Biphenylenes. Part 32.[1] A New, General Synthesis of Mono- and Poly-benzobiphenylenes from Substituted Benzocyclobutene-1,2-diones and *ortho*-Bis(cyanomethyl)arenes

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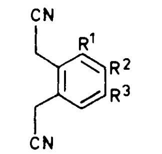
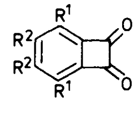
Thirteen examples (including eight novel ring systems) are described of a new, general synthesis of polycyclic biphenylenes from substituted benzocyclobutene-1,2-diones and *ortho*-bis(cyanomethyl)arenes (benzene, naphthalene, and phenanthrene). Some related condensations are described together with studies on the hydrolysis and decarboxylation of some of the di- and tetra-carbonitriles.

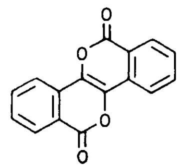
Eleven mono- and poly-benzobiphenylene ring systems have so far been described.† The parent hydrocarbons and/or substitution products were made by three main methods: pyrolysis of a mixture of 2,2′-biaryl and cuprous oxide at *ca.* 350 °C,[3-5] annulation of biphenylene with the anhydrides of succinic, phthalic, and naphthalene-2,3-dicarboxylic acids,[6-8] and dimerisation or crossed-coupling of arynes.[9,10] A few benzobiphenylene hydrocarbons and substituted derivatives of them have also been made by a variety of non-general methods.[11] As part of our research work on biphenylenes [1] and benzocyclobutene-1,2-diones [12] we record here a new, and more general, synthesis of condensed biphenylenes, together with some studies on the hydrolysis of aromatic polycarbonitriles.



(1) $R^1 = R^2 = R^3 = H$
(2) $R^1 = H, R^2R^3 =$ Benzo
(3) $R^1R^2 =$ Benzo, $R^3 = H$
(4) $R^1 = H, R^2 = R^3 = CH_2CN$
(5) $R^1 = R^2 = CH_2CN, R^3 = H$



(6) $R^1 = R^2 = H$
(7) $R^1 = H, R^2 =$ MeO
(8) $R^1 = H, R^2R^2 =$ Benzo
(9) $R^1R^2 =$ Benzo



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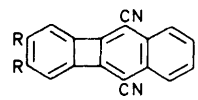
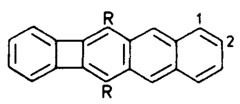
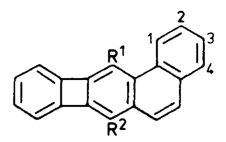


(11) R = H
(12) R = MeO



(13) R = CN
(14) R = $CONH_2$
(15) R = CO_2H
(16) R = CO_2Me
(17) R = H



(18) $R^1 = R^2 = CN$
(19) $R^1 = R^2 = CONH_2$
(20) $R^1 = CONH_2, R^2 = CO_2H$
(21) $R^1 = R^2 = H$

Results and Discussion

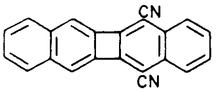
Hinsberg [13] found that the condensation of 1,2-bis(cyanomethyl)benzene (1) with benzil in the presence of sodium ethoxide gave 4-cyano-2,3-diphenylnaphthalene-1-carboxamide. A similar reaction using phenanthrene-9,10-quinone, in place of benzil, gave the corresponding cyano-carboxamide. More recently Moureu [14] observed that the condensation of compound (1) with five other 1,2-diketones, using piperidine as catalyst, gave polynuclear dinitriles or cyano-carboxamides in 30—67% yields. We wished to condense benzocyclobutene-1,2-dione (BBD) (6) and its derivatives with *ortho*-bis(cyanomethyl) compounds but the choice of base (as catalyst) is limited. BBD reacts with sodium hydroxide to give the sodium salt of formylbenzoic acid, and it reacts with many primary amines to give products in which the CO–CO bond has been cleaved.[1,15] In the hope of avoiding this ring cleavage, by using a tertiary amine, we tested the stability of BBD towards 1,5-diazabicyclo[4·3·0]non-5-ene (DBN). When one drop of this catalyst was added to a solution of BBD in acetonitrile a rapid reaction occurred to give one of the known [16] photodimers (10) of BBD in 73% yield. The dimer (10) is formed photochemically in 4% yield and had previously been obtained (in *ca.* 5% yield) during the preparation if BBD by the reaction of triethylamine with *cis*- or *trans*-benzocyclobutene-1,2-diol dinitrate.[17] Fortunately, DBN preferentially catalysed the reaction of BBD with the bis-cyanomethyl compound (1) and the desired product (11) (16% yield) was readily separable from a small amount of the dimer (10) which was simultaneously formed. Later it was found that the use of 1,8-diazabicyclo[5·4·0]undec-7-ene (DBU) gave the biphenylene (11) in 25% yield, whereas the use of sodium methoxide in methanol gave a 5% yield only. DBU was therefore used as catalyst for all the condensation reactions reported in this paper.

