69. *Phenanthrene Chemistry. Part II.* Reactions of 9,9′-Biphenanthryl.*

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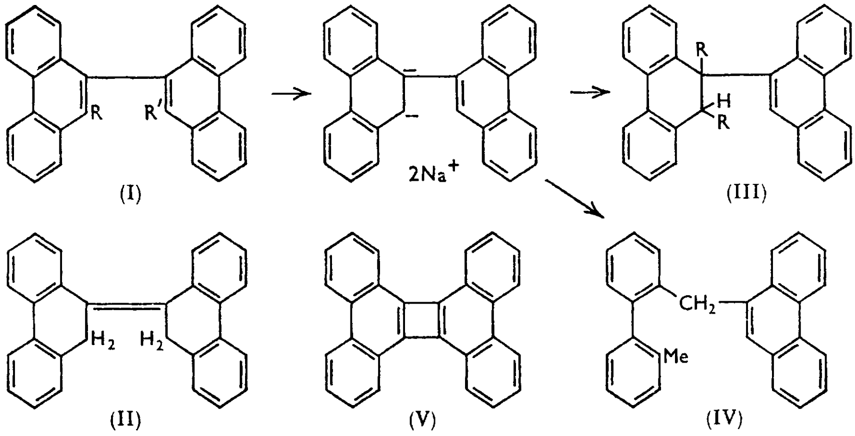
9,9′-Biphenanthryl in 1,2-dimethoxyethane adds sodium at the 9,10-positions: some reactions of the disodio-derivative are described. The reduction, oxidation, nitration, bromination, and iodination of 9,9′-biphenanthryl have been investigated.

Attempts to prepare tetrabenzobiphenylene (bi-9,10-phenanthrylene) by several reactions were unsuccessful. Calculations by the Hückel molecular-orbital method indicate that this derivative of cyclobutadiene should be highly unstable and reactive.

The reaction of 9-bromophenanthrene with potassium amide in liquid ammonia yields tetrabenzophenazine and 9-phenanthrylamine.

The chemistry of 9,9′-biphenanthryl (I; R = R′ = H) has been relatively little studied. The compound has been prepared by a Krizewski–Turner reaction of 9-phenanthrylmagnesium bromide with cupric chloride,[1] by the Ullmann reaction of 9-bromophenanthrene at 350°,[2] and by reaction of 9-chlorophenanthrene with sodium.[3] We have prepared it by the first of these methods, and conveniently also by the thermal decomposition of 9,9′,10,10′-tetrahydro-10-nitro-9,9′-biphenanthryl-10′-yl nitrate, as will be described later.

Addition of sodium to 9,9′-biphenanthryl in diethyl ether has been described by Bergmann and Bergmann.[4] Hydrolysis of the violet-black solution gave a compound which they concluded was 10,10′-dihydro-9,9′-biphenanthrylene (II), described as yellow and having m. p. 303°.



(I) (III)

(II) (V) (IV)

Such terminal addition of metal to the 9,10:9′,10′-diene system is not necessarily to be expected. There is little electronic interaction between the phenanthryl units in 9,9′-biphenanthryl, and the 9,10,9′,10′-system can hardly be conjugated. Thus, a model suggests that approach to near-co-planarity of the phenanthryl units is opposed by considerable steric resistance. The ultraviolet absorption spectrum of 9,9′-biphenanthryl is

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* Part I, Carey and Millar, *J.*, 1962, 3278.

[1] Bachmann, *J. Amer. Chem. Soc.*, 1934, **56**, 1363.

[2] Zinke and Ziegler, *Ber.*, 1941, **74**, 115.

[3] Union Carbide Corp. and D. J. Foster, G.P. 1,114,193/1961 (*Chem. Abs.*, 1962, **57**, 2166).

[4] Bergmann and Bergmann, *J. Amer. Chem. Soc.*, 1937, **59**, 1443.

very similar in form to that of phenanthrene,[5] and almost identical with that of 9-methylphenanthrene; [6] the molecular refractivity indicates that the mobility of the π-electrons is restricted to each phenanthryl unit; [6] and the thermochemical stabilization energy is twice that of phenanthrene.[7] 9,9′-Biphenanthryl does not add maleic anhydride.[4]

Our attempts to obtain reaction between sodium and 9,9′-biphenanthryl in diethyl ether were unsuccessful. However, we found reaction in 1,2-dimethoxyethane, addition occurring at the 9,10-positions, as with phenanthrene on addition of lithium, sodium, or potassium in the same solvent.[8] Hydrolysis of the disodio-derivative gives 9,10-dihydro-9,9′-biphenanthryl (III; R = H) (colourless, m. p. 209—210°) in nearly quantitative yield; and reaction with carbon dioxide gives 9,10-dihydro-9,9′-biphenanthryl-9,10-dicarboxylic acid (III; $R = CO_2H$) (probably the *trans*-CO_2H form).[8] These structures are in accord with the infrared spectra of the compounds, and, for the hydrocarbon (III; R = H) with the ultraviolet spectrum and the proton magnetic resonance spectrum; also with the visible-absorption spectrum of the complex formed with tetracyanoethylene. The ultraviolet spectrum and the colour of the complex indicate the presence of an unreduced phenanthryl unit. With iodine the disodio-compound regenerates 9,9′-biphenanthryl.

With triphenylboron the disodio-compound undergoes reductive fission, giving on hydrolysis a small yield of a hydrocarbon formulated as 2′-methyl-2-9′-phenanthrylmethyl biphenyl (IV) on the basis of its infrared, ultraviolet, and proton magnetic resonance spectra.

