiling glacial acetic acid gave (−)-2 : 2′-bisbromomethyl-1 : 1′-dinaphthyl (III), $[\alpha]^{23}_{5461}$ −199·1° in benzene. This rather drastic treatment was not, apparently, accompanied by appreciable racemisation, probably because the replacement reaction was very fast and the dibromide crystallised almost at once from the boiling solution. The (−)-dibromide was added to an ethereal solution of phenyl-lithium and, after treatment with water and evaporation of the ether at room temperature, impure (+)-9 : 10-dihydro-3 : 4-5 : 6-dibenzophenanthrene (IV) was isolated. The recrystallised material had the surprisingly high specific rotation of $[\alpha]^{22}_{5461}$ +1496° in benzene. A preliminary account of this part of the work has been given in *Chem. and Ind.*, 1953, 1177. In benzene solution the hydrocarbon was optically stable at 60° and only very slowly racemised (sealed tube) at 100°. It had a half-life of 218 min. in boiling toluene and of 13 min. in boiling ethylbenzene. It melted at 183° with complete and rapid racemisation.



(I) (II) (III) (IV)

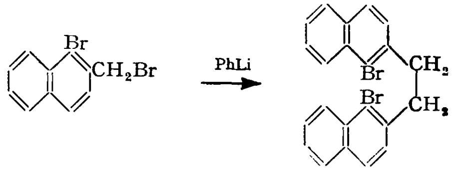
Similar treatment of the acid ($[\alpha]^{20}_{5461}$ +124·2° in 0·1N-sodium hydroxide) obtained from the more soluble quinine salt gave the (+)-diol, $[\alpha]^{23}_{5461}$ +83·1° in acetone, and thence the (+)-dibromide, $[\alpha]^{23}_{5461}$ +198·8° in benzene, and the (−)-hydrocarbon, $[\alpha]^{22}_{5461}$ −1500° in benzene.

In a similar series of reactions starting with optically active 6 : 6′-dimethyl-2 : 2′-diphenic acid, Wittig and Zimmermann (*loc. cit.*) obtained (after distillation) optically inactive 9 : 10-dihydro-4 : 5-dimethylphenanthrene from the active dibromide; but they nevertheless demonstrated indirectly that the molecule of this hydrocarbon is dissymmetric since they isolated two racemic and three of the four possible optically active forms of 9 : 10-dihydro-4 : 5-dimethylphenanthryltrimethylammonium iodide.

When we had completed all but the last stage of the trial synthesis of the racemic compound, Bergmann and Szmuszkovicz (*loc. cit.*) published a similar synthesis of the racemic compound, differing from ours only in certain experimental details. Attention is drawn to these in the Experimental section. In particular we found that the yield of 1-bromo-2-naphthaldehyde from 1-bromo-2-bromomethylnaphthalene (Hewett, *J.*, 1940, 293) was much improved by the use of the technique for the Sommelet reaction described by Angyal, Morris, Tetaz, and Wilson (*J.*, 1950, 2141).

We also investigated a number of short cuts and one alternative synthesis of (±)-dihydrodibenzophenanthrene, but all were unsuccessful. Thus, neither 1-bromo-2-methylnaphthalene nor 1-bromo-2-bromomethylnaphthalene could be oxidised to 1-bromo-2-naphthoic acid. A Grignard reagent was made from 1-bromo-2-methylnaphthalene and treated with anhydrous cupric chloride but no crystalline product was isolated. 1-Bromo-2-naphthaldehyde was heated with copper powder but no solid product was obtained. The aldehyde failed to undergo a Cannizzaro reaction and was extremely resistant to the usual oxidising agents (chromic anhydride in glacial acetic acid; nitric acid; hydrogen peroxide; aqueous potassium permanganate). Oxidation was achieved by the use of an excess of aqueous potassium permanganate in acetone solution at $\not>$70°, and under these conditions was rapid and practically quantitative. As an alternative route we prepared

1 : 2-di-(1-bromo-2-naphthyl)ethane by the action of phenyl-lithium on 1-bromo-2-bromomethylnaphthalene and tried to induce ring closure to dihydrodibenzophenanthrene by the action of various metals :



The dibromo-compound was unaffected by magnesium turnings or by copper bronze at 290°. The use of copper at higher temperatures gave a gum. Sodium in boiling toluene or, better, boiling di-*n*-butyl ether, removed the bromine without ring-closure, producing 1 : 2-di-2′-naphthylethane. Kenner and Wilson (*J.*, 1927, 1108) found that the interaction of 2 : 2′-dibromodibenzyl and sodium in ether was similarly accompanied by removal of bromine, giving more than 50% of dibenzyl. [1 : 2-Di-2′-naphthylethane has been confused in the literature (*e.g.*, Bamberger and Lodter, *Ber.*, 1888, **21**, 51) with 1 : 2-di-2′-naphthylethylene, m. p. 254°, a confusion which persists in recent work (Buu-Hoï and Hoán, *J. Org. Chem.*, 1949, **14**, 1023).]