The structure of the benzo[*b*]biphenylene (11) follows from its method of preparation and its elemental analysis. It is confirmed by its i.r. spectrum which contains a band at 2 235 cm^{-1} (C≡N) but no bands corresponding to $CONH_2$; its u.v. spectrum which is similar to that of the parent hydrocarbon; and its n.m.r. spectrum which shows two multiplets, each corresponding to 4 aromatic protons (see Experimental section for details of the i.r., u.v., and n.m.r. spectra).

The structures of all the other new biphenylenes follow from the same kind of evidence. Moreover the mass spectra of all new compounds in this paper were measured and provided supporting evidence, however, they are not recorded here except where other evidence is lacking.

Condensation of BBD with 2,3-bis(cyanomethyl)naphthalene (2) gave the anthracene derivative (13) in 48% yield,

† The *X*-ray crystal and molecular structures of four other poly-benzo-derivatives of biphenylene have been published but the method by which they were prepared was not recorded.[2]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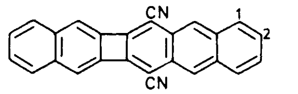
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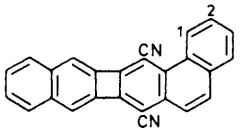
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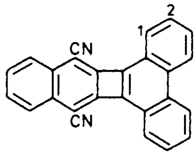
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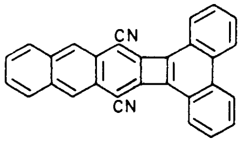
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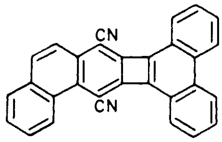
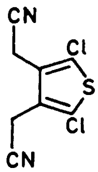

(27)

which was later raised to 62% by adding calcium hydride to the reaction mixture in order to remove the water produced in the reaction. Calcium hydride was used as a dehydrating agent in two more condensations (see Table) and if its use had been discovered earlier it would probably have led to increased yields in the other condensations. The reactions of 4,5-dimethoxy-BBD (7) with the bis(cyanomethyl) compound (1) and of cyclobuta[*b*]naphthalene-1,2-dione (8) with compounds (1) and (2) gave the corresponding linear polycyclic biphenylenes (12), (22), and (23) respectively. Similarly, reaction of BBD and the naphthalenedione (8) with 1,2-bis(cyanomethyl)naphthalene (3) gave the angular polycyclics (18) and (24), while reaction of the phenanthrenedione (9) with compound (1) and the bis(cyanomethyl)naphthalenes (2) and (3) gave the corresponding hexacyclic compound (25) and heptacyclic compounds (26) and (27). We tried to extend our new synthesis to derivatives of thiophen. However 2,5-dichloro-3,4-bis(cyanomethyl)thiophen (28) [18] is sensitive to bases and a solution of it in acetonitrile rapidly blackened when a few drops of DBU were added. Nevertheless, the thiophen (28) reacted with BBD to give a low yield (4%) of the biphenylenothiophen (29), although it failed to condense with biacetyl or with benzil to give derivatives of cyclobutenothiophen. We were unable to prepare 2,3-bis(cyanomethyl)thiophen from 2,3-bis(bromomethyl)thiophen [19] under the conditions used for thiophen (28). As expected, the electronic absorption spectrum of the biphenyleno[2,3-*c*]thiophen (29) is very different from that of the related compound (11) (see Experimental section) whereas the u.v. spectrum of biphenyleno[2,3-*b*]thiophen [20] closely resembles that of benzo[*b*]biphenylene.[6] Similarly it is known that the u.v. spectrum of benzo[*c*]thiophen [21] is quite different from that of its isomer benzo[*b*]thiophen [22] whose absorption is like that of naphthalene.

Until now, no compounds containing two fused biphenylene ring systems have been prepared. We have made two such compounds. Condensation of BBD with 2,3-bis(cyanomethyl)biphenylene (30) gave the biphenyleno[2,3-*b*]biphenylene (31) in 34% yield, and condensation of 2 equivalents of BBD with 1,2,4,5-tetrakis(cyanomethyl)benzene (4) gave the benzodibiphenylene (32) (24% yield). However, a similar attempt to condense BBD with 1,2,3,4-tetrakis(cyanomethyl)benzene (5) failed. In related experiments the tetracarbonitrile (4) reacted with biacetyl to give the tetramethylanthracene (33) (56% yield) whereas the isomeric tetracarbonitrile (5) gave only a 2% yield of the tetramethylphenanthrene (35). Presumably the severe steric compression produced by the two carbonitrile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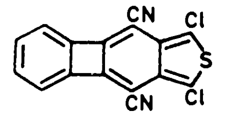
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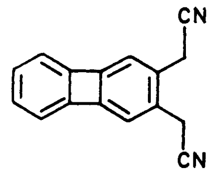
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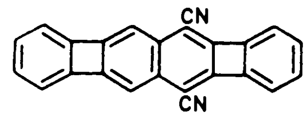
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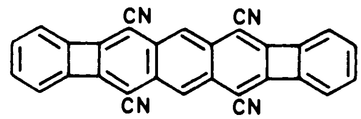
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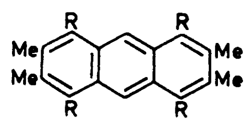
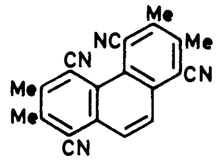

