# Polycyclic Biphenylenes. Part IV.[1] Biphenylenes derived from 9,10-Phenanthryne

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The amination of phenanthro[9,10-*d*]triazole gives mixtures of the 1-amino-1*H*- and 2-amino-2*H*-derivatives [(I; R = NH₂) and (V)], the latter predominating. In oxidations of compound (I; R = NH₂) with lead tetra-acetate, products derived from 9,10-phenanthryne (II) were obtained but the dimer of (II), tetrabenzo[*a,c,g,i*]bi-phenylene (III), was not found. 'Crossed' aryne couplings of (II) with benzyne and 2,3-naphthalyne gave dibenzo[*a,c*]- and tribenzo[*a,c,h*]-biphenylene; that with 1,2-naphthalyne failed. The results are discussed with regard to the stabilities of these annelated biphenylenes.

In a previous paper [1] it was shown that the dimerisation and 'crossed' coupling of arynes generated from 1-amino-1*H*-triazolo-arenes provided satisfactory routes to certain otherwise inaccessible dibenzobiphenylenes,

notably the dibenzo[*a,g*]- and dibenzo[*a,i*]-isomers, which are of low stability. The present paper describes the generation of 9,10-phenanthryne (II) from 1-amino-1*H*-phenanthro[9,10-*d*]triazole (I; R = NH₂). This aryne (II) would be expected to dimerise to the un-known tetrabenzo[*a,c,g,i*]biphenylene (III). It is now

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well established that the angular annelation of benzene nuclei to biphenylene leads to systems of reduced stability due to increased bond order in the four-membered ring,[2] and it is of interest to determine where the stability



(I)                            (II)

(III)                          (IV)
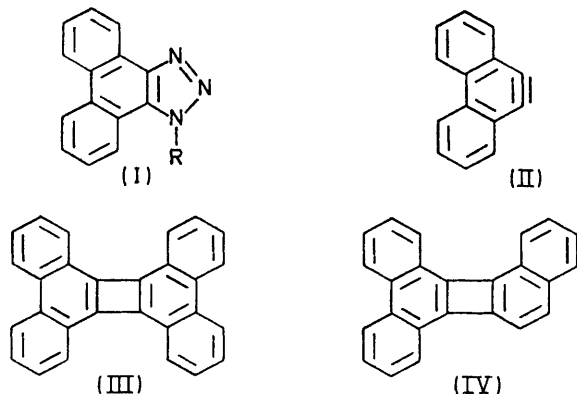
limit lies, *i.e.* whether tetrabenzo[*a,c,g,i*]biphenylene (III) or tribenzo[*a,c,g*]biphenylene (IV) may be obtained under normal conditions. Calculations of the bond orders for the series dibenzo[*b,h*]-, parent, dibenzo[*a,i*]-, and tetrabenzo[*a,c,g,i*]-biphenylene [3] have suggested that the last of these should be considerably less stable than the [*a,i*]-isomer, which is isolable. Unfortunately, a more recent theoretical treatment of a wider range of compounds [4] of this type does not include (III) and (IV).

Some other reactions which might give compound (III) have been examined previously. The Lothrop [5] pyrolysis of 10,10′-di-iodo-9,9′-biphenanthryl with copper(I) oxide at various temperatures between 210 and 400° gave only 9,9′-biphenanthryl.[3] The generation of 9,10-phenanthryne (II) from organometallic precursors has also been studied,[6,7] although the conditions under which it was generated were such that dimerisation to (III) would not be a particularly favourable process.