From these and other reactions of the disodio-compound, a small amount (*ca.* 1%) of 2,3:10,11-dibenzoperylene was also isolated. This compound has previously been prepared from 9,9′-biphenanthryl by dehydrogenation, *e.g.*, with aluminium and stannic chlorides in boiling benzene.[9]

Bergmann and Bergmann's 10,10′-dihydro-9,9′-biphenanthrylene formed a brown-black perbromide ($C_{28}H_{18}Br_4$) with bromine, interpreted by them as evidence for the structure (II). 9,10-Dihydro-9,9′-biphenanthryl fails to react with bromine in chloroform, and gives only a weak colour with tetranitromethane; but it adds chlorine to give 9,10-dichloro-9,′10′-dihydro-9,9′-biphenanthryl which shows the ultraviolet absorption typical of a biphenyl. Like 9,9′-biphenanthryl and its halogen-substituted derivatives described below, 9,10-dihydro-9,9′-biphenanthryl forms a complex with 2,4,7-trinitrofluorenone, in which one molecule of the reagent forms a complex with each electronically independent polycyclic unit.

With chromic anhydride in acetic acid 9,9′-biphenanthryl gives only phenanthraquinone.

9,9′-Biphenanthryl is readily nitrated by nitric acid in acetic anhydride, but some dinitro-compounds are formed even in conditions where much of the hydrocarbon is unattacked; and separation of the isomeric mono- and di-nitro-compounds is difficult. The lack of selectivity is similar to that of phenanthrene in nitration.[10] 10-Nitro-9,9′-biphenanthryl can be prepared in excellent yield by reaction of the biphenanthryl in benzene solution with anhydrous nitric acid. These results, and addition reactions to phenanthrene to be reported later, suggest that this reaction may proceed by an addition–elimination mechanism. The 10-nitro-compound is also obtained in high yield by use of dinitrogen trioxide or nitrogen dioxide in benzene, and in lower yields by use of nitryl chloride in benzene. From the 10-nitro-compound, other 10-substituted biphenanthryls are available, by reduction and diazotization. The 10,10′-dinitro-compound has been

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[5] Henri and Bergmann, *Nature*, 1939, **143**, 278.

[6] Bigot and van Krevelen, *Trans. Faraday Soc.*, 1960, **56**, 322.

[7] Magnus and Becker, *Erdöl und Kohle*, 1951, **4**, 115; Magnus, Hartmann, and Becker, *Z. phys. Chem.*, 1951, **197**, 75.

[8] Jeanes and Adams, *J. Amer. Chem. Soc.*, 1937, **59**, 2608.

[9] Clar and Zander, *J.*, 1958, 1861.

[10] Dewar and Warford, *J.*, 1956, 3570.

prepared in small yield by an Ullmann reaction of 9-bromo-10-nitrophenanthrene,[11] despite earlier failures.[12]

9,9′-Biphenanthryl is brominated at the 10-position by *N*-bromosuccinimide in acetic acid with a ferric chloride catalyst, and iodinated by iodine and iodic acid in acetic and sulphuric acid. Iodination occurs successively at the 10- and the 10′-position, and the mono- and the di-iodo-compound can be isolated. The biphenanthryl resists bromination by a variety of other reagents, in conditions where phenanthrene undergoes substitution, and iodination by other reagents.

The unknown hydrocarbon tetrabenzobiphenylene (V) is of interest, insofar as analogy with the properties of the known benzo- and dibenzo-biphenylenes suggests that it might be highly reactive or not isolable in normal conditions. Thus, angularly annellated benzologues of biphenylene are sensitive to heat, air, and light, whereas the linear benzologues are not.[13] Kekulé-type bond distributions in the 9,10-phenanthrylene units of tetrabenzobiphenylene would conflict with the tendency, in biphenylenes, to shun a true cyclobutadienoid bond distribution in the four-membered ring system. The similar conclusions drawn from these simple arguments are supported by calculations by Hückel molecular-orbital approximation methods (see below).

These conclusions are supported by some negative experiments. No evidence for the formation of tetrabenzobiphenylene was obtained on reaction of 10,10′-di-iodo-9,9′-biphenanthryl with cuprous oxide; comparable reactions have been employed to afford biphenylene and a variety of benzo- and other substituted biphenylenes, albeit in small yields.[13] The only product isolated was 9,9′-biphenanthryl (which would be the expected reduction product from tetrabenzobiphenylene).

Biphenylene and 2,6-dimethylbiphenylene have been obtained by reaction of *o*-bromoiodobenzene[14] and 3-bromo-4-iodotoluene,[15] respectively, with magnesium in ether: these reactions doubtless involve the effective dimerization of a benzyne or toluyne intermediate, respectively. 2-Bromo-3-iodonaphthalene failed to react with magnesium, but 2,3:6,7-dibenzobiphenylene has been prepared from it by reaction with copper bronze in dimethylformamide.[16] However, 9,10-dichlorophenanthrene with magnesium in tetrahydrofuran gives, not tetrabenzobiphenylene, but hexabenzotriphenylene, which very probably results from condensation reactions of 9,10-phenanthryne;[17] the formation of 9,10-phenanthryne in these conditions is supported by the evidence of experiments in which it was trapped by Diels–Alder reaction with anthracene, giving 2,3:4,5-dibenzotriptycene.[18]

9-Bromo-10-iodophenanthrene reacts vigorously with magnesium in diethyl ether; carboxylation gave a small yield of acid, probably 9,9′-biphenanthryl-10,10′-dicarboxylic acid, and a complex mixture of neutral products from which only 9,9′-biphenanthryl was definitely identified. Reaction of 9-bromo-10-iodophenanthrene with copper bronze in dimethylformamide gave similar neutral products. 9,10-Dibromophenanthrene failed to react with magnesium in diethyl ether or tetrahydrofuran. 9-Bromo-10-fluorophenanthrene with lithium amalgam in ether gave only a polymeric product.[18]

We have also investigated the reaction of 9-bromophenanthrene in liquid ammonia with potassium amide, as a possible route to tetrabenzobiphenylene *via* dimerization of phenanthryne. The major product isolated was tetrabenzophenazine, but some 9-phenanthrylamine was also formed and when an excess of potassium amide was used the yield

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[11] Braithwaite and Holt, *J.*, 1959, 3025.