(33) R = CN
(34) R = H


(35)

groups at positions 4 and 5 of the phenanthrene ring are largely responsible for the failure of the reaction of (5) with BBD and the low yield in the reaction with biacetyl. Finally, attempts to condense biphenylene-2,3-quinone [23] with 1,2-bis(cyanomethyl)benzene (1) failed because the quinone was decomposed too rapidly by DBU.

Hydrolysis of Polycarbonitriles.—Having devised a satisfactory synthesis of polycyclic biphenylene derivatives, we turned our attention to the protio-decyanation of our new compounds in order to prepare the parent hydrocarbons. Mosby [24] had found that treatment of 2,3,6,7-tetramethylnaphthalene-1,4-dicarbonitrile with polyphosphoric acid at 200 °C had given a 'good yield' of 2,3,6,7-tetramethylnaphthalene, which had formed as a sublimate in the reflux condenser. When we applied this method to the anthracenetetracarbonitrile (33) we obtained the hydrocarbon (34) in 21% yield; however, a similar reaction with the biphenylenobiphenylene (31) gave no sublimate. Instead extensive decomposition occurred and the reaction mixture yielded only a trace of the desired hydrocarbon (31; with H in place of CN). We, therefore, turned to a stepwise sequence of hydrolysis followed by decarboxylation. Unfortunately, 2,6-disubstituted benzonitriles and benzamides are usually resistant to hydrolysis, and thus when the dicarbonitrile (13) was boiled with potassium hydroxide in aqueous digol it gave the diamide (14) (92%) after 6 h, but prolonged hydrolysis (48 h) led to darkening of the reaction mixture and formation of an intractable tar. The diamide (14) was insoluble in digol but proved to be soluble in acetic acid. It was, therefore, refluxed with hydrochloric acid in the latter solvent and gave the dicarboxylic acid (15) in 99% yield. The acid was characterised as its dimethyl ester (16). Decarboxylation of the diacid (15) was effected by heating it with copper bronze and thereby gave the known[7] hydrocarbon (17) (54%). We then tried the same reaction sequence with the angular isomer (18) in the hope of preparing the unknown hydrocarbon (21). Alkaline hydrolysis of compound (18) gave the diamide (19) (89%) after 12 h but prolonged heating did not bring about further hydrolysis. When the diamide (19) was boiled with hydrochloric acid in acetic acid for 10 days no reaction occurred. However, when the diamide (19) was boiled with 50% sulphuric acid for 18 h it gave a monocarboxylic acid. This is considered to be the 7-carboxylic acid (20) since the 7-carboxamide group is less sterically hindered than that at position 12. Prolonged heating under the same conditions gave an intractable tar. We did not attempt hydrolyses with stronger sulphuric acid because biphenylene undergoes disulphonation very easily with concentrated sulphuric acid.[25]

Experimental

Unless otherwise stated the following conditions apply. I.r. and u.v. spectra were measured in Nujol mulls and in dichloromethane respectively. ^{1}H N.m.r. spectra were recorded on a Varian HA-100 or a Jeol JNM-PS-100 spectrometer as solutions in deuteriochloroform with tetramethylsilane as internal standard. T.l.c. was carried out on Kieselgel G (Merck) and column chromatography on silica gel M.F.C. (Hopkin and Williams). Petroleum refers to light petroleum (b.p. 60—80 °C).

Sources of Diones.—Small amounts of benzocyclobutene-1,2-dione (BBD) are conveniently made by pyrolysis of indane-1,2,3-trione,[26] larger amounts are better made by Cava's method[17] with the improvements noted by Cracknell *et al.*[27] Diones (7),[28] (8),[29] and (9)[12] were made as previously described.

Sources of Biscyanomethyl Compounds.—1,2-bis(cyanomethyl)-benzene and -naphthalene,[30] 2,3-bis(cyanomethyl)-naphthalene,[31] and 2,5-dichloro-3,4-bis(cyanomethyl)-thiophen[18] were made by reaction of the corresponding bisbromomethyl compounds with sodium cyanide in dimethyl sulphoxide (method of Helmers[18]).