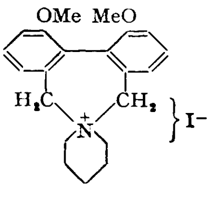
The large-scale optical resolution of 1 : 1′-dinaphthyl-2 : 2′-dicarboxylic acid differed in a number of features from the small-scale resolution described by Kuhn and Albrecht (*loc. cit.*). The latter authors crystallised the quinine salt (from 0·8 g. of acid) from ethanol–ether and obtained crops with $[\alpha]^{22}_{D}$ +230·4°, $[\alpha]^{24}_{D}$ +301·6° and, by total evaporation, $[\alpha]^{22\cdot5}_{D}$ +15·4° in chloroform. Decomposition of the second and third crops gave the acid with $[\alpha]^{22}_{D}$ −101·6° and $[\alpha]^{22}_{D}$ +46° in 0·1N-sodium hydroxide. We found that once the two diastereoisomerides had been obtained crystalline, they could be crystallised from ethanol without the addition of ether, but the resolution was complicated by the following factors : (*a*) the specific rotation of the salts in chloroform was extremely sensitive to the presence of traces of ethanol, *e.g.*, a crop with $[\alpha]_{5461}$ −29·1° in " B.P." chloroform had $[\alpha]_{5461}$ +10·0° in chloroform which had been freed from ethanol; (*b*) both salts were solvated with ethanol and thus the specific rotation in chloroform was affected by the actual weight of salt used for determining the specific rotation (after this had been discovered, all specific rotations were determined in acetone solution); and (*c*) the specific rotation of the salt of the (−)-acid had a fairly large temperature coefficient, the salt becoming more lævorotatory with rise in temperature.

The less soluble salt had $[\alpha]^{23}_{5461}$ about −36° in washed chloroform and −103·5° in acetone. It seems likely that Kuhn and Albrecht's salt was not solvated and that the strong dextrorotation which these authors observed is that of the unsolvated salt in chloroform entirely free from ethanol. That this corresponds to our *lævo*-salt is shown by the fact that both gave the *lævo*-acid. Our acid had $[\alpha]^{22}_{5461}$ −125·2°, $[\alpha]^{22}_{5791}$ −108·6°, and theirs had $[\alpha]^{22}_{D}$ −101·6°, all in 0·1N-sodium hydroxide. Our more soluble salt had $[\alpha]^{22}_{5461}$ about +75° in washed chloroform and +11·6° in acetone. It would presumably be much more strongly dextrorotatory in chloroform entirely free from ethanol (*i.e.*, if unsolvated salt could be used). Kuhn and Albrecht describe the more soluble salt as having $[\alpha]_{D}$ +15° in chloroform, but it is apparent from the quantities given that they in fact used an excess of quinine, which would be present in the total material obtained on evaporation and would account for the very low dextrorotation. Decomposition of our more soluble salt gave acid with $[\alpha]^{20}_{5461}$ +124·2°, $[\alpha]^{20}_{5791}$ +107·2° in 0·1N-sodium hydroxide. Kuhn and Albrecht were, of course, concerned only in showing that the acid could exist in enantiomorphic forms.

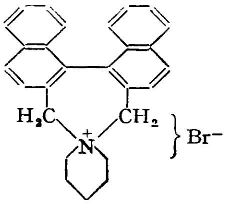
1 : 1′-Dinaphthyl-2 : 2′-dicarboxylic acid is optically highly stable (Kuhn and Albrecht, *loc. cit.*; Hall, Ridgwell, and Turner, *J.*, 1954, 2498) and we have so far failed to racemise it. For example, the rotation was unchanged after the acid had been heated in *N*-methylformamide at *ca.* 175° for 8 hr. and, although the solution developed an intense fluorescence, the acid appeared to be mainly unchanged chemically. It remained optically active after being in solution for 2 hr. in boiling tetralin; the development of colour in the solution and

the low solubility of the acid in cold tetralin made it impossible to discover if slight racemisation had occurred. In boiling ethylene glycol solution, however, the acid underwent chemical change with some loss of optical activity.

Discussion of Specific Rotations and Optical Stabilities.—2 : 7-Dihydro-4′ : 1″-dimethoxy-3 : 4-5 : 6-dibenzazepinium-1-*spiro*-1‴-piperidinium iodide (V) has a very small specific rotation ($[\alpha]^{22}_{5461}$ +4·0° and −3·8°) (Beaven, Hall, Lesslie, and Turner, *J.*, 1952, 854) and it seemed possible that this might be a common property of diphenyls bridged in the 2 : 2′-positions to form 6- and 7-membered rings. This expectation is not borne out by the large specific rotation of 9 : 10-dihydro-3 : 4-5 : 6-dibenzophenanthrene. We therefore prepared (+)-2 : 7-dihydrodinaphtho(2′ : 1′-3 : 4)(1″ : 2″-5 : 6)azepinium-1-*spiro*-1‴-piperidinium bromide (VI) and (+)-1 : 1-diallyl-2 : 7-dihydrodinaphtho(2′ : 1′-3 : 4)(1″ : 2″-5 : 6)azepinium iodide (VII) in which the 2 : 2′-positions are linked to form 7-membered heterocyclic rings. These compounds have $[\alpha]^{20}_{5461}$ +306·5° and +205·3° respectively in ethanol.



(V)



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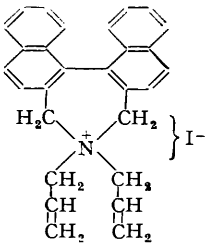


(VII)

It is likely that the high values of [α] observed with the spirans (VI) and the closely related compound (VII) compared with the value for (V) are associated with larger contributions to the optical rotatory power from the absorption bands nearest the visible region.

In each case the *lævo*-dibromide (III) gave a *dextro*-compound on cyclisation (IV, VI, and VII).