[12] Mosby, *J. Org. Chem.*, 1959, **24**, 421.

[13] Ginsburg, " Non-Benzenoid Aromatic Compounds," Interscience Publ., Inc., New York, 1959, p. 90.

[14] Heaney, Mann, and Millar, *J.*, 1957, 3930.

[15] Hinton, Mann, and Millar, *J.*, 1958, 4704.

[16] Ward and Pearson, *J.*, 1961, 515.

[17] Carey and Millar, *J.*, 1959, 3144.

[18] Wittig, Uhlenbrock, and Weinhold, *Chem. Ber.*, 1962, **95**, 1692.

of this amine was 20%; this is readily isolated and the method constitutes a preparative route to the amine superior to earlier multi-step syntheses.

The mechanism by which the phenazine is formed is uncertain. Neither 9,10-diaminophenanthrene nor phenanthraquinone is apparently an intermediate, as they fail to give the phenazine under the same conditions. It is likely that 9-bromophenanthrene is converted into 9,10-phenanthryne, which by addition of amide ion would give an anion derived from 9-phenanthrylamine, and that this is converted into *NN*-dihydrotetrabenzophenazine; this is known to be very readily oxidized to tetrabenzophenazine.

EXPERIMENTAL

Compounds are colourless unless otherwise described. M. p.s were determined on a Kofler hot stage, and absorption spectra with a Unicam S.P. 700 spectrophotometer. Infrared spectra were determined for Nujol mulls unless otherwise stated, usually with a Perkin-Elmer Infracord spectrophotometer. Chromatographic separations were carried out on alumina columns unless otherwise specified, with the usual sequence of eluting solvents.

9,9′-*Biphenanthyryl* (I).—When prepared as described by Bachmann [1] and recrystallized twice from methanolic chloroform, this compound was isolated in 50% yield, with m. p. 187—188°. When the crude product was chromatographed in benzene and eluted with benzene–light petroleum (b. p. 60—80°) (1 : 1) it was isolated in 60% yield, with m. p. 185—186°; recrystallization from ethanolic chloroform then gave m. p. 190—192° (lit.,[1] 184—185°). The *bis*-2,4,7-*trinitrofluorenone complex*, prepared in benzene, formed red needles, m. p. 224—226° (Found: C, 66·2; H, 2·9; N, 9·0. $C_{54}H_{28}N_6O_{14}$ requires C, 65·9; H, 2·9; N, 8·6%). We failed to induce reaction of the biphenanthryl with sodium in diethyl ether, even on prolonged boiling. The infrared spectrum of 9,9′-biphenanthryl shows a strong band at 895 cm.$^{-1}$ (single aromatic CH).

9,10-*Dihydro*-9,9′-*biphenanthryl* (III; R = H).—9,9′-Biphenanthryl (5 g.) in purified 1,2-dimethoxyethane (150 ml.) was added to sodium powder (2·2 equiv.) under diethyl ether (20 ml.) and stirred at room temperature under nitrogen for 3 hr. (in some cases reaction was slow; it was then apparently catalysed by a trace of benzoyl peroxide). The dark solution was filtered from the excess of sodium and hydrolysed by addition of an aqueous solution of the ether. The solvents were removed under reduced pressure and the residue dissolved in benzene, dried (Na_2SO_4), and chromatographed, giving the *dihydro-compound*, m. p. 200—205° (3·8 g., 95%). Recrystallized twice from ethyl acetate, this had m. p. 209—210° (3·35 g., 83%) (Found: C, 94·0; H, 5·8%; *M*, 360. $C_{28}H_{20}$ requires C, 94·35; H, 5·65%; *M*, 356). The *bis*-2,4,7-*trinitrofluorenone complex* crystallized from benzene as red needles, m. p. 238—240° (Found: C, 66·7; H, 3·15; N, 8·3. $C_{54}H_{30}N_6O_{14}$ requires C, 66·5; H, 3·0; N, 8·3%).

The last chromatographic fraction gave 2,3 : 10,11-dibenzoperylene (0·002 g.), yellow crystals (from benzene), m. p. 345—346° (lit.,[9] 330—332°); the m. p. and infrared and ultraviolet spectra were identical with those of a sample prepared by Clar and Zander's method.[9] The ultraviolet spectrum determined in 1,4-dioxan shows $\lambda_{max.}$ 438 (4·58), 414 (4·56), 390 (4·28), 302 (4·66), 292 (4·55), and 240 mμ (5·1) ($\log_{10} \varepsilon$ in parentheses here and below). These values do not differ greatly from those determined by Clar and Zander [9] for benzene and ethanol solutions.

The ultraviolet absorption spectrum of 9,10-dihydro-9,9′-biphenanthryl shows the presence of a phenanthrene chromophore. In 1,4-dioxan solution, it shows $\lambda_{max.}$ 246 (4·69), 252 (4·94), 257 (5·06), 300 (4·2), 326 (2·57), 334 (2·72), 342 (2·54), 350 (2·70), and $\lambda_{min.}$ 234 (4·35) and 296 mμ (4·15).

