Cyclobutarenes. Part 4.[1] Biphenyleno[2,1-*a*]biphenylene

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Flash vacuum thermolysis of [5,6]phenanthrolino[4,3-*c*][5,6]phenanthroline **6** gave biphenyleno-[2,1-*a*]biphenylene **2**. The properties of this system are compared with those of the previously reported biphenylenobiphenylenes **3** and **4**, and are in accord with expectations from simple resonance theory.

The physical properties of two of the four possible biphenylenobiphenylenes **1**–**4** have been described in the literature. Biphenyleno[2,3-*b*]biphenylene **4** and its derivatives are pale yellow and exhibit high thermal stability,[2–4] in contrast to the bright yellow [2,3-*a*]-isomer **3**, which decomposes when heated > 250 °C.[3] These differences have been attributed to the higher π-bond order in the four-membered rings of compound **3**, and were predicted to become even more pronounced on moving to the remaining isomers **1** and **2**. A calculation of the REPE (resonance energy per π-electron) values for compounds **1**–**4** using Randic's conjugated circuit method[5] gives values of −0.0025, −0.0025, +0.013 and +0.052 eV, respectively.[6] As expected, the [1,2-*a*]- and [2,1-*a*]-isomers **1** and **2** are predicted to be the least stable of the four, having overall negative resonance energies. The low values reflect the fact that the naphthalene unit must contribute one double bond to either or both of the four-membered rings in all the Kekulé forms for **1** and **2**, whereas for both **3** and **4**, a single Kekulé representation can be drawn containing all double bonds exocyclic to the respective four-membered rings (see Fig. 1). Here, the preparation of biphenyleno[2,1-*a*]biphenylene **2** and some preliminary approaches to biphenyleno[1,2-*a*]biphenylene are described.

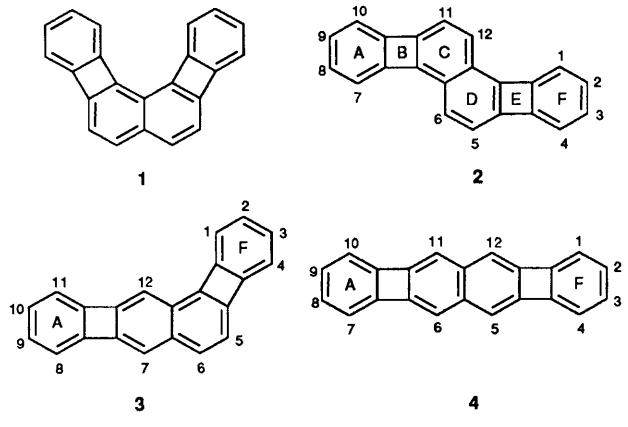
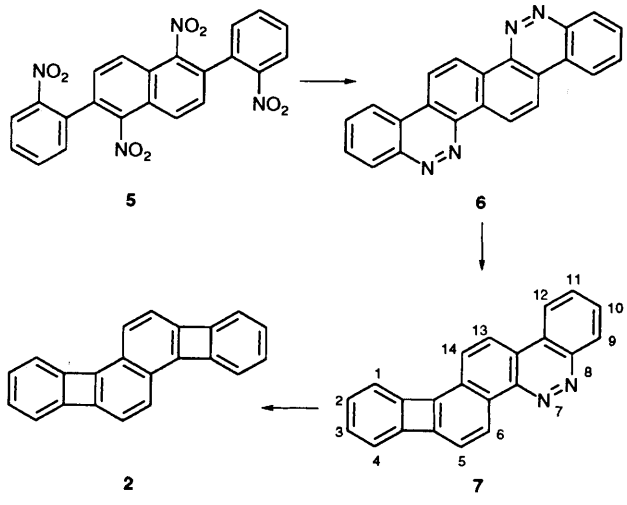


Fig. 1 The four possible biphenylenobiphenylenes with the numbering schemes employed