Compound (VI) underwent racemisation in hot ethylene glycol solution. It had a half-life of the order of 26 hr. at 172°. In *N*-methylformamide solution at the same temperature racemisation was much faster, being complete in about 6 hr., but was accompanied by chemical change and none of the original bromide could be recovered.

The optical stability of 9 : 10-dihydro-3 : 4-5 : 6-dibenzophenanthrene is of particular interest. On the one hand it is much more stable optically than 3 : 4-5 : 6-dibenzophenanthrene-9 : 10-dicarboxylic acid, the morphine salt of which exhibits mutarotation in chloroform solution but gives an optically inactive acid (Bell and Waring, *loc. cit.*). On the other hand, both the hydrocarbon and the corresponding 7-membered-ring compound (VI) are less stable optically than the non-bridged 1 : 1′-dinaphthyl-2 : 2′-dicarboxylic acid; but it is probably not valid to compare the effect of linked methylene groups with that of free carboxyl groups and a more interesting comparison would be with the so far unknown 2 : 2′-dimethyl-1 : 1′-dinaphthyl. Enlargement of the bridging ring from 6 atoms in (IV) to 7 atoms in (VI) leads to a considerable increase in optical stability; the groups causing steric interference are the same in both compounds but much greater distortion is required to enable the 7-membered ring to pass through the planar configuration. This is reflected in the optical stability of the azepinium compound (V) in which the substituents in the 4 : 5-positions are methoxyl groups instead of benzene rings. This compound, although less optically stable than its analogue (VI), is nevertheless more stable than the hydrocarbon (IV), despite the fact that the purely blocking effects of its *ortho*-substituents are much smaller. [The half-life of (V) is of the order of 3—4 hr. at 160°; cf. Beaven, Hall, Lesslie, and Turner, *loc. cit.*).] This confirms us in our view that the optical activity and high optical stability of the spiran (V) are primarily due to the configurational stability of the 7-membered ring.

It thus appears that the passage through the planar configuration of a molecule of the *ortho*-substituted diphenyl type is facilitated by the joining of two of the blocking groups into a ring; and, further, that the planar configuration is more easily achieved when the angle between the ring planes is already small, as in compound (IV), than when it is of the order of 50°, as in compounds (V) and (VI).

The case of 4 : 5-disubstituted phenanthrenes is rather different, since the phenanthrene system is distorted from the preferred coplanar configuration (*e.g.*, 3 : 4-5 : 6-dibenzophenanthrene in the crystal; McIntosh, Robertson, and Vand, *Nature*, 1952, **169**, 322; *J.*, 1954, 1661) and therefore has a greater inducement to become flat than has a substituted dihydrophenanthrene in which the *preferred* configuration is non-planar.

EXPERIMENTAL

In all polarimetric readings $l = 2$.

1 : 2-*Di*-(1-*bromo*-2-*naphthyl*)*ethane*.—1-Bromo-2-methylnaphthalene (Adams and Binder, *J. Amer. Chem. Soc.*, 1941, **63**, 2773; Hall and Mitchell, *J.*, 1951, 1375) was brominated with *N*-bromosuccinimide (Newman and Kosak, *J. Org. Chem.*, 1949, **14**, 375). 1-Bromo-2-bromomethylnaphthalene (48 g.), dissolved in ether (800 c.c.), was added to a solution of phenyllithium, prepared from lithium (1·5 g.) and bromobenzene (16 g.) in ether (75 c.c.). The solution became red but the colour was lost as the reaction proceeded. Most of the product crystallised during the reaction and a little more was obtained from the ethereal solution. 1 : 2-*Di*-(1-*bromo*-2-*naphthyl*)*ethane* (21 g., 60%) crystallised from benzene in rectangular plates, m. p. 192·5—193·5° (Found : Br, 36·2. $C_{22}H_{16}Br_2$ requires Br, 36·3%).

Action of Metals on 1 : 2-*Di*(1-*bromo*-2-*naphthyl*)*ethane*.—(a) *Copper*. The dibromo-compound was heated with copper bronze at 270—290° for 1 hr. and the resulting mixture extracted with acetone. Only unchanged dibromo-compound could be isolated. When reaction was carried out at 310—320° very little of the dibromo-compound was recovered and the product was a gum.

(b) *Magnesium*. The dibromo-compound did not form a Grignard reagent with magnesium in boiling di-*n*-butyl ether (14 hr.).

(c) *Sodium*. The dibromo-compound (1·65 g.) was dissolved in warm di-*n*-butyl ether (30 c.c.), and sodium (1 g.) added. Reaction started on warming; the ether was slowly heated to the b. p. and gentle boiling was continued for 5 hr. The mixture was filtered hot; the filtrate deposited a bromine-free solid (0·5 g.) which, after crystallisation from light petroleum (b. p. 60—80°), had m. p. 185—186° (Found : C, 93·2; H, 6·4. Calc. for $C_{22}H_{18}$: C, 93·6; H, 6·4%), and gave a picrate, m. p. 198—199°. 1 : 2-Di-2′-naphthylethane has m. p. 182—184° and its picrate m. p. 198° (Friedmann, *Ber.*, 1916, **49**, 1352).