The infrared absorption spectrum determined in carbon tetrachloride shows bands at 3070 and 3030 (due to aromatic CH) and 2940 and 2831 (C–H in CH_2) and 2892 cm.$^{-1}$ (tertiary aliphatic C–H stretching): and, in Nujol, at 885 cm.$^{-1}$ (single aromatic C–H). The proton magnetic resonance spectrum showed the presence of methine CH and of a single methylene unit.

Treatment with tetracyanoethylene in chloroform gave a blue-purple colour ($\lambda_{max.}$ 547 mμ), very similar to that shown by 9-methylphenanthrene and contrasting with the colours given by biphenyl and by stilbene. The development of colour, due to the formation of a charge-transfer complex, when tetracyanoethylene is mixed with various aromatic compounds in a non-hydroxylic solvent has been described previously.[19] The colour, and wavelength of principal absorption maximum in the visible region, produced when a solution of a polycyclic aromatic compound in chloroform is mixed with one equivalent of the reagent, is given below. The visible colours are those given by an ~3% solution of the compound and an equivalent of the reagent in 3% solution in chloroform. The wavelengths of principal absorption maxima are given for 0·04M-solutions in chloroform unless otherwise specified, and an equivalent of reagent in 0·04M-solution in chloroform. Benzene, yellow (3895 Å); biphenyl, red (3690, 4910); dimethyl biphenate, pale yellow (3708); stilbene, cobalt-blue (5960); biphenylene, turquoise (3850, 6570); phenanthrene, purple (5300); 9-methylphenanthrene, deeper purple (0·02M; 5380); 9,10-dimethylphenanthrene, deep blue (5515); 9,10-dihydrophenanthrene, violet-black (4170, 5520); 9-nitrophenanthrene, colourless; 9-phenanthroic acid, pink (0·002M; 5220); methyl 9-phenanthroate, pale pink (0·004M; broad absorption); 9,9′-biphenanthryl, deep purple (3895, 5220); 10-nitro-9,9′-biphenanthryl, pale yellow-brown (0·02M; 4880, 6910); naphthalene, violet-black (4340, 5520); anthracene, green (rapidly forming colourless adduct); fluorene, deep green (3230, 4410, 6380); acenaphthene, green (3230, 3385, 4450, 6420); acenaphthylene, red-brown (4745); fluoranthene, purple (5560); chrysene, purple-blue (0·02M; 3795, 4380, 5320); triphenylene, bright purple (0·02M; 4520, 5825); 1,2-benzanthracene, blue-black (0·01M; 3795, 5340, 6725) slowly forming colourless adduct; pyrene, dark violet (4910, 6975, 7125); *o*-, pale pink (4260, 5135), *m*-, deeper pink (3960, 5020), and *p*-terphenyl, pale blue (3850, 5580).

It will be seen that very broadly, for aromatic hydrocarbons, the colour deepens with increasing number of aromatic rings, and, to a small extent, with alkyl substitution: *i.e.*, with increasing electron-donor properties. The colour can be used to distinguish quickly, *e.g.*, a biphenyl chromophore from a phenanthrene chromophore. Thus, 9,10-dihydrophenanthrene behaves much as biphenyl; and 9,10-dihydro-9,9′-biphenanthryl gives a colour intermediate between those given by biphenyl and by phenanthrene. Electron-withdrawing substituents, conjugated with an aromatic ring, inhibit complex formation and lighten the colour, as expected.

9,10-*Dihydro*-9,9′-*biphenanthryl*-9,10-*dicarboxylic Acid* (III; R = CO_2H).—Carbon dioxide was passed into a solution of the disodio-compound prepared as above from 9,9′-biphenanthryl (4 g.). The dark solution became brownish-pink with suspended solid. When no further colour change appeared (30 min.) the gas stream was stopped, the solvent removed under reduced pressure, and the residue extracted with water (200 ml.) for 2 hr. The water-insoluble residue was dissolved in benzene and extracted with water. The *acid* was precipitated from the combined aqueous extracts by hydrochloric acid, and recrystallized successively from acetic acid and light petroleum (b. p. 60—80°); it formed nearly colourless crystals, m. p. 265—270° (0·86 g., 16%) (Found: C, 80·95; H, 5·3. $C_{30}H_{20}O_4$ requires C, 81·05; H, 4·55%), $\nu_{max.}$ 1690 (C=O), 940 (carboxyl OH), 750 and 726 (four adjacent aromatic CH), and 885 cm.$^{-1}$ (single aromatic CH).

Chromatography of the benzene extract gave 9,9′-biphenanthryl (55%) and 2,3 : 10,11-dibenzoperylene (1·2%).

Reaction of 9,10-*Disodio*-9,9′-*biphenanthryl with Iodine*.—To the disodio-compound, prepared as above from 9,9′-biphenanthryl (5 g.), a solution of iodine (2 mol.) in 1,2-dimethoxyethane was added dropwise at room temperature. A vigorous reaction occurred, and the solution became clear pale red. The solvent was removed and the residue extracted from sodium iodide with benzene. Chromatography in benzene, and elution with 1 : 1 light petroleum (b. p. 60—80°)–benzene gave 9,9′-biphenanthryl (3·5 g., 70%) and 9,10-dihydro-9,9′-biphenanthryl (0·2 g., 4%); 2,3 : 10,11-dibenzoperylene (0·04 g., 1·6%) was eluted by ether; all were identified by m. p. mixed m. p., and infrared spectra.