2,3-*Bis(cyanomethyl)biphenylene* (30).—2,3-Dimethylbiphenylene[26] was boiled with 2-equivalents of *N*-bromosuccinimide and a small amount of dibenzoyl peroxide in carbon tetrachloride. The resulting 2,3-bis-(bromomethyl)-biphenylene (58%), m.p. 139 °C was converted into compound (30) by the method used for 2,3-bis(cyanomethyl)naphthalene. The crude product was chromatographed on a column of dry silica gel, with dichloromethane as eluant, and gave 2,3-*bis(cyanomethyl)biphenylene* (30) (31%) as pale yellow plates (ethanol), m.p. 152—154 °C (decomp.) (Found: C, 83.2; H, 4.4; N, 11.7. $C_{16}H_{10}N_2$ requires C, 83.45; H, 4.4; N, 12.2%), $\nu_{max.}$ 2 250, 863, and 759 cm^{-1}; δ 3.53 (s, 2 × CH_2), 6.67 (s, 1-, 4-H) and 6.75 (m, 5-, 6-, 7-, 8-H).

1,2,4,5-*Tetrakis(cyanomethyl)benzene* (4).—Powdered 1,2,4,5-tetrakis(bromomethyl)benzene[32] (9.0 g) was added during 20 min to a stirred suspension of sodium cyanide (4.16 g) in dimethyl sulphoxide (90 ml) and acetonitrile (90 ml) at 5—7 °C. The mixture was then added dropwise to 1M-hydrochloric acid (1 l) (CAUTION, HCN evolved) containing sodium chloride (30 g). The resulting precipitate (4.0 g) was washed well with water, dried, and then chromatographed on two dry alumina columns (100 × 2.5 cm, activity 3—4). Elution with dichloromethane–ethyl acetate (4 : 1) gave the *cyanomethyl compound* (4) (0.81 g, 18.5%) as plates (from acetonitrile), m.p. 213—215 °C (Found: C, 71.9; H, 4.4; N, 23.8. $C_{14}H_{10}N_4$ requires 71.8; H, 4.3; N, 23.9%), δ (CD_3CN) 3.88 (s, CH_2) and 7.60 (s, ArH).

1,2,3,4-*Tetrakis(cyanomethyl)benzene* (5).—This compound was prepared from 1,2,3,4-tetrakis(bromomethyl)benzene,[33] and purified, in the same way as for its 1,2,4,5-isomer. The cyanomethyl compound (5) (5% yield) formed plates (from acetone–pentane), m.p. 208—209 °C (Found: C, 71.5; H, 4.2; N, 23.6%), δ (CD_3CN) 3.88 (s, CH_2), 3.92 (s, CH_2), and 7.51 (s, ArH).

Dimerisation of BBD by DBN.—1,5-Diazabicyclo[4·3·0]-non-5-ene (1 drop) was added to BBD (66 mg) in acetonitrile (2 ml). A crystalline precipitate began to form almost immediately. This was collected and washed with acetonitrile and then with methanol. The crystals (48 mg, 73%) consisted of the dimer (10), m.p. 335—340 °C (lit.,[16] 333—335 °C); $\nu_{max.}$ 1 752, 1 612, 1 260, and 767 cm^{-1}; *m/z* 264 (M^+, 100%), 236(28%), 208(26%), 180(32%), and 152(23%).

General Method for Reaction of Diones with Bis(cyanomethyl) Compounds.—The dione (alone or dissolved in dry CH_3CN) was added to a warm solution of the bis(cyanomethyl) compound and DBU (*ca.* 0.15 ml) in dry MeCN. The mixture was boiled under reflux, then allowed to cool and the polycyclic biphenylene was collected. The crude products were purified by recrystallisation except for compound (27) (see below). The Table records the amounts of reactants used together with yields and analytical data. Three examples are given in detail below to show small variations in the general procedure.

Benzo[b]*biphenylene*-5,10-*dicarbonitrile* (11).—A solution of BBD (6) (132 mg) in hot acetonitrile (10 ml) was added dropwise, during 5 min, to a hot solution of 1,2-bis(cyanomethyl)-benzene (180 mg) and DBU (5 drops) in hot acetonitrile (15 ml). The mixture was heated under reflux for 10 min, cooled, and filtered. The solid was purified by chromatography on a dry alumina column (20 cm) using toluene as eluant. The *biphenylene* (11) (63 mg, 25%) formed bright yellow needles (from toluene), m.p. 324 °C (decomp); $\nu_{max.}$ 2 235, 1 143, 765, and 750 cm^{-1}; $\lambda_{max.}$ (EtOH) 252, 259, 283, 300, 373, 393, and 417 nm (log ε 4.29, 4.39, 4.45, 4.31, 3.62, 3.92, and 4.07); δ 7.54 (m, 6-, 7-, 8-, 9-H) and 7.86 (m, 1-, 2-, 3-, 4-H). A solution of biphenylene (11) in CH_2Cl_2 shows a blue fluorescence.