1-*Bromo*-2-*naphthaldehyde*.—1-Bromo-2-bromomethylnaphthalene (90 g.) was dissolved in chloroform (400 c.c.), and powdered hexamine (46·5 g.) added in several lots to the boiling solution. The hexaminium salt (128 g.) separated in a few minutes and was filtered off and then boiled in 50% acetic acid (650 c.c.) for 1 hr. Concentrated hydrochloric acid (105 c.c.) was added and the solution boiled for 5 min. The aldehyde (41 g., 58%), m. p. 119—120°, crystallised on cooling. The *semicarbazone*, m. p. >270°, crystallised from glacial acetic acid (Found : N, 12·1; Br, 22·7. $C_{12}H_{10}ON_3Br,CH_3{\cdot}CO_2H$ requires N, 11·9; Br, 22·7%).

1-*Bromo*-2-*naphthoic Acid*.—A solution of 1-bromo-2-naphthaldehyde (11 g.) in acetone (275 c.c.) was heated in a bath kept at 60—68°; a hot aqueous solution of potassium permanganate (14 g. in 330 c.c.) was added during ½ hr. and heating was continued for a further ½ hr. Sulphur dioxide was passed in at once and the clear solution poured into water (1·5 l.). The crude acid from 30 oxidations was taken through the ammonium salt (the sodium salt was very sparingly soluble in water) and reprecipitated, giving 307 g. (87%), m. p. 189—191°. Bergmann and Szmuszkovicz (*loc. cit.*), using different experimental conditions, obtained a rather lower yield of acid, m. p. 186°.

Dimethyl 1 : 1′-*Dinaphthyl*-2 : 2′-*dicarboxylate*.—1-Bromo-2-naphthoic acid was esterified by boiling methanol and sulphuric acid (yield 89%), and the ester heated with copper bronze at 270—280° for *ca.* 20 min. While still hot the mixture was extracted with toluene; the filtrate deposited crystals on cooling. A further crop was obtained by removal of some of the solvent. After one recrystallisation from ethanol the ester had m. p. 158° (yield 78%). (Martin, *J.*, 1941, 679, obtained a lower yield of the ester by heating for 5 hr. at 190°.)

1 : 1′-*Dinaphthyl*-2 : 2′-*dicarboxylic acid*, obtained by hydrolysis of the ester, crystallised from ethanol in a solvated form; prolonged heating on a steam-bath gave the anhydrous acid, m. p. 272—274°.

2 : 2′-*Bishydroxymethyl*-1 : 1′-*dinaphthyl*.—The above ester (20 g., 1 mol.) was ground and washed with ether (500 c.c.) into lithium aluminium hydride (5·4 g., 2·6 mols.) in ether (350 c.c.). After ½ hour's boiling the mixture was treated with water and sulphuric acid (2N), and the ether was distilled off. The diol was filtered off from the residual aqueous solution and crystallised from ethanol, giving 16 g. (94%), m. p. 191—192·5°.

2 : 2′-*Bisbromomethyl*-1 : 1′-*dinaphthyl*.—The above diol (10 g.) was dissolved in boiling glacial acetic acid (250 c.c.), and boiling hydrobromic acid (*d* 1·49; 75 c.c.) was added. The initial cloudiness disappeared but reappeared after ½ min. as the dibromide began to separate as an oil. The mixture was boiled for 15 min.; more hydrobromic acid (50 c.c.) was added and the boiling continued for another ½ hr. During this process the oil solidified and, after cooling, the solid was separated and crystallised from ethyl methyl ketone (yield 12 g., 86%). The dibromide formed large crystals, melting over a range of 10°, presumably owing to poor thermal conduction. When ground it melted at 151—153° to an opaque liquid which cleared at 155° (Found: C, 59·9; H, 4·0; Br, 36·1. Calc. for $C_{22}H_{16}Br_2$: C, 60·0; H, 3·7; Br, 36·3%). Bergmann and Szmuszkovicz (*loc. cit.*) obtained a product with m. p. 148—149·5° by treating the diol with phosphorus tribromide in benzene.

9 : 10-*Dihydro*-3 : 4-5 : 6-*dibenzophenanthrene*.—The above dibromide (25 g., 0·8 mol.) was added as a suspension in ether (500 c.c.) to a solution of phenyl-lithium, prepared from lithium (1·07 g.) and bromobenzene (11 g.) in ether (50 c.c.). After being heated for 1 hr., the solution was decanted through glass wool and treated with water and dilute acid. 9 : 10-Dihydro-3 : 4-5 : 6-dibenzophenanthrene crystallised from the ethereal solution, and more was obtained by evaporation of the solvent. It recrystallised from benzene or ethyl methyl ketone as needles, m. p. 215—216° (yield of pure material 9·5 g., 59%) (Found: *M*, 260. Calc. for $C_{22}H_{16}$: *M*, 280). Bergmann and Szmuszkovicz (*loc. cit.*) give m. p. 212—213°.