Reaction of 9,10-*Disodio*-9,9′-*biphenanthryl with Triphenylboron*.—A violet-black solution of the disodio-compound, prepared as above from 9,9′-biphenanthryl (4 g.) in 1,2-dimethoxyethane (120 ml.) was siphoned under nitrogen into a flask containing a stirred suspension of triphenylboron (2 equiv.) in the ether (30 ml.). The solution, now golden-yellow with a blue-green fluorescence, was stirred for 12 hr. and then hydrolysed by dropwise addition of water, before addition of aqueous 25% sodium hydroxide (75 ml.) with stirring. The organic layer was separated, and benzene (100 ml.) added, causing separation of an aqueous layer. This aqueous layer was further extracted with benzene; the combined organic layers and benzene

[19] Merrifield and Phillips, *J. Amer. Chem. Soc.*, 1958, **80**, 2778; Ozolins and Schenk, *Analyt. Chem.*, 1961, **33**, 1035, 1562; Schenk, *Talanta*, 1961, **8**, 109; *Analyt. Chem.*, 1963, **35**, 167; Farnum, Atkinson, and Lothrop, *J. Org. Chem*, 1961, **26**, 3204.

extracts were dried and the solvents removed. The residue in benzene was then chromatographed, elution being with light petroleum (b. p. 60—80°), benzene, and diethyl ether successively. The fractions collected were evaporated and the residues recrystallized from ethanol–chloroform. 9,9'-Biphenanthryl (50%) was isolated from the early fractions, followed by 9,10-dihydro-9,9'-biphenanthryl (5%), and ultimately by 2,3 : 10,11-dibenzoperylene (*ca.* 1%); all were identified as above. The ethanol–chloroform mother-liquors from these recrystallizations were combined and evaporated, and the residue rechromatographed, yielding 2'-*methyl*-2-9'-*phenanthrylmethylbiphenyl*, m. p. 122·5° [from light petroleum (b. p. 40—60°)] (0·8 g., 16%). (Found: C, 93·8; H, 6·1%; *M*, 358. $C_{28}H_{22}$ requires C, 93·8; H, 6·2%; *M*, 358). The *bis*-2,4,7-*trinitrofluorenone complex*, prepared in, and recrystallized from, cyclohexane, formed orange-red needles, m. p. 269° (Found: N, 8·6. $C_{54}H_{32}N_6O_{14}$ requires N, 8·5%). The hydrocarbon in dioxan gave an ultraviolet absorption spectrum similar to that of phenanthrene: $\lambda_{max.}$ 256 (4·81), 287 (4·04), 297 (4·11), 318 (2·53), 326 (2·47), 333 (2·61), 342 (2·42), and 350 mμ (2·64). The infrared spectrum determined in Nujol showed bands at 764, 746, and 728 cm.$^{-1}$ (four adjacent aromatic CH); and in CCl_4 at 3060, 3020, 2952, and 2920 cm.$^{-1}$ (aromatic, methyl, and methylene CH).

The hydrocarbon with tetracyanoethylene in chloroform gave a pale purple colour. Proton magnetic resonance peaks were observed at τ 7·85 (one CH_3), 5·82 (one CH_2 attached to two aromatic rings), and a complex aromatic region corresponding to 17 aromatic H.

9,10-*Dichloro*-9,9',10,10'-*tetrahydro*-9,9'-*biphenanthryl*.—A solution of 9,10-dihydro-9,9'-biphenanthryl (0·2 g.) and chlorine (0·04 g.) in carbon tetrachloride was exposed to sunlight for 10 min. Removal of solvent and recrystallization of the residue successively from ethanol and light petroleum (b. p. 60—80°) gave the *dichloro-compound*, m. p. 159—160° (63%) (Found: C, 78·2; H, 4·3. $C_{28}H_{20}Cl_2$ requires C, 78·5; H, 4·7%). The infrared spectrum showed bands at 685 (C–Cl stretching) and 733 and 765 cm.$^{-1}$ (four adjacent aromatic CH). The ultraviolet spectrum was similar to that of biphenyl ($\lambda_{max.}$ 248 mμ) with a large bathochromic shift; in 1,4-dioxan solution, it shows $\lambda_{max.}$ 268 (4·01) and $\lambda_{min.}$ 244·5 mμ (3·76).

The hydrocarbon (III; R = H) failed to add bromine in chloroform or carbon tetrachloride.

Oxidation of 9,9'-*Biphenanthryl*.—Chromic anhydride (3·5 g.) in 50% aqueous acetic acid (4·4 ml.) was added to a suspension of 9,9'-biphenanthryl (2·2 g.) in acetic acid (10 ml.) at 60°, and the mixture was boiled under reflux for 1½ hr. Dilution with ice–water then gave a solid which was collected, washed with water, dried, and chromatographed, giving 9,9'-biphenanthryl (0·25 g.) and phenanthraquinone (0·5 g., 40%), m. p. and mixed m. p. 201—202°. If the oxidation was carried out at 85°, only 9,9'-biphenanthryl (80%) was isolated on recrystallization from methanol–benzene.

10-*Nitro*-9,9'-*biphenanthryl* (I; R = H, R' = NO_2).—Freshly distilled anhydrous or fuming nitric acid (2 ml., 2½ mol.) was added dropwise with stirring to 9,9'-biphenanthryl (5 g.) in benzene (100 ml.) at 15—20°. After complete addition (15 min.) the suspension was set aside for 36 hr.; filtration then gave the *nitro-compound*, m. p. 277—281° (4 g., 72%). Recrystallization from ethyl acetate or methanol–chloroform, or sublimation at 240°/0·03 mm., raised the m. p. to 284—286°. The filtrate, on evaporation and addition of light petroleum, gave more 10-nitro-9,9'-biphenanthryl (Found: C, 83·95; H, 4·1; N, 3·7. $C_{28}H_{17}NO_2$ requires C, 84·2; H, 4·3; N, 3·5%).