Results

Biphenylene has been prepared by vacuum thermolysis of benzo[*c*]cinnoline,[7] as have a number of heterocyclic biphenylenes,[8–11] and, pertinent to this paper, the two isomers of the benzocyclobutabiphenylenes.[12,13] The yields are normally low, but failures have only been encountered in those rare cases where the product is unstable at the high temperatures used[14] or more favourable fragmentation pathways are available.[10,15] It was expected that the phenanthrolinophenanthroline precursors to **1** and **2** would be accessible *via* reductive cyclisations of appropriately substituted tetranitro derivatives, as illustrated in Scheme 1.



Scheme 1

2,6-Dibromonaphthalene was prepared by decomposition at 340 °C of the complex obtained from naphthalene-2,6-diol with dibromotriphenylphosphorane (2 equiv.). The dinitration of 2,6-dichloronaphthalene with fuming nitric acid at −30 °C has been described by Piggott *et al.*,[16] and under these conditions the 2,6-dibromide gave 2,6-dibromo-1,5-dinitronaphthalene in high yield. A conventional crossed Ullmann reaction between this dibromide and an excess of 1-chloro-2-nitrobenzene with copper bronze at 250 °C gave very poor yields (< 5%) of 1,5-dinitro-2,6-bis(2′-nitrophenyl)naphthalene **5**. This was raised to *ca.* 15% by using 1-bromo-2-nitrobenzene, but the results were not reproducible and purification of the desired product proved impractical on a preparative scale. 2,2′-Dinitrobiphenyl was the only identifiable product from an analogous coupling with 1-iodo-2-nitrobenzene. However, the triaryl **5** can be obtained in near-quantitative yield by heating a mixture of 2,6-dibromo-1,5-dinitronaphthalene, 1-bromo-2-nitrobenzene, 4-(dimethylamino)pyridine and copper in acetonitrile. This procedure has been developed from that described by Cornforth *et al.*,[17] who reported that 2,2′-dinitrobiphenyl can be obtained in high yield from 1-iodo-2-nitrobenzene by stirring it with copper in an ammoniacal acetone–acetonitrile solvent at room temperature. The method described here has the advantage that bromonitroaryls couple as readily as the corresponding iodo compounds and formation of the by-products encountered with the latter procedure, nitro- and aminonitro-aryls, are reduced.

Hydrogenation of **5** over palladium oxide gave the pale yellow [5,6]phenanthrolino[4,3-*c*][5,6]phenanthroline **6** in 12% yield (see Scheme 1). The insolubility of this product

precluded recording its solution NMR spectra, but its mass spectrum, which showed fragmentation peaks at *m/z* 304 and 276, encouraged the prospect of obtaining **2** by sequential dinitrogen extrusion. Flash vacuum thermolysis of the phenanthrolinophenanthroline **6** at 800 °C gave the mono-extrusion product, the bulk of the starting material being recovered unchanged. Biphenyleno[1,2-*c*][5,6]phenanthroline **7** forms yellow–orange crystals which are stable to temperatures > 300 °C. The ^{1}H NMR spectrum ($CDCl_3$) is in accord with that expected by analogy with benzo[*a*]biphenylene[18] and benzo[*c*]cinnoline,[19] showing multiplets at δ 6.62 (1 H, m, 4-H), 6.73 (3 H, m, 1- to 3-H), 7.27 (1 H, d, 5-H, $J_{5,6}$ 7.88), 7.80 (1 H, dd, 14-H), 7.90 (2 H, m, 10-, 11-H), 8.26 (1 H, d, 13-H, $J_{13,14}$ 9.16), 8.51 (1 H, m, 12-H), 8.72 (1 H, m, 9-H) and 9.37 (1 H, dd, 6-H, $J_{6,14}$ 0.73). The lowfield shift of 2-H can be explained by the proximity of the 'bay' 13-nitrogen, but, somewhat surprisingly, 9- to 12-H resonate to lowfield of the corresponding protons in benzo[*c*]cinnoline. This is contrary to the observations of Barton and Rowe,[18] who note that the shielding effect associated with an unsaturated four-membered ring usually extends to annelated rings which are remote from the biphenylene nucleus: the 1- to 4-hydrogens in biphenyleno[2,3-*c*]cinnoline, for example, resonate to highfield of those in benzo[*c*]cinnoline by over 0.1 ppm.[8] Thermolysis of the phenanthrolinophenanthroline **6** at 850 °C gave an approximately 50:50 mixture of **7** and **2**, whilst at 900 °C, biphenyleno[2,1-*a*]biphenylene **2** was the only identifiable product. The deep red hydrocarbon **2** is stable in the solid state but decomposes over a period of hours (in benzene) to days (in chlorinated solvents), apparently by formation of a mixture of dimers (see Experimental section). The ^{1}H NMR spectrum of **2** is compared with those of the other biphenylenobiphenylenes in the discussion.