Resolution of 1 : 1′-*Dinaphthyl*-2 : 2′-*dicarboxylic Acid*.—The de-solvated acid (46·8 g., 1 mol.) and anhydrous quinine (44·3 g., 1 mol.) were dissolved together in ethanol (455 c.c.), and ether (455 c.c.) was added. The solution was kept at 4° and eventually deposited a salt (57 g.) which was subsequently recrystallised 3 times from ethanol to constant specific rotation (4 g.). The mother-liquor from the first crop was evaporated to dryness and the residue crystallised from ethanol. The more soluble salt was crystallised from highly concentrated ethanolic solutions. Intermediate crops were repeatedly recrystallised. Altogether 27·5 g. of the less soluble salt and 13·4 g. of the more soluble salt were obtained, apparently optically pure or nearly so. The less soluble *quinine salt* had m. p. 178° (decomp.), $[\alpha]^{23}_{5461}$ −103·5°, $[\alpha]^{23}_{5791}$ −89·8° (*c*, 1·101 in acetone) (Found: C, 74·15; H, 6·4. $C_{42}H_{38}O_6N_2,C_2H_5{\cdot}OH$ requires C, 74·1; H, 6·2%). The more soluble *quinine salt* had m. p. 184—190° (decomp.) with previous softening, $[\alpha]^{22}_{5461}$ +11·6°, $[\alpha]^{22}_{5791}$ +8·6° (*c*, 0·989 in acetone) (Found: C, 73·2; H, 6·4. $C_{42}H_{38}O_6N_2,1{\cdot}5C_2H_5{\cdot}OH$ requires C, 73·45; H, 6·4%). Several crops of the more soluble salt were obtained with $[\alpha]_{5461}$ about +21°, but decomposition gave acid which was not optically pure. Some of the (+)-acid with the highest [α] was therefore converted into the quinine salt and this had $[\alpha]^{22}_{5461}$ +11·6°. The higher dextrorotations obtained for the optically impure salt remain anomalous.

(−)-1 : 1′-*Dinaphthyl*-2 : 2′-*dicarboxylic Acid*.—A solution of the less soluble quinine salt (3·5 g.) in chloroform (35 c.c.) was extracted 3 times with N-potassium hydroxide. The combined extracts were washed with chloroform and poured into dilute hydrochloric acid. The precipitated (−)-1 : 1′-*dinaphthyl*-2 : 2′-*dicarboxylic acid* was crystallised from aqueous acetone (yield, 1·6 g.) and had $[\alpha]^{23}_{5461}$ −125·2°, $[\alpha]^{22}_{5791}$ −108·6° (*c*, 1·023 in approx. 0·1N-NaOH). It was hydrated, the analysis corresponding to about $0{\cdot}5H_2O$, and had m. p. *ca.* 120° (decomp.) (Found: C, 74·9; H, 4·5. $C_{22}H_{14}O_4,0{\cdot}5H_2O$ requires C, 75·2; H, 4·3%). It lost water when heated for some hours at 100° *in vacuo* but the anhydrous acid was very hygroscopic; to ensure reproducible results samples (*e.g.*, those obtained by precipitation) were always crystallised from aqueous acetone and air-dried at room temperature before their specific rotations were measured. The active *acid* also crystallised in needles, solvated with carbon tetrachloride, but apart from this could not be crystallised from anhydrous solvents (Found: C, 60·5; H, 3·6. $C_{22}H_{14}O_4,0{\cdot}7CCl_4$ requires C, 60·6; H, 3·1%).

(+)-1 : 1′-*Dinaphthyl*-2 : 2′-*dicarboxylic Acid*.—Similar decomposition of the more soluble quinine salt gave (+)-*acid*, m. p. *ca.* 120° (decomp.), $[\alpha]^{20}_{5461}$ +124·2°, $[\alpha]^{20}_{5791}$ +107·2° (*c*, 1·115 in approx. 0·1N-NaOH) (Found: C, 74·9; H, 4·6. $C_{22}H_{14}O_4,0{\cdot}5H_2O$ requires C, 75·2; H, 4·3%). Decomposition of the salt with $[\alpha]_{5461}$ *ca.* +21° gave acid with $[\alpha]_{5461}$ +84°, from which it proved possible to extract more highly active acid ($[\alpha]_{5461}$ +117°) with ether, the racemic acid being very sparingly soluble.

Attempted Racemisation of (+)-1 : 1′-*Dinaphthyl*-2 : 2′-*dicarboxylic Acid*.—(*a*) A solution of the acid in 0·1N-sodium hydroxide, having α^{20}_{5461} +1·89°, was boiled under reflux for 10 hr. and then heated at 140° (sealed tube) for 5 hr. It then had α^{20}_{5461} +1·88°.

(*b*) A solution of the acid in *N*-methylformamide (α^{21}_{5461} +4·24°) was maintained at *ca.* 175° in an electrically heated bath. The solution became yellow and fluorescent. After 1·5 hr. it had α^{22}_{5461} +4·32° and after 8 hr. α^{24}_{5461} +4·3° ± 0·1°. (The small initial increase in α resulted from slight loss of solvent into the condenser.) Solid was recovered from the solution, and almost all of it dissolved readily in sodium hydrogen carbonate solution and was reprecipitated by acid.

(*c*) The acid ($[\alpha]_{5461}$ +110° in 0·1N-NaOH) dissolved in warm tetralin but crystallised out at room temperature. A 1% solution was heated at the b. p. for 2 hr., then cooled, and the acid was extracted with 0·1N-sodium hydroxide. The alkaline solution, which was green, was made up to 20 c.c. and had α_{5461} *ca.* 2·0°, corresponding to $[\alpha]_{5461}$ *ca.* 100°, indicating that little, if any, racemisation had occurred.

(*d*) The acid was boiled under reflux in ethylene glycol solution for 6 hr. Attempted recovery of the acid gave a gum, most of which was insoluble in alkali. The soluble part formed a colloidal solution, which cleared on the addition of acetone and was optically inactive.