*N*-Aminotriazoloarenes such as (I; R = NH₂) have been obtained by two methods, either by the diazotisation of suitably protected *o*-aminoarylhydrazines followed by removal of the protecting group,[8,9] or by direct amination of the parent triazole,[9] in this case (I; R<sup>tion</sup>H). The former method is usually preferred, as direct amination can occur at any of the triazole ring nitrogen atoms, but in this series direct amination was used because difficulties were encountered in the preparation of the required nitrophenanthrylhydrazine derivatives from diazotised 9-amino-10-nitrophenanthrene.[10]

Phenanthro[9,10-*d*]triazole (I; R = H) had previously been prepared in very low yield by the diazotisation of 9,10-diaminophenanthrene in aqueous acetic acid,[11] the main products being phenanthrazine and phenanthrene-9,10-quinone. Much higher yields were obtained by changing to aprotic diazotisation in benzene. Following an observation by Cava *et al.*,[12] who found that the reaction of phenanthrene-9,10-quinone with toluene-*p*-sulphonohydrazide gives 9-diazo-10-phenanthrone, we tried to obtain the triazole (I; R = H) by an analogous reaction on phenanthrene-9,10-quinone monoimine, but only complex mixtures of products were obtained. Similarly, the triazole derivatives (I; R = OH) and (I; R = NH·CO·NH₂) could not be isolated from the corresponding reactions of the quinone mono-oxime and monosemicarbazone, respectively. The diazo-phenanthrone failed to condense further with toluene-*p*-sulphonohydrazide and with *N*-aminophthalimide.

The amination of phenanthro[9,10-*d*]triazole (I; R = H) with hydroxylamine-*O*-sulphonic acid in aqueous potassium hydroxide yielded mainly unchanged material and less than 20% of a mixed product, most of which proved to be the 2-amino-2*H*-derivative (V); this contrasts with methylation by dimethyl sulphate which is reported to give the 1-methyl-1*H*-derivative (I; R = Me) exclusively.[11]

Amination was much more complete when the sodium salt of (I; R = H) was treated with *O*-(2,4-dinitrophenyl)hydroxylamine. This hydroxylamine derivative,[13] which has a very good leaving group attached to nitrogen,[14] has the added advantage of being more stable than the *O*-sulphonic acid, although it is not so accessible. The resulting mixture contained 1-amino-1*H*-phenanthro[9,10-*d*]triazole (I; R = NH₂) and the 2-amino-2*H*-isomer (V) in the approximate ratio 1 : 3, identifiable by differences in their i.r. spectra. The spectrum of (I; R = NH₂) showed two sharp N–H stretching bands, at 3300 and 3120 cm⁻¹, a weak N–H deformation band at 1640 cm⁻¹, and very weak absorption in the region 1000—940 cm⁻¹, whereas that of isomer (V) showed multiple N–H bands from 3350 to 3170 cm⁻¹, no absorption at 1640 cm⁻¹ and strong multiple bands in the region 1000—940 cm⁻¹; similar differences are observable in the spectra of other 1- and 2-amino-benzo- and naphtho-triazoles.[15] The structures assigned to the two monoaminophenanthrotriazoles were confirmed by oxidation of the compounds with lead tetra-acetate, the 1-amino-compound giving products derived from 9,10-phenanthryne (see later) while the 2-isomer gave 2,2′-dicyanobiphenyl in high yield (*cf.* ref. 9).

Oxidation of 1-amino-1*H*-phenanthro[9,10-*d*]triazole

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(I; R = NH$_2$) with lead tetra-acetate brought about a rapid evolution of nitrogen, and when 2,3,4,5-tetra-phenylcyclopentadienone was present as an aryne trap the known 1,2,3,4-tetraphenyltriphenylene (VI) [16] was
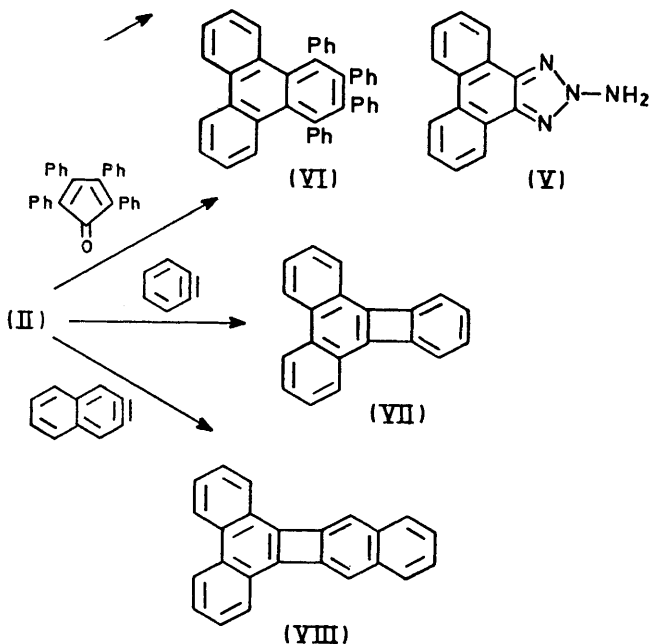