Benzo[3,4]*cyclobut*[1,2-b]*anthracene*-6,11-*dicarbonitrile* (13).—BBD (264 mg) in acetonitrile (20 ml) was added dropwise, during 10 min, to a mixture of 2,3-bis(cyanomethyl)naphthalene (420 mg), DBU (3 drops), and calcium hydride (500 mg) in warm acetonitrile (20 ml). The mixture was heated under reflux for 10 min, cooled, and the precipitate collected by filtration. The solid was extracted overnight in a Soxhlet apparatus with CH_2Cl_2. Removal of the solvent gave the *anthracene* (13) (373 mg, 62%) as bright yellow needles (from toluene) which sublimed at 340—350 °C; $\nu_{max.}$ 2 240, 1 600, 890, and 755 cm^{-1}; $\lambda_{max.}$ 233, 247, 260, 268sh, 280, 294, 305, 325, 337, 372, 393, 415, and 440 nm (log ε 4.65, 4.60, 4.49, 4.51, 4.67, 4.73, 4.83, 4.62, 4.83, 3.99, 4.05, 4.14, and 4.08); δ 7.37 (m, 7-, 8-, 9-, 10-H), 7.58 (m, 2-, 3-H), 7.95 (m, 1-, 4-H), and 8.34 (s, 5-, 12-H).

Phenanthro[2,3-c]*cyclobuta*[1,2-l]*phenanthrene*-9,16-*dicarbonitrile* (27).—The dione (9) (30 mg) in hot acetonitrile (15 ml) was added during 10 min to the dinitrile (3) (30 mg), calcium hydride (100 mg), and DBU (3 drops) in hot aceto-

Table. Experimental conditions for the preparation of condensed biphenylenes

Dione and mass used (mg)	Dicyanide and mass used (mg)	Total volume of CH_3CN (ml)	Product and yield (%)	Refluxed (min)	Analysis C [a]	H [a]	N [a]	C [b]	H [b]	N [b]
(6) 132	(1) 180	25	(11) 25	10	85.6	3.2	11.1	85.7	3.2	11.1
(6) 264	(2) 420 [c]	40	(13) 62	10	87.3	3.6	9.1	87.4	3.3	9.3
(6) 60	(3) 110 [d]	15	(18) 73	10	87.1	3.1	9.4	87.4	3.3	9.3
(7) 30	(1) 20	10	(12) 31	10		(M^+ 312.089)			(M 312.089)	
(8) 40	(1) 40	15	(22) 49	10	87.6	3.8	9.1	87.4	3.3	9.3
(8) 25	(2) 40	15	(23) 48	10	88.6	3.7	7.8	88.6	3.4	8.0
(8) 30	(3) 30	15	(24) 70	10	88.8	3.7	8.1	88.6	3.4	8.0
(9) 90	(1) 90	70	(25) 31	20	88.7	3.4	7.9	88.6	3.4	8.0
(9) 30	(2) 30	30	(26) 31	10	89.9	3.5	7.2	89.5	3.5	7.0
(9) 30	(3) 30 [e]	30	(27) 30	20		(M^+ 402.115)			(M 402.115)	
(6) [f] 252	(28) 441	20	(29) 4	(16 h) [g]		(M^+ 224.035)	8.5		(M 224.037)	8.6
(6) 66	(30) 115	4	(31) 34	(5 h) [g]	88.1	3.2	8.4	88.3	3.1	8.6
(6) 132	(4) 59	5	(32) 24	(10 h) [g]	84.9	2.6	13.2	84.5	2.4	13.1
						(M^+ 426.091)			(M 426.090)	
Biacetyl 86	(4) 59	5	(33) 56	(10 h) [g]	78.9	4.3	16.3	79.0	4.2	16.8
Biacetyl [f] 220	(5) 75	5	(35) 2	(24 h) [g]		(M^+ 334.121)			(M 334.122)	

[a] Found (%). [b] Required (%). [c] Also CaH_2 (500 mg). [d] Also CaH_2 (200 mg). [e] Also CaH_2 (100 mg). [f] This experiment was done by Dr. P. V. C. Cass. [g] Mixture was kept at room temperature.

nitrile (15 ml). After being heated under reflux for 20 min the mixture was cooled and filtered. The solid was extracted overnight with dichloromethane in a Soxhlet apparatus. The solvent was evaporated and the solid was heated to 200—220 °C at 0.01 Torr to remove volatile impurities. Finally the solid was washed thoroughly with dichloromethane thereby giving the *dicarbonitrile* (27) (15 mg, 30%) as a red solid which did not melt up to 360 °C; $\nu_{max.}$ 3 070, 2 215, 1 600, 860, 820, 755, 750, and 725 cm^{-1}; $\lambda_{max.}$ (saturated solution in warm CH_2Cl_2) 237, 277, 285, 302sh, 339, 352, 366sh, 387, 415, 435, and 462 nm (% relative ε, 100, 18.3, 35.5, 14.4, 31.7, 31.7, 23.9, 10.6, 8.3, 15.0, and 18.3).