(−)-2 : *2′-Bishydroxymethyl*-1 : *1′-dinaphthyl.*—The (−)-acid (12·0 g.), dissolved in ether (400 c.c.), was added to lithium aluminium hydride (5·1 g., 4 mols.) in ether (300 c.c.). The mixture was boiled for 1½ hr. Ethyl acetate was added, followed by water and 2N-sulphuric acid. The ethereal layer was separated, the solvent removed, and the residue crystallised twice from benzene. (−)-2 : *2′-Bishydroxymethyl*-1 : *1′-dinaphthyl* (9·1 g., 85%) was obtained as thick hexagonal plates, m. p. 168—169°, and also as solvated rods which readily lost solvent at 100° and then also had m. p. 168—169° (Found : C, 84·5; H, 5·7. $C_{22}H_{18}O_2$ requires C, 84·05; H, 5·8%). The diol had $[\alpha]^{23}_{5461}$ −83·0°, $[\alpha]^{23}_{5791}$ −72·3° (*c*, 0·9815 in acetone). The melted diol solidified on cooling and remelted at 168°, showing that racemisation had not occurred on melting.

(+)-2 : *2′-Bishydroxymethyl*-1 : *1′-dinaphthyl.*—Similar reduction of the (+)-acid (5·8 g.) gave the (+)-*diol* (4·5 g.), m. p. 167—168°, $[\alpha]^{21}_{5461}$ +83·1°, $[\alpha]^{21}_{5791}$ +72·2° (*c*, 1·1495 in acetone) (Found : C, 84·2; H, 6·0%).

(−)-2 : *2′-Bisbromomethyl*-1 : *1′-dinaphthyl.*—The (−)-diol (7·85 g.) was dissolved in boiling glacial acetic acid (195 c.c.), and boiling hydrobromic acid (*d* 1·49; 60 c.c.) was added. The solution cleared on shaking, then became cloudy and, after a few minutes' boiling, crystals separated. More hydrobromic acid (40 c.c.) was added and heating was continued for a total time of 7 min. after first adding hydrobromic acid. After cooling, the solid was filtered off, washed with water and dried *in vacuo* over sodium hydroxide. The crude *dibromide* (10·8 g., 98%) had m. p. 184—186°, $[\alpha]^{21}_{5461}$ −196·9° in C_6H_6, and was used without further purification. Some was recrystallised from ethyl methyl ketone and had m. p. 185·5—186·5°, $[\alpha]^{23}_{5461}$ −199·1°, $[\alpha]^{23}_{5791}$ −169·4° (*c*, 1·095 in C_6H_6) (Found : C, 59·7; H, 3·95; Br, 36·1. $C_{22}H_{16}Br_2$ requires C, 60·0; H, 3·7; Br, 36·3%).

(+)-2 : *2′-Bisbromomethyl*-1 : *1′-dinaphthyl.*—Similar treatment of the (+)-diol (3·7 g.) gave the (+)-*dibromide* which, after crystallisation from ethyl methyl ketone, had m. p. 185·5—186·5°, $[\alpha]^{23}_{5461}$ +198·8°, $[\alpha]^{23}_{5791}$ +169·9° (*c*, 1·089 in C_6H_6) (Found : C, 60·0; H, 4·1; Br, 36·0%).

(+)-9 : *10-Dihydro*-3 : 4-5 : *6-dibenzophenanthrene.*—The (−)-dibromide (4·0 g., 0·8 mol.) was added as a suspension in ether (100 c.c.) to a solution of phenyl-lithium, prepared from lithium (0·17 g.) and bromobenzene (1·8 g.) in ether (8 c.c.). After being heated for 35 min. the ethereal solution was decanted through glass wool and treated with water and dilute acid. The ethereal layer was separated and the ether removed at *ca.* 5°. The residual solid was crystallised twice from ethyl methyl ketone and yielded (+)-9 : *10-dihydro*-3 : 4-5 : *6-dibenzophenanthrene*, $[\alpha]^{22}_{5461}$ +1496°, $[\alpha]^{22}_{5791}$ +1302° (*c*, 0·5285 in C_6H_6) (Found : C, 94·0; H, 5·9. $C_{22}H_{16}$ requires C, 94·25; H, 5·75%), as thick hexagonal plates. These melted at 183° and at once resolidified as needles which then melted at 215—216° (the m. p. of the racemate).

(−)-9 : *10-Dihydro*-3 : 4-5 : *6-dibenzophenanthrene* was prepared similarly from the (+)-dibromide (3·85 g.). It had m. p. 183° (with second melting at 215—216°), $[\alpha]^{22}_{5461}$ −1500°, $[\alpha]^{22}_{5791}$ −1307° (*c*, 0·5250 in C_6H_6) (Found : C, 94·1; H, 6·0%).

Racemisation of (+)- *and* (−)-9 : *10-Dihydro*-3 : 4-5 : *6-dibenzophenanthrene.*—(*a*) No racemisation occurred with a solution of the (+)-compound in benzene at 60° for 24 hr.

(*b*) When a solution of the (+)-compound in benzene was heated in a sealed tube at 100° for 35 min. a small fall in rotation (*ca.* 3%) occurred.

(*c*) The rate of racemisation in boiling toluene solution was measured by using a solution (30 c.c.) containing 0·0803 g. of the (+)-compound. The temperature of the solution was raised rapidly to the b. p. and, after a suitable interval, the solution was rapidly cooled in ice-water. Polarimetric readings were taken at room temperature (22°) and the solution returned to the flask and re-heated for a further period. α_{5461} fell from +6·86° to 0° during 35 hr. By this method values for the times were subject to a small but cumulative error since racemisation would be continuing for short periods during the heating and cooling of the solution. The straight line of the log plot and the constancy of k showed that this error was small: k, 3·18 (±0·01) $\times 10^{-3}$ min.$^{-1}$; half-life, 218 ± 1 min.