obtained in high yield. The use of N-bromosuccinimide as oxidant [17] gave 9,10-dibromophenanthrene, again indicating the intermediacy of 9,10-phenanthryne (II). In the absence of an aryne trap, however, the dimeric product (III) was not found, only small amounts of 9-acetoxyphenanthrene and a yellow material, m.p. >400°, were observed. The former presumably resulted by addition of acetic acid (from the lead tetra-acetate) to the aryne and the latter by the trimerisation of (II) (mass spectrum), although its properties differ from those previously reported for hexabenzotriphenylene.[6] Triphenylenes have been isolated in a number of reactions of o-dihalogenoarenes with metals, and the trimerisation of an intermediate aryne has been suggested to account for their formation,[18] Heaney[19] postulates a stepwise mechanism for triphenylene formation in organometallic reactions and points out that a concerted trimerisation is highly improbable on energetic grounds and at best could only give very low yields of trimer. Where benzyne is produced in relatively high concentration, as in the flash photolysis[20] of benzenediazonium-2-carboxylate and in the lead tetra-acetate oxidation of 1-amino-1H-benzotriazole,[9] biphenylene is the major product and triphenylene is formed in very low yield, possibly by a

near-concerted reaction; thus a small amount of trimer derived from (II) might be expected here.

That 'crossed' aryne coupling reactions of (II) are possible was demonstrated by generating it in the presence of benzyne and 2,3-naphthalyne, when dibenzo[a,c]biphenylene (VII)[21] and the hitherto unknown tribenzo[a,c,h]biphenylene (VIII) were obtained in yields of 15 and 31%, respectively. In contrast, no tribenzo[a,c,g]biphenylene (IV) could be isolated when the aryne (II) was generated in the presence of 1,2-naphthalyne under the same conditions. It is thus tempting to assume that the failures of this reaction and of the dimerisation of compound (II) are due to the instability of compounds (IV) and (III), i.e. that the angular annelation of more than two benzene nuclei to biphenylene leads to compounds which are unstable under these reaction conditions.

EXPERIMENTAL

*Phenanthro[9,10-d]triazole.*—Butyl nitrite (16·5 ml) was added during 45 min to a refluxing mixture of 9,10-diaminophenanthrene dihydrochloride[22] (31·3 g) and anhydrous sodium acetate (10·4 g) in benzene (410 ml). After 1·5 h the mixture was cooled and diluted with light petroleum (b.p. 40—60°). The solid was collected and extracted with warm dilute sodium hydroxide. Neutralisation of the extracts with acetic acid gave the triazole (13·5 g, 55%) as an off-white solid, m.p. 294—298° (lit.,[11] m.p. 306°). It was used without further purification.