Properties of Polycyclic Biphenylene Derivatives.—(Compound, solvent crystallisation, i.r., u.v., and ^{1}H n.m.r. spectra). 7,8-*Dimethoxybenzo*[b]*biphenylene*-5,10-*dicarbonitrile* (12) (CH_2Cl_2–petroleum) yellow needles, m.p. 309—311 °C (decomp.); $\nu_{max.}$ 3 090, 2 230, 880, 840, and 770 cm^{-1}; $\lambda_{max.}$ 275, 296sh, 314sh, 321, 383sh, 401, 424, and 450 nm (log ε 4.44, 4.06, 4.30, 4.33, 3.65, 4.05, 4.34, and 4.45 respectively); δ 3.95 (OMe), 6.86 (s, 6-, 9-H), 7.46 (m, 2-, 3-H), and 7.68 (m, 1-, 4-H). *Benzo*[3,4]*cyclobuta*[1,2-b]*phenanthrene*-7,12-*dicarbonitrile* (18) (toluene) green–yellow needles, m.p. 321—322 °C; $\nu_{max.}$ 3 070, 2 240, 2 230, 1 600, 1 580, 830, 750, and 720 cm^{-1}; $\lambda_{max.}$ 236, 276, 290, 325, 339, 374sh, 397, 419, and 435 nm (log ε 4.45, 4.65, 4.58, 4.33, 4.40, 3.63, 3.79, 4.13, and 4.31); δ 7.21 (m, 8-, 9-, 10-, 11-H), 7.69 and 7.93 (m, 6ArH). *Dibenzo*[b,h]*biphenylene*-5,12-*dicarbonitrile* (22) (sublimation at 165—175 °C at 0.01 Torr) yellow solid, m.p. 305—307 °C (decomp.); $\nu_{max.}$ 3 090, 3 040, 2 240, 1 600, 880, 765, and 750 cm^{-1}; $\lambda_{max.}$ 233, 247, 258sh, 265, 283sh, 308, 324, 337sh, 363, 390, 413, and 442 nm (log ε 4.45, 4.30, 4.37, 4.51, 4.30, 4.97, 4.74, 4.26, 4.11, 3.91, 4.30, and 4.57); δ 7.56—7.78 (m, 2-,3-, 7-,8-,9-,10-H), 7.63 (s, 6-,11-H), and 8.01 (q, 1-,4-H). *Naphtho*-[2,3-c]*cyclobut*[1,2-b]*anthracene*-6,13-*dicarbonitrile* (23) (toluene) orange needles which did not melt up to 360 °C; $\nu_{max.}$ 3 070, 3 040, 2 240, 890, and 755 cm^{-1}; $\lambda_{max.}$ 232, 249, 260sh, 266sh, 284, 315sh, 327, 348, 380, 404, 428, and 458 nm (log ε 4.66, 4.61, 4.54, 4.23, 4.52, 4.86, 5.13, 4.82, 3.82, 3.07, 3.38, and 3.56); δ 7.64 (m) and 8.03 (m, 1-,2-,3-,4-,8-,9-,10-, 11-H), 7.77 (s, 7-,12-H), and 8.48 (s, 5-,14-H). *Naphtho*[2,3-c]*cyclobuta*[1,2-b]*phenanthrene*-7,14-*dicarbonitrile* (24) (toluene) orange plates which sublime at 315—325 °C and melt at 330 °C (decomp.); $\nu_{max.}$ 3 090, 2 230, 1 615, 885, 825, and 750 cm^{-1}; $\lambda_{max.}$ 234, 258, 268, 286, 303sh, 328, 366, 409sh, 434, and 464 nm (log ε 4.75, 3.50, 3.50, 4.61, 4.32, 4.82, 4.12, 3.70, 4.25, and 4.58); δ 7.21 (m, 8-,9-,10-,11-H), 7.69 m and 7.93s (6ArH).