A parallel investigation directed towards the preparation of biphenyleno[1,2-*a*]biphenylene **1** foundered at the hydrogenation step. Dinitration of 2,7-dibromonaphthalene as described above for the 2,6-isomer gave 2,7-dibromo-1,8-dinitronaphthalene, which on coupling with 1-bromo-2-nitrobenzene in the presence of copper and 4-dimethylaminopyridine gave 1,8-dinitro-2,7-bis(2′-nitrophenyl)naphthalene in moderate yield. Attempts to reduce this product to [5,6]phenanthrolino[3,4-*c*]-[5,6]phenanthroline were unsuccessful, possibly as a consequence of the proximity of the two heterocyclic rings in the envisgaged product.

Discussion

Simple resonance theory, in terms of counting Kekulé structures, cannot be applied to the cyclobutarenes in the straightforward manner used for polycyclic benzenoid systems. The properties of these systems are better interpreted in terms of their algebraic structure counts (ASCs), where the ASC is the total number of Kekulé representations minus those of opposing parity.[20,21] Herndon has determined the Pauling bond orders (PBOs) for a number of annelated cyclobutadienes using this approach. While the values for biphenylene correspond well with those from simple molecular orbital calculations, anomalous positive and negative PBOs are obtained for the four-membered rings on moving to the benzo- and dibenzo-biphenylene series.[22] This is a consequence of the large number of cyclobutadienoid contributors to these systems, coupled with the assumption that all Kekulé forms must contribute equally, albeit some in a negative sense, to the resonance hybrid. The anomaly disappears if the weighting of these contributors is reduced and, since they are equal and opposite in number and parity, the remaining PBOs for a given derivative remain unchanged. These values, here referred to as invariant PBOs, are illustrated for the biphenylenobiphenylenes **2–4** in Fig. 2.

^{1}H NMR data for compounds **2–4** are collected in Table 1. The published spectrum for **3** did not allow unambiguous distinction between the different ring protons and has been redetermined for this investigation.

Helson *et al.* interpreted the spectrum of the [2,3-*b*]-isomer **4** as evidence for a significant degree of bond-fixation in the naphthalene unit,[2] in accord with the predictions of the model used here. The central 5-, 6-, 11- and 12-H resonate at δ 6.73, to highfield of those in the terminal (A and F) rings, which form a tightly grouped AA′BB′ multiplet at δ 6.84. The unusual degree of shielding experienced by the naphthalene protons is in part due to geometric distortions imposed by the B and E rings; the analogous hydrogens in 2,3,6,7-tetrahydrodicyclobuta[*b*,*g*]naphthalene also resonate to highfield of those in naphthalene, by *ca.* 0.5 ppm, at δ 7.28.[23] The benzenoid protons are shifted to lowfield with respect to biphenylene and this, coupled with the comparatively small difference in shift between the α- and β-positions, appears to be characteristic of systems which can minimise $4n$ π-electron effects by localisation of an adjacent ring.[6] This lowfield shift may also be indicative of a higher diatropic current in the terminal rings than that in biphenylene, owing to their higher degree of delocalisation (invariant PBOs 0.38 and 0.62, *cf.* biphenylene, 0.33 and 0.67).