The infrared spectrum shows bands at 1530 (aromatic NO), 895 (single aromatic CH) and at 718 and 752 cm.$^{-1}$ (four adjacent aromatic CH). Its orientation was also established by oxidation to phenanthraquinone (below). The ultraviolet spectrum showed the presence of a phenanthrene chromophore: in tetrahydrofuran, $\lambda_{max.}$ 2260 (4·75), 2380 (5·0) 2545 (5·02) 2732 (4·52) 2860 (4·34) and 2975 Å (4·29).

In a similar experiment with anhydrous nitric acid (1 mol.) the yield of nitro-compound was 0·56 g. (48%); 4 mol. gave 45% yield. Nitration with nitric acid in acetic anhydride at 50° gave a complex mixture of mono- and di-nitro-9,9'-biphenanthryls, partly separated but not rendered isomerically pure by chromatography on charcoal, and unchanged hydrocarbons.

Nitration with dinitrogen trioxide (from nitric acid and arsenious oxide) or with purified nitrogen dioxide was carried out by passing a rapid stream of the gas into 9,9'-biphenanthryl (1 g.) in benzene (20 ml.) at 25—30°. When gas absorption ceased the suspension was set aside for 24 hr. before removal of the nitro-compound, m. p. 281—285° (0·8 g.). Evaporation of the filtrate and recrystallization of the residue from methanol–benzene gave a further 0·3 g., m. p. 284—286° (total yield 1 g., quantitative).

In another experiment, nitryl chloride (0·8 g., 2 mol.) was added to 9,9′-biphenanthryl (1·7 g.) in benzene (40 ml.) dropwise at room temperature. Removal of the solvent and chromatography of the residue gave 9,9′-biphenanthryl (0·1 g.), the 10-nitro-compound (0·7 g., 33%), and an unidentified dinitro-compound (0·35 g.). An experiment with nitryl chloride (4 mol.) gave similar results.

Oxidation of 10-*Nitro*-9,9′-*biphenanthryl.*—The nitro-compound (0·5 g.), suspended in acetic acid (20 ml.), was oxidized by chromic anhydride (2 g.) in 50% aqueous acetic acid (4 ml.). After boiling for 2 hr. the mixture was poured into water, and the solid deposited on storage was collected and extracted with aqueous sodium hydrogen sulphite, yielding, on basification, phenanthraquinone, m. p. and mixed m. p. 207—209° (0·35 g., 75%).

Reduction of 10-*Nitro*-9,9′-*biphenanthryl.*—The nitro-compound was reduced by lithium aluminium hydride in tetrahydrofuran to give the crude amine; this, when diazotized and treated with aqueous potassium iodide in the usual way, gave the 10-iodo-compound (I; R = H, R′ = I) identical with that prepared by iodination of biphenanthryl, as described below.

10-*Bromo*-9,9′-*biphenanthryl* (I; R = H, R′ = Br).—A mixture of 9,9′-biphenanthryl (1·5 g.), *N*-bromosuccinimide (1·5 g.), and anhydrous ferric chloride (2 g.) in acetic acid (40 ml.) was shaken, and then boiled for 15 hr. The mixture was then poured into ice–water and the solid collected, washed with aqueous sodium hydroxide and water, dried, and chromatographed, giving a yellow *bromo-compound*, m. p. 168—170° (from ethanol) (1·6 g., 88%) (Found: C, 77·3; H, 4·05; $C_{28}H_{17}Br$ requires C, 77·6; H, 3·95%). The *bis*-2,4,7-*trinitrofluorenone complex*, prepared in benzene, formed red needles, m. p. 212° (Found: C, 62·05; H, 3·1. $C_{54}H_{27}BrN_6O_{14}$ requires C, 61·95; H, 2·6%). The infrared spectrum was in accord with the assigned structure; the ultraviolet spectrum was similar to that of 9,9′-biphenanthryl, with slight bathochromic shift. A sample oxidized by chromic anhydride in acetic acid gave phenanthraquinone (50%).

9,9′-Biphenanthryl was recovered in good yield, after attempted bromination with *N*-bromosuccinimide in carbon tetrachloride at the b. p. with or without addition of benzoyl peroxide, and after attempted bromination by bromine in carbon tetrachloride in the presence of pyridine or iron.

10-*Iodo*-9,9′-*biphenanthryl.*—9,9′-Biphenanthryl (5 g.) in acetic acid (125 ml.) was shaken with iodine (1·4 g.) and iodic acid (0·5 g.) in water (5 ml.), carbon tetrachloride (5 ml.), and concentrated sulphuric acid (5 ml.), then stirred at 85—90° for 15 hr. The mixture was poured into very dilute aqueous sodium hydrogen sulphite and ice, and the solid collected, washed with aqueous sodium hydroxide and water, and dried (6·1 g.). This solid was extracted with 5 : 1 benzene–light petroleum (b. p. 60—80°) and the extract chromatographed, giving the *iodo-compound*, m. p. 176—178° (from ethanol) (5·8 g., 85%) (Found: C, 70·05; H, 3·9. $C_{28}H_{17}I$ requires C, 70·1; H, 3·55%). The bis-2,4,7-trinitrofluorenone complex, prepared in benzene, formed red crystals, m. p. 221—222° but was too unstable for satisfactory analysis. The infrared spectrum was in accord with the assigned structure; the ultraviolet spectrum was very similar to that of 10-bromo-9,9′-biphenanthryl.

This compound was also prepared from 10-amino-9,9′-biphenanthryl as described above.

Attempts to iodinate 9,9′-biphenanthryl with iodine and sodium persulphate in acetic acid, iodine monochloride in acetic acid, iodine and nitric acid in dioxan, or iodine and silver sulphate in a mixture of sulphuric acid and cyclohexane gave the unchanged hydrocarbon as the only identified product.