Naphtho[2,3-c]*cyclobuta*[1,2-l]*phenanthrene*-9,14-*dicarbonitrile* (25) (toluene) yellow needles which did not melt up to 360 °C; $\nu_{max.}$ 3 070, 2 215, 1 630, 755, and 720 cm^{-1}; $\lambda_{max.}$ 248, 256, 266sh, 280sh, 290sh, 318, 329, 343, 354sh, 375, 396, 417, 442, and 464sh nm (log ε 4.45, 4.49, 4.32, 4.23, 4.13, 4.25, 4.53, 4.64, 4.02, 4.06, 3.78, 4.09, 4.19, and 3.41); δ 7.20 (m), 7.45 (m), and 7.76 (m) (8 × ArH), 8.21 (m, 10-,13-H), and 8.65 (m, 4-,5-H). *Anthra*[2,3-c]*cyclobuta*[1,2-l]*phenanthrene*-9,16-*dicarbonitrile* (26) (toluene) orange needles which began to decompose at 340 °C but did not melt up to 360 °C; $\nu_{max.}$ 3 070, 2 240, 1 600, 890, 760, 750, and 730 cm^{-1}; $\lambda_{max.}$ 251, 258, 301sh, 305, 318, 332sh, 345sh, 357, 370, 384, 400sh, 423, 440sh, 465sh, and 480sh (log ε 4.61, 4.62, 4.23, 4.28, 4.45, 4.31, 4.67, 4.84, 4.78, 4.54, 4.24, 4.10, 3.94, 3.63, and 3.30). 1,3-*Dichlorobiphenyleno*[2,3-b]*thiophen*-4,9-*dicarbonitrile* (29) (CH_3CN) yellow crystals, m.p. 330—331 °C; $\nu_{max.}$ 2 220, 1 305, 1 032, and 747 cm^{-1}; $\lambda_{max.}$ (EtOH) 277sh, 281, 307, 319, 362sh, 380, 401, and 426 nm (log ε 4.45, 4.56, 4.49, 4.56, 3.76, 3.99, 4.15, and 4.05); δ 7.44 (s, ArH). *Biphenyleno*[2,3-b]-*biphenylene*-5,12-*dicarbonitrile* (31) (1,4-dioxan) orange needles, m.p. *ca.* 360 °C; $\nu_{max.}$ 2 230, 1 141, 868, and 746 cm^{-1}; $\lambda_{max.}$ ($CHCl_3$) 282sh, 298, 305sh, 320sh, 350, 418, 443, and 473 nm (log ε 4.55, 4.81, 4.71, 4.35, 3.49, 3.77, 4.15, and 4.37). *Benzo*[1,2-b:4,5-b′]*dibiphenylene*-5,7,12,14-*tetracarbonitrile* (32) (impurities removed by subliming them out at 340 °C and 0.01 Torr) greenish orange crystals, m.p. *ca.* 360 °C; $\nu_{max.}$ 2 230, 1 138, 890, and 746 cm^{-1}. 2,3,6,7-*Tetramethylanthracene*-1,4,5,8-*tetracarbonitrile* (33) (impurities removed from the almost insoluble solid with ethanol) orange crystals which did not melt up to 360 °C; $\nu_{max.}$ 2 232, 1 189, 1 034, and 884 cm^{-1}; $\lambda_{max.}$ ($CHCl_3$) 270, 343, 362, 380, 399, and 422 nm (log ε 5.26, 3.57, 4.01, 4.34, 4.18, and 4.12). 2,3,6,7-*Tetramethylphenanthrene*-1,4,5,8-*tetracarbonitrile* (35) ($CHCl_3$) pale yellow solid, m.p. 321—323 °C; $\nu_{max.}$ ($CHCl_3$) 2 222 cm^{-1};

$\lambda_{max.}$ (EtOH) 237, 259, 275, 318, and 341sh (log ε 4.87, 4.57, 4.60, 4.76, and 4.31); δ 2.84 (s, 2 Me), 2.88 (s, 2 Me), and 8.32 (s, 9-,10-H).

2,3,6,7-*Tetramethylanthracene* (34).—The tetracyanoanthracene (33) (47 mg) and polyphosphoric acid (2 ml) were heated under reflux at 200 °C until no further crystals collected in the condenser. The sublimate (7 mg, 21%) was identified as 2,3,6,7-tetramethylanthracene by its u.v. spectrum [34] and its mass spectrum, *m/z*: 234 (M^+, 100%), 219(44%), 204(8%), 189(9%), and 117(11%).

Reaction of the Biphenylenobiphenylene (31) *with Polyphosphoric Acid*.—Finely powdered compound (31) (23 mg) and polyphosphoric acid (2 g) were kept at 200 °C until the mixture blackened. The mixture was then cooled, diluted with water, and extracted three times with CH_2Cl_2. The combined extracts were washed with water, dried, and the solvent removed. The residual reddish solid (*ca.* 5 mg) was probably biphenyleno[2,3-*b*]biphenylene (31; with H in place of CN). The mass spectrum showed two peaks only, namely *m/z* 276 (M^+, 100%) and 138 (M^{2+}, 16%). When the experiment was repeated at a lower temperature unchanged dicarbonitrile (31) was recovered.

Benzo[3,4]*cyclobut*[1,2-b]*anthracene*-6,11-*dicarboxamide* (14).—The dicarbonitrile (13) (370 mg), potassium hydroxide (400 mg), water (10 ml), and digol (50 ml) were boiled under reflux for 6 h. The cooled solution was poured into water (300 ml) and acidified with hydrochloric acid. The precipitate was collected, washed with water, and allowed to dry. It consisted of the *dicarboxamide* (14) (380 mg, 92%) and formed yellow crystals (from dimethyl sulphoxide) which decomposed at 358 °C without melting (Found: M^+, 338.105. $C_{22}H_{14}N_2O_2$ requires *M*, 338.105); $\nu_{max.}$ 3 400, 3 200, 1 640, 1 580, 910, and 745 cm^{-1}.