(*d*) The rate of racemisation in boiling ethylbenzene solution was determined in a similar way. The solution (25 c.c.) contained 0·1419 g. of the (−)-compound and α_{5461} changed from −17·47° to 0° during 109 min. Owing to the higher b. p. of this solvent, errors in the values for the times were greater than in the previous experiment: k, 5·3 (±0·2) $\times 10^{-2}$ min.$^{-1}$; half-life, 13 ± 1 min.

The values of k obtained in experiments (*c*) and (*d*) give a value for the activation energy of about 34 kcal./mole.

(±)-2 : 7-*Dihydrodinaphtho*(2′ : 1′-3 : 4)(1″ : 2″-5 : 6)*azepinium*-1-spiro-1‴-*piperidinium Bromide*.—Piperidine (1·9 g., 2·2 mols.) in benzene was added to a warm benzene solution of (±)-2 : 2′-bisbromomethyl-1 : 1′-dinaphthyl (4·4 g., 1 mol.). After ½ hr. the benzene was decanted and the residual gum crystallised from water, in which it was sparingly soluble. The *bromide* (3·75 g.) was obtained as hair-like needles, melting at *ca.* 250° to an opaque liquid (Found: C, 69·1; H, 6·4; Br, 16·95. $C_{27}H_{26}NBr,1{\cdot}5H_2O$ requires C, 68·8; H, 6·2; Br, 16·95%). The *picrate*, crystallised from acetone or ethanol, had m. p. 276—277° (block) (Found: C, 65·8; H, 4·8; N, 9·4. $C_{33}H_{28}O_7N_4$ requires C, 66·9; H, 4·8; N, 9·5%).

(+)-2 : 7-*Dihydrodinaphtho*(2′ : 1′-3 : 4)(1″ : 2″-5 : 6)*azepinium*-1-spiro-1‴-*piperidinium Bromide* (VI).—Similar treatment of (−)-2 : 2′-bisbromomethyl-1 : 1′-dinaphthyl (1·1 g.) gave the (+)-quaternary *bromide*, which crystallised from water in hexagonal plates, melting at *ca.* 237° to an opaque liquid (Found: C, 67·0; H, 6·5; Br, 16·6. $C_{27}H_{26}NBr,2H_2O$ requires C, 67·5; H, 6·3; Br, 16·6%), $[\alpha]^{20}_{5461}$ +306·5°, $[\alpha]^{20}_{5791}$ +268·8° (*c*, 1·088 in EtOH). The (+)-compound was much more soluble in water than the racemic compound. The *picrate* crystallised from ethanol in plates, m. p. 222° (Found: C, 65·3; H, 4·8; N, 9·5%). (The low carbon analysis for this and for the racemic compound must result from partial solvation. Insufficient material was available for a quantitative investigation.)

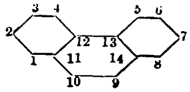
Racemisation of the (+)-*Bromide*.—A solution of the (+)-bromide (0·1868 g.) in ethylene glycol (20 c.c.) was heated quickly to 172° and then transferred to a heating mantle, pre-set so that the temperature of the solution remained at 172°. At suitable intervals the racemisation was stopped by rapid external cooling and polarimetric readings were taken at room temperature. α_{5791} fell from +5·04° to +3·98° during 8½ hr. but after this it was no longer possible to make polarimetric readings of the solution. The results indicated $k \sim 4{\cdot}5 \times 10^{-4}$ min.$^{-1}$, and half-life ~26 hr. The solution was treated with aqueous picric acid. The precipitated picrate was extracted three times with ethanol (in which the racemic picrate is sparingly soluble). The first extract deposited the optically active picrate, m. p. 221°, mixed m. p. 222°. The third extract deposited the racemic picrate, m. p. 275—276° (block), mixed m. p. 276—277° (block).

(±)-1 : 1-*Diallyl*-2 : 7-*dihydrodinaphtho*(2′ : 1′-3 : 4)(1″ : 2″-5 : 6)*azepinium Bromide*.—(±)-2 : 2′-Bisbromomethyl-1 : 1′-dinaphthyl and diallylamine were allowed to react together in warm benzene solution during several hours. The solid *bromide* which separated was collected; it crystallised from water in flattened needles, m. p. *ca.* 135° (decomp.) (Found: C, 68·3; H, 6·2; Br, 16·3. $C_{28}H_{26}NBr,2H_2O$ requires C, 68·3; H, 6·1; Br, 16·2%). On attempted recrystallisation from water it separated in very fine needles which formed a gel with the solvent.

(+)-1 : 1-*Diallyl*-2 : 7-*dihydrodinaphtho*(2′ : 1′-3 : 4)(1″ : 2″-5 : 6)*azepinium Iodide* (VII).—The interaction of (−)-2 : 2′-bisbromomethyl-1 : 1′-dinaphthyl and diallylamine in warm benzene solution gave a gum which became crystalline on treatment with water but on attempted recrystallisation from water gave a gel. It was dissolved in hot water and treated with aqueous potassium iodide. The quaternary *iodide* separated and crystallised from dilute aqueous ethanol in plates, m. p. *ca.* 115° (decomp.) (Found: C, 62·2; H, 5·6; I, 23·6. $C_{28}H_{26}NI,2H_2O$ requires C, 62·3; H, 5·6; I, 23·5%), $[\alpha]^{20}_{5461}$ +205·3°, $[\alpha]^{20}_{5791}$ +182·2° (*c*, 1·062 in EtOH).