*Amination of Phenanthro[9,10-d]triazole.*—(a) A solution of the triazole (10 g) and potassium hydroxide (2·8 g) in water (40 ml) was stirred at room temperature while freshly prepared hydroxylamine-O-sulphonic acid[23] (9 g) in water (15 ml) and potassium hydroxide (11·2 g) in water (30 ml) were added in portions during 1 h, the temperature rising to ca. 30°. After stirring overnight, water was added to dissolve the precipitated potassium salts and the resulting solution was continuously extracted with ether for 24 h. On neutralisation with acetic acid the aqueous solution gave starting material (8·5 g). The ethereal extracts were evaporated and fractionally crystallised from methanol and benzene, giving 2-amino-2H-phenanthro[9,10-d]triazole (1·1 g, 69% based on reacted triazole) as silvery leaflets, m.p. 177—179° (decomp) (Found: C, 71·9; H, 4·5; N, 24·2. C$_{14}$H$_{10}$N$_4$ requires C, 71·8; H, 4·3; N, 23·9%). The mother liquors gave 1-amino-1H-phenanthro[9,10-d]triazole (0·1 g, 6%) as dull yellow needles which darkened above 220°, m.p. 261—263° (decomp) [from benzene–light petroleum (b.p. 60—80°)] (Found: C, 71·8; H, 4·7; N, 24·5%) [m/e 234 (60% of base peak, m/e 176)].

(b) The sodium salt of phenanthro[9,10-d]triazole (7·2 g) was stirred in dry NN-dimethylformamide (30 ml) at 0—5° while O-(2,4-dinitrophenyl)hydroxylamine[13] (6·0 g) was added in portions. After 15 min the resulting reddish-brown solution was allowed to come to room temperature and poured into water (1 l). The precipitate was collected, washed with dilute sodium hydroxide and water, then

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fractionally crystallised as in (*a*), giving 1-amino-1*H*-phenanthro[9,10-*d*]triazole (0·9 g, 13%), 2-amino-2*H*-phenanthro[9,10-*d*]triazole (2·3 g, 33%), and a residue of mixed material.

*Oxidations of* 1-*Amino*-1H-*phenanthro*[9,10-d]*triazole*.—(i) *With* N-*bromosuccinimide*. A stirred suspension of the triazole (0·45 g) in dry methylene chloride was treated with *N*-bromosuccinimide (1·0 g). After 2—3 min gas evolution commenced and solution of the triazole was complete after 1 h. The solvent was evaporated, the residue triturated with warm water containing a little sodium disulphite, then crystallised from ethanol (charcoal) giving 9,10-dibromophenanthrene as needles (0·34 g, 52%), m.p. 182—183° (and mixed m.p. with an authentic sample [24]).

(ii) *With lead tetra-acetate in the presence of* 2,3,4,5-*tetraphenylcyclopentadienone*. A solution of the triazole (0·23 g) and 2,3,4,5-tetraphenylcyclopentadienone (0·76 g) in warm, dry benzene (40 ml) was added to a stirred suspension of lead tetra-acetate (0·9 g) in benzene (8 ml). After 45 min a few drops of ethylene glycol were added to destroy excess of oxidant and the mixture was filtered. The solvent was evaporated off and the residue chromatographed on silica. Elution with n-hexane gave 1,2,3,4-tetraphenyltriphenylene (0·27 g, 50%), m.p. 300—302° (lit.,[16] 292—293°), $m/e$ 532·217 (Calc. for $C_{42}H_{28}$: $M$, 532·219).

(iii) *With lead tetra-acetate in the absence of an aryne trap*. The triazole (0·3 g) was oxidised in benzene as in experiment (ii), but without the addition of tetraphenylcyclopentadienone. After filtration, the solution was concentrated *in vacuo* and the residue applied to an alumina column, all operations being carried out in subdued light. Elution with benzene gave first a pale yellow solid, possibly hexabenzotriphenylene (2 mg), m.p. >400°, $m/e$ 528·183 (Calc. for $C_{42}H_{24}$: 528·188), followed by 9-acetoxyphenanthrene (55 mg, 18%), m.p. 77—78°, identical with a sample prepared by the acetylation of 9-phenthrol.[25]