Benzo[3,4]*cyclobut*[1,2-b]*anthracene*-6,11-*dicarboxylic Acid* (15).—The dicarboxamide (14) (300 mg), concentrated hydrochloric acid (50 ml), water (50 ml), and acetic acid (150 ml) were boiled under reflux for 48 h. The mixture was cooled and diluted with water (500 ml). The precipitate (300 mg, 99%) gave the *dicarboxylic acid* (15) as yellow needles (from acetic acid) which sublimed at 310—315 °C (Found: C, 77.9; H, 3.6. $C_{22}H_{12}O_4$ requires C, 77.6; H, 3.6%); $\nu_{max.}$ 3 070, 3 040, 3 020, 1 700, 1 650, 910, 750, and 700 cm^{-1}; $\lambda_{max.}$ (EtOH) 220, 250, 280sh, 293, 304, 331, 370, 389, 412, and 438 nm (log ε 4.58, 4.50, 4.68, 4.75, 4.78, 4.74, 4.04, 4.02, 4.01, and 3.86).

Dimethyl Benzo[3,4]*cyclobut*[1,2-b]*anthracene*-6,11-*dicarboxylate* (16).—Diazomethane solution (5 ml) was added to a solution of the dicarboxylic acid (15) (10 mg) in tetrahydrofuran (20 ml). After removal of the solvent, the residue was purified by preparative t.l.c. (CH_2Cl_2 as eluant). The yellow band (R_F *ca.* 0.8) was extracted with CH_2Cl_2. Removal of the solvent and crystallisation from methanol gave the *dimethyl ester* (16) (8 mg, 77%) as yellow needles, m.p. 254—255 °C (Found: C, 78.5; H, 4.4. $C_{24}H_{16}O_4$ requires C, 78.3; H, 4.4%); δ 7.24 (m, 7-,8-,9-,10-H), 7.50 (m, 2-,3-H), 7.85 (m, 1-,4-H), and 9.31 (s, 5-,12-H).

Benzo[3,4]*cyclobut*[1,2-b]*anthracene* (17).—The dicarboxylic acid (15) (100 mg) was mixed with copper bronze (1 g) and heated in a Pyrex test-tube, in a metal bath, at 300—350 °C for 30 min. The test-tube was cooled and the contents were extracted in a Soxhlet apparatus with CH_2Cl_2 for 6 h. The extract was evaporated and the residue was chromatographed on a column (40 cm) of silica gel using light petroleum–toluene (3 : 1) as eluant. The yellow band was collected and the solid obtained from it gave the anthracene (17) as yellow crystals (from toluene) (40 mg, 54%) which sublimed at 320—330 °C (lit.,[7] 310—330 °C). The i.r. and u.v. spectra of the anthracene (17) were identical with those previously recorded.[7]

Benzo[3,4]*cyclobuta*[1,2-b]*phenanthrene*-7,12-*dicarboxamide* (19).—The dicarbonitrile (18) (100 mg), potassium hydroxide (100 mg), water (10 ml), and digol (25 ml) were boiled under reflux for 12 h. The mixture was cooled, diluted with water (200 ml), and then acidified with hydrochloric acid. The resulting percipitate (100 mg, 80%) was recrystallised from dimethyl sulphoxide and gave the *diamide* (19) as yellow crystals which did not melt up to 360 °C (Found: M^+, 338.104. $C_{22}H_{14}N_2O_2$ requires *M*, 338.105); $\nu_{max.}$ 3 345, 3 200, 1 640, 840, and 750 cm^{-1}.

12-*Carbamoylbenzo*[3,4]*cyclobuta*[1,2-b]*phenanthrene*-7-*carboxylic Acid* (20).—The dicarboxamide (19) (50 mg), acetic acid (75 ml), water (50 ml), and concentrated sulphuric acid (50 ml) were boiled under reflux for 18 h. The cooled reaction mixture was poured into water (200 ml). The precipitate (25 mg, 40%) (too sparingly soluble to be recrystallised) is assumed to be the *amido-acid* (20) (Found: M^+, 339.089. $C_{22}H_{13}NO_3$ requires *M*, 339.089); $\nu_{max.}$ 3 390, 3 240, 1 710, 1 640, 845, 815, 780, and 750 cm^{-1}. When the above mixture was refluxed for 48 h complete decomposition took place whereas no hydrolysis occurred when the dicarboxamide (19) (100 mg) was refluxed for 10 days with acetic acid (100 ml), water (20 ml), and concentrated hydrochloric acid (50 ml).

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