APPENDIX (by K. E. HOWLETT)

In the racemisation of an optically active dihydrophenanthrene, the molecules will probably pass through a planar transition state and the activation energy for the rearrangement will therefore be similar in magnitude to the difference in energy between the



equilibrium state and the planar configuration. Although the strain of the transition state would undoubtedly be spread over the whole molecule, it is reasonable to assume that the benzenoid rings involve more rigid bonds than the bridge links. Also it seems unlikely that the strain can be relieved by deformation of the 4–12–13 and 5–13–12 angles in the plane of the transition state because this would bring the 4- and the 5-hydrogen atom into even closer proximity. Therefore, in order to make a first approximation to the potential-energy difference between initial and transition states, one need only consider bond-bending effects of the carbon skeleton of the bridge at the 11-, 14-, 9-, and 10-positions, together with a compression of the 9—10 carbon–carbon bond.

Certain other activation energy increments may be noted. Whilst the bridge hydrogen atoms experience a part of the ethane energy barrier in passing the eclipsed position, the 4- and the 5-hydrogen atom will suffer half the repulsive forces experienced for an equal twisting motion in diphenyl, and further the coplanarity of the benzenoid rings in the transition state implies a gain in delocalisation energy. These effects, however, are probably small for the low angle of rotation necessary, and moreover the last acts in the opposite sense to the others.

If the vibrational motion of the atoms is assumed to be simple harmonic, *i.e.*, the variation of potential energy with oscillation is of the form :

$$V = V_0 + \Sigma \tfrac{1}{2} k_r \Delta r^2 + \Sigma \tfrac{1}{2} k \, \Delta\theta^2$$

(where V_0 is the potential energy of the equilibrium state of the molecule, k_r and k_θ are respectively bond-stretching and bond-bending constants, and Δr and $\Delta\theta$ are the respective deformations), then the energy barrier to be surmounted may be calculated if the force constants are known. In the calculations described here, the <CCC bending constant is assumed to be $0{\cdot}5 \times 10^{-11}$ dyne-cm./radian^2 (cf. Crawford and Brinkley, *J. Chem. Phys.*, 1941, **9**, 69) and the C–C stretching constant 5×10^5 dyne/cm. (cf. Linnett, *Quart. Rev.*, 1947, **1**, 85). The potential energies of a number of planar configurations have been calculated on the assumptions that in the equilibrium state the bond lengths 12–13, 11–12, 10–11, and 9–10 are respectively 1·50, 1·40, 1·54, and 1·54 Å, whilst the appropriate inter-bond angles are 120° and 109° 28′. The results are set out in tabular form.

θ	ϕ	r (9–10) (Å)	V_θ (cal.)	V_ϕ (cal.)	V_r (cal.)	Total energy (cal.)
120°	120°	1·360	0	2430	23,310	25,740
122	118	1·454	90	1600	5,320	7,010
123	117	1·502	200	1250	1,040	2,490
124	116	1·550	350	950	70	1,370
125	115	1·598	550	670	2,420	3,640
126	114	1·647	800	450	8,260	9,510

θ and ϕ refer to the angles 10–11–12 and 9–10–11 respectively.

The lowest energy pass between the antipodal equilibrium configurations of dihydrophenanthrene is about 1·4 kcal./mole above the ground state. It seems, therefore, that the simple dihydrophenanthrene is likely to be configurationally too unstable to permit of optical resolution. Thus, for example, this energy barrier is similar in magnitude to those separating rotational isomers which are not isolable as chemically distinct species (cf. Pitzer, *J. Amer. Chem. Soc.*, 1948, **70**, 2140). Even the barrier of 10 kcal./mole thought to separate the boat and the chair form of *cyclo*hexane (Shoppee, *J.*, 1946, 1138) is insufficient to allow of chemical separation. In fact 15—18 kcal./mole is probably a lower limit for an energy barrier which would enable optically active species to be studied by observing a mutarotational change (cf. Jamison and Turner, *J.*, 1938, 1652, who found the mutarotation of the cinchonidine salt of *N*-benzoyl-4 : 6 : 4′-tribromodiphenylamine-2-carboxylic acid to have a half-life of 15 min. at 17·6° and an activation energy for the mutarotation process of 21 kcal./mole).

The calculation indicates, incidentally, that the 9–10 bond is probably shortened by only about 0·01 Å in the transition state whilst the original tetrahedral angles of the bridge are opened to about 116°. Thus *a posteriori* it can be appreciated (*a*) that the assumption of simple harmonic motion is unlikely to be seriously in error for a bond oscillation of the order of 0·1 radian, and (*b*) that neglect of compression in the other bridge links (which would be even less than in the 9–10 bond) is justified.

The application of a calculation, similar to that employed for dihydrophenanthrene, to a diphenyl derivative with a seven-membered carbocyclic bridging ring has been attempted. By assuming as a further approximation in this case that the planar transition state causes no compressional effects in the bridge bonds, the activation energy for racemisation is estimated to be 19 kcal./mole. This figure is in qualitative agreement with the known optical stability of the azepinium salt (V).

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