In contrast, the corresponding A and F rings in biphenyleno[2,1-*a*]biphenylene **2** resonate to highfield of the C and D rings, the two sets giving multiplets in the range δ 6.40–6.58 and 6.87–7.05, respectively. Moreover, the coupling constant $J_{5,6}$ between the central ring protons is, at 7.70 Hz, markedly

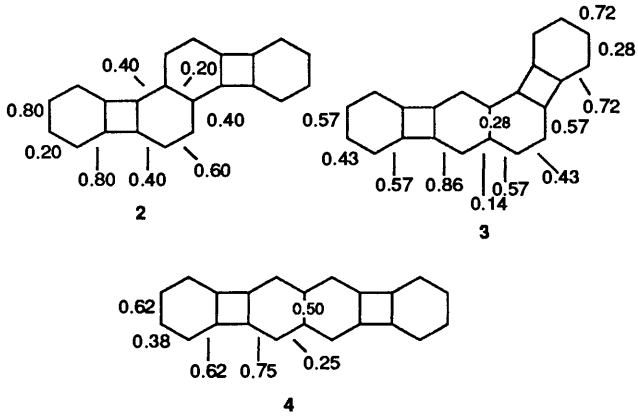


Fig. 2 Invariant Pauling bond orders (PBOs) for the biphenylenobiphenylenes **2–4**

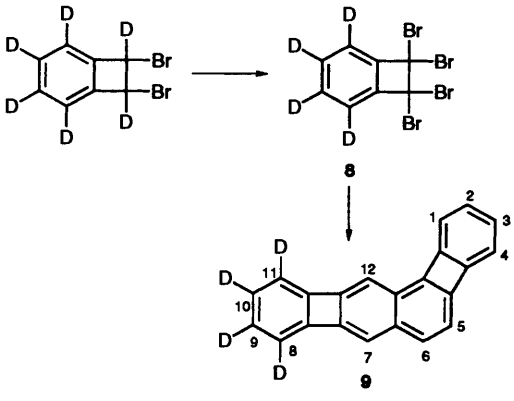
Table 1 ^{1}H NMR spectra of the biphenylenobiphenylenes **2–4** in $CDCl_3$; the numbering system employed is given in Fig. 1

	δ_H(multiplicity)		
^{1}H Nucleus	**2**	**3**	**4**[c]
1	6.40 (m)	6.62 (m)	
2	6.58 (m)	6.68 (m)	6.84 (m)
3			
4	6.49 (m)	6.54 (m)	
5	7.05 (d)[a]	6.66 (d)[b]	6.73 (s)
6	6.87 (d)[a]	6.92 (d, br)[b]	
7	6.40 (m)	6.67 (s, br)	
8	6.58 (m)	7.01 (m)	(6.84 m)
9			
10	6.49 (m)		
11	7.05 (d)		6.73 (s)
12	6.87 (d)	6.70 (s)	

[a] $J_{5,6}$ 7.70 Hz. [b] $J_{5,6}$ 7.33 Hz. [c] Data for compound **4** are taken from the literature.[2]

lower than that in naphthalene itself, at 8.28 Hz (*cf.* benzene, 7.54 Hz).[34] This reduction does not appear to be a consequence of framework distortions, since $J_{3,4}$ values in derivatives of 1,2,5,6-tetrahydrodicyclobuta[*a*,*f*]naphthalene are very similar to those in naphthalene, at 8.31 Hz.[1] Biphenyleno[2,1-*a*]biphenylene **2** minimises paratropic effects by a redistribution of electron density in the central rings so as to effectively 'delocalise' the periphery of the naphthalene unit (the PBOs for naphthalene are 0.67 and 0.33). The A and F rings are more localised than those in biphenylene, but are also shielded to a greater extent by the paratropic B and E rings; 1- and 7-H resonate to high field of the adjacent β-protons by nearly 0.2 ppm (*cf.* biphenylene, 0.1 ppm). A similar line of argument, advanced to explain the difference between the spectra of the angular and linear benzocyclobutabiphenylenes,[18] was subsequently confirmed by X-ray crystal structure analyses.[25,26]