' *Crossed* ' *Coupling Reaction of* 9,10-*Phenanthryne with Benzyne*.—A solution of 1-amino-1*H*-phenanthro[9,10-*d*]-triazole (0·45 g) and 1-amino-1*H*-benzotriazole [9] (1·02 g) in hot benzene (250 ml) was added dropwise to a stirred suspension of lead tetra-acetate (5 g) in benzene (50 ml). The suspension was then stirred for a further 10 min, treated with ethylene glycol, and filtered. The solution was concentrated *in vacuo* to *ca.* 10 ml, diluted with an equal volume of n-hexane and applied to a silica column. Elution with benzene–hexane (1 : 1) gave biphenylene (0·45 g), m.p. 110—111°, followed by an orange solid, contaminated with traces of biphenylene. Treatment of this with 2,4,7-tri-nitrofluorenone in benzene–methanol gave the complex of dibenzo[*a,c*]biphenylene (0·16 g, 15%) as deep purple

needles, m.p. 212—214°. Chromatographic ιvage of the complex in benzene solution on alumina gave dibenzo-[*a,c*]biphenylene as orange-red needles (75% recovery), m.p. 183—184° (from hexane), identical with an authentic sample.[21]

' *Crossed* ' *Coupling Reaction of* 9,10-*Phenanthryne with* 2,3-*Naphthalyne*.—The oxidation of a mixture of 1-amino-1*H*-phenanthro[9,10-*d*]triazole (0·3 g) and 1-amino-1*H*-naphtho[2,3-*d*]triazole [1] (0·945 g) was carried out as in the previous experiment. On concentration the reaction solution deposited crystals of dibenzo[*b,h*]biphenylene, and benzene extraction of the lead residues gave further crops (total 0·38 g). Chromatography of the residue from the mother liquor on alumina in benzene–hexane (1 : 1) gave *tribenzo*[a,c,h]*biphenylene* (0·12 g, 31%) as bright yellow needles, m.p. 228·5—230° (from hexane), $m/e$ 302·108 (base peak) ($C_{24}H_{14}$ requires $M$, 302·109), $\lambda_{max.}$ (EtOH) 247·5, 252·5sh, 272, 280·5, 290, 302, 314, 334, 359, 378, 393, 403, 414, and 442 nm (log ε 5·37, 5·25, 5·03, 5·09, 5·16, 5·31, 5·39, 4·47, 3·96, 4·11, 4·25, 4·14, 4·29, and 3·78). Combustion analyses gave consistently low carbon values for this hydrocarbon. It was characterised as the 2,4,7-*trinitrofluorenone complex*, which formed grey-purple needles, m.p. 260—262° (from benzene–methanol) (Found: C, 72·1; H, 3·1; N, 7·2. $C_{37}H_{19}N_3O_7$ requires C, 71·9; H, 3·1; N, 6·8%).

*Oxidation of* 2-*Amino*-2H-*phenanthro*[9,10-d]*triazole with Lead Tetra-acetate*.—Lead tetra-acetate (1·2 g) was added to a stirred suspension of the triazole (0·3 g) in benzene (20 ml). After 20 min the mixture was treated with a few drops of ethylene glycol, filtered, and evaporated. Crystallisation of the residue from light petroleum (b.p. 60—80°) gave 2,2′-dicyanobiphenyl (0·21 g, 81%) as needles, m.p. 171—172° (lit.,[26] 172°), identical with a sample prepared by the following alternative method.

2,2′-*Dicyanobiphenyl*.—2,2′-Di-iodobiphenyl (12 g) and copper(I) cyanide (4 g) in dry pyridine (8 ml) were heated at 150° (bath) for 3 h. The cooled semi-solid mass was extracted with portions of benzene and aqueous ammonia [1 : 1 $NH_4OH$ (*d* 0·880)–$H_2O$]. The benzene extracts were dried and evaporated and the residue was crystallised from benzene–light petroleum (b.p. 60—80°) giving 2,2′-dicyano-biphenyl (3·0 g, 50%) as needles, m.p. 171—172°. The residue from the mother liquor was chromatographed on alumina with benzene as eluant giving starting material (0·9 g) then 2-*cyano*-2′-*iodobiphenyl* (1·7 g, 19%) as prisms, m.p. 73—74° [from light petroleum (b.p. 60—80°)] (Found: C, 51·3; H, 2·8; N, 4·4. $C_{13}H_8NI$ requires C, 51·1; H, 2·6; N, 4·6%).

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