9,10,9′,10′-*Tetrachloro*-10-(*dichloroiodo*)-9,10,9′,10′-*tetrahydro*-9,9′-*biphenanthryl.*—An excess of chlorine was passed into a solution of the above iodo-compound in chloroform at −5°. Removal of solvent at 0° in a rotary evaporator gave the *compound* as light yellow-green crystals, decomp. >115° or on attempted recrystallization (Found: C, 49·25; H, 2·15; I, 18·3. $C_{28}H_{16}Cl_6I$ requires C, 48·6; H, 2·3; I, 18·35%).

10,10′-*Di-iodo*-9,9′-*biphenanthryl* (I; R = R′ = I).—The monoiodide (5 g.) was treated with iodine (1·06 g.), iodic acid (0·366 g.) in water (5 ml.), carbon tetrachloride (5 ml.), and sulphuric acid (5 ml.) in acetic acid (125 ml.) in the same conditions as for monoiodination. Chromatography and recrystallization from ethanol gave the *di-iodo-compound*, m. p. 143—144° (4·9 g., 80%) (Found: C, 54·9; H, 2·8. $C_{28}H_{16}I_2$ requires C, 55·5; H, 2·7%). The infrared spectrum was in accord with the assigned structure; the ultraviolet spectrum was similar to that of 9,9′-biphenanthryl. A solution in ethanol showed a blue fluorescence. A bis-2,4,7-trinitrofluorenone complex, prepared in benzene, formed red crystals, m. p. 180—181° (decomp.), but was very unstable and decomposed in a vacuum.

A sample of the di-iodo-compound, oxidized with chromic anhydride in acetic acid, gave phenanthraquinone (50%).

Reaction of 10,10′-*Di-iodo*-9,9′-*biphenanthryl with Cuprous Oxide.*—The di-iodo-compound, mixed with ten times its weight of cuprous oxide, was pyrolysed at temperatures between 210° and 400°. In all these experiments, chromatography gave only products shown by elemental analysis, molecular-weight determination, and ultraviolet and infrared spectra to be mixtures of the di-iodo-compound and 9,9′-biphenanthryl.

Reaction of 9-*Bromo*-10-*iodophenanthrene with Magnesium.*—9-Bromo-10-iodophenanthrene (4·5 g.) in ether (300 ml.) was stirred with magnesium (0·65 g.) under nitrogen; reaction was induced by the addition of a crystal of iodine. After 8 hours' stirring at room temperature, the green solution was decanted from magnesium (0·34 g.) and poured on solid carbon dioxide. Working-up in the usual way gave an acid, probably 9,9′-*biphenanthryl* 10,10′-*dicarboxylic acid* (I; R = R′ = CO_2H), m. p. 329° (from chloroform, ethanol, and light petroleum) (0·2 g.) (Found: C, 81·6; H, 4·8. $C_{30}H_{18}O_4$ requires C, 81·45; H, 4·1%), $\nu_{max.}$ 2620, 1700, and 950 cm.$^{-1}$ (CO_2H) and 722 and 758 cm.$^{-1}$ (four adjacent aromatic CH).

Chromatography of the neutral product gave 9,9′-biphenanthryl (1·6 g.), mixtures of halogenated biphenanthryls, and an unidentified yellow crystalline compound (0·1 g.), m. p. 360—365° (from benzene) (blue-green fluorescence) raised to 365—367° by sublimation at 320°/2 × 10^{-3} mm. This halogen-free compound (Found: C, 89·0, 89·4; H, 4·8, 5·1%) showed infrared bands at 740 and 721 cm.$^{-1}$ (four adjacent aromatic CH), and in the ultraviolet spectrum $\lambda_{max.}$ 2540, 2910, 3020, and 4620 Å (in dioxan). Its low solubility in phenanthrene, and decomposition in camphor, prevented Rast determination of the molecular weight.

9,10-Dibromophenanthrene failed to react substantially with magnesium in ether or tetrahydrofuran.

Reaction of 9-*Bromo*-10-*iodophenanthrene with Copper Bronze.*—The halogen compound (5 g.) in dimethylformamide (50 ml.) was boiled under reflux with copper bronze (6·5 g.) for 3 hr. The hot solution was decanted from solid into water; the precipitated solid, on chromatography, gave the same neutral products as in the previous experiment.

Reaction of 9-*Bromophenanthrene with Potassium Amide.*—9-Bromophenanthrene (10 g.) in light petroleum (b. p. 40—60°; 250 ml.) was added to a solution of potassium amide (from 8 g., 5 equiv. of the metal) in liquid ammonia (300 ml.); powdered ammonium nitrate (1·55 g., 0·5 mol.) was added, before stirring for 1 hr. The ammonia was then allowed to evaporate, the residue boiled, and the petroleum replaced under reflux by benzene. The insoluble product was collected, washed with hot benzene, methanol, and water, and dried; recrystallization from 1,2,4-trichlorobenzene gave yellow crystalline tetrabenzophenazine, m. p. *ca.* 450° (1·57 g., 63%), identified by comparison of its infrared and ultraviolet spectra with those of an authentic specimen.

The benzene extract was dried and hydrogen chloride passed through it, precipitating 9-phenanthrylamine hydrochloride (2·0 g., 22·5%), identified by basification and comparison of the free base with an authentic specimen.

In a similar experiment with 0·2 equiv. of potassium amide, a trace of 9-phenanthrylamine was isolated and 9-bromophenanthrene was recovered almost quantitatively.

When 1 equiv. of the amide was used, the phenazine and 9-phenanthrylamine were formed in poor yield and 9-bromophenanthrene (75%) was recovered. In similar experiments in which the bromophenanthrene was replaced by 9,10-diaminophenanthrene or by phenanthraquinone, these compounds were recovered and no phenazine was formed.

APPENDIX

Theoretical Study of Tetrabenzobiphenylene by the Molecular-orbital Method.—Owing to the approximations in the Hückel molecular-orbital theory, absolute stability cannot be evaluated; only relative stability in a series of molecules of related type can be predicted.

Ali and Coulson [20] studied biphenylenes and the related compounds (VI), (VII), and (VIII) by the Hückel molecular-orbital method with some refinements and showed that their relative stability could be understood from a study of the bond orders in the central cyclobutadiene-like ring of these molecules: similarly the bond orders of compound (V) obtained by the Hückel molecular-orbital method would provide some information about the general properties.

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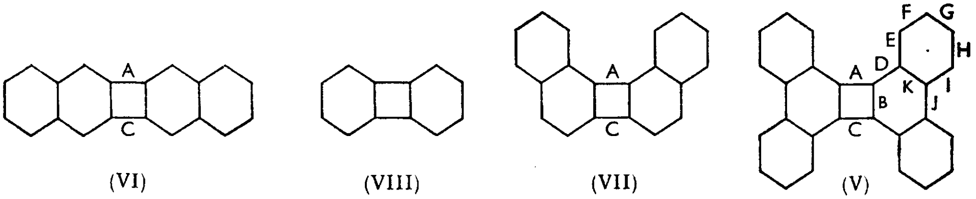
[20] Ali and Coulson, *Tetrahedron*, 1960, **10**, 41.

Since we are primarily interested in the difference of bond orders in the central part of molecule (V) and other related molecules (VI)—(VIII), it was necessary to relax the contraint of putting all " resonance integrals " between nearest neighbour atoms β_{rs} equal to β. Instead, the dependence of β_{rs} on the length l of the bond r–s was allowed for by using the relation suggested by Longuet-Higgins and Salem: [21]



(VI) (VIII) (VII) (V)

[All C_6 rings aromatic.]

$$\beta(l) = -\beta e^{-l/a} \qquad (a = 0{\cdot}3106 \text{ Å})$$

such that β (1·40 Å) $= \beta_0 = -25{\cdot}56$ kcal./mole.

A self-consistent set of bond orders were obtained by using an iterative technique starting from the bond orders obtained from a Hückel calculation with all $\beta_{rs} = \beta$, the length of a bond being derived from the linear relation suggested by Longuet-Higgins and Salem: [21]

$$l = (1{\cdot}50 - 0{\cdot}15 \text{ p}) \text{ Å}$$

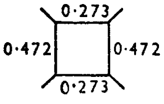
where p is the π bond order of the bond.

The set of bond orders obtained is assumed to be self-consistent when the lengths derived are reproducible to an accuracy of 0·001 Å. The results of the calculation for the molecule (V) are shown in Table 1 for the different stages of iteration. The nomenclature of the bonds is shown above. We show also the self-consistent bond orders of the central cyclobutadiene-like part in (V)—(VIII). This shows that the degree of bond-fixation increases in the order: (VI) < (VIII) < (VII) < (V). The central four-membered ring in (V) has the pronounced diene character of all the molecules studied here and since the conjugation energy gained by delocalization is small, the molecule would tend to split into two phenanthrene units or a biphenanthryl molecule. Even if the 9,10-bonds were to become pseudo-triple bonds, there might easily be a gain in energy on separation into halves.[22] Splitting into two phenanthrene units involves rupture of a σ-bond and also a π-bond, but we can assume that the σ-bond-fission

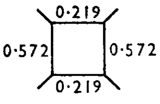
TABLE 1.

Bond orders in tetrabenzobiphenylene.

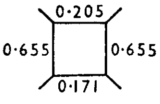
Bond	1st iteration	2nd iteration	3rd iteration	4th iteration	Final length (Å)
A	0·207	0·159	0·151	0·149	1·478
B	0·678	0·720	0·729	0·731	1·390
D	0·527	0·526	0·520	0·519	1·422
E	0·554	0·552	0·550	0·548	1·418
F	0·719	0·732	0·735	0·737	1·389
G	0·607	0·593	0·588	0·586	1·412
H	0·707	0·720	0·725	0·727	1·391
I	0·584	0·579	0·575	0·572	1·414
J	0·483	0·469	0·465	0·465	1·430
K	0·510	0·531	0·540	0·542	1·419



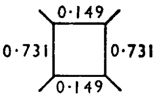
(VI)



(VIII)



(VII)



(V)

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[21] Longuet-Higgins and Salem, *Proc. Roy. Soc.*, 1959, *A*, **251**, 172.
[22] Personal communication from Professor C. A. Coulson, F.R.S.

energy would be almost identical in these molecules. The relative ease of fission would, therefore, be related to change in π-electron energy on fission. We have used Coulson and Longuet-Higgins's simple perturbation theory [23] to calculate the energies required to break, first, the π-bond (C) and, secondly, both bonds (A) and (C) in these molecules, with the results given in Table 2. These indicate that molecule (V) would be much more labile than (VI)—(VIII). However, it is not suggested that (V) cannot be synthesized.

TABLE 2.

	VI	VII	(V)
Energy reqd. to break bond (C)	$0{\cdot}451\beta_0$	$0{\cdot}269\beta_0$	$0{\cdot}232\beta_0$
,, ,, bonds (A) & (C)	$0{\cdot}903\beta_0$	$0{\cdot}598\beta_0$	$0{\cdot}464\beta_0$

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[23] Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39.