A completely different type of ground-state structure is predicted for biphenyleno[2,3-*a*]biphenylene **3**. The A and D rings are delocalised, whereas the other benzenoid rings exhibit some bond-fixation, this being particularly marked for the C ring. This appears to be supported by the ^{1}H NMR spectrum of **3**, in that while the A ring protons give rise to a tightly grouped multiplet at δ 7.01, the F ring protons resonate at much higher field, in the range δ 6.54–6.68. These assignments were confirmed by the absence of the lowfield multiplet in an independently prepared sample of [8,9,10,11-$^2H_4$]biphenyleno-[2,3-*a*]biphenylene **9** (Scheme 2). The C ring gives two singlets



Scheme 2

at *ca.* δ 6.7 (cf. the [2,3-*b*]-isomer **4** above) and the D ring an AB doublet, $J_{5,6}$ 7.33 Hz, at δ 6.66 and 6.92. The low value of the coupling constant is in accord with the invariant PBO at this point, but the observation that these protons resonate at higher field than the corresponding 5- and 6-H in biphenyleno-[2,1-*a*]biphenylene **2** requires some comment. Firstly, the magnitude of the shielding 4*n* π-electron paratropic current in adjacent E ring may be greater in **3** than in **2**. This seems unlikely, considering the relative effect of the two E rings on the respective F rings. Secondly, the D ring in **3** could be more localised than that in **2**, leading to a reduction in diatropism and pointing to a limitation of the bond order model used here. Finally, the D ring in **3** may be deshielded by the C ring to a smaller extent than that in **2**, as a consequence of the high degree of bond fixation in this region. However, it should be noted that in the absence of a suitable reference system, such as 1,2,6,7-tetrahydrocyclobuta[*a*,*g*]naphthalene, no allowance has been made for the differing degrees of geometric distortion in the carbon frameworks of **2** and **3**.

In the ^{1}H NMR spectra of all such compounds, distinguishing between the influence of localised ring currents, bond fixation and annelated rings is by no means straightforward. Current work is being directed towards the preparation of systems which will enable a clearer delineation of these effects.

Experimental

Unless stated otherwise, the following conditions apply: ^{1}H and ^{13}C NMR spectra were recorded for solutions in deuteriochloroform containing tetramethylsilane as an internal standard, on a Brucker AM 250 spectrometer. *J* Values are quoted in Hz. Other details have been described previously.[27] 1,2-Bis(dibromomethyl)biphenylene,[3] 2,7-dibromonaphthalene[28] and 1,2-dibromo[1,2,3,4,5,6-$^2H_6$]1,2-dihydrobenzocyclobutene[29] were prepared by literature methods.

2,6-*Dibromonaphthalene*.—Naphthalene-2,6-diol (5.0 g) was added in one portion to dibromotriphenylphosphorane [prepared by addition of bromine (10.0 g) to triphenylphosphine (16.4 g) in MeCN (30 cm^3)]. The white suspension dissolved and then reprecipitated as a brownish solid. This mixture was heated, initially causing the solvent to evaporate, to an internal temperature of *ca.* 340 °C. The residual solid turned black and melted at 300 °C, and HBr evolution became rapid above 310 °C. After being maintained at 340 °C for 5 min, the mixture was cooled and suspended in refluxing EtOH (200 cm^3), and the suspension was then filtered and evaporated to *ca.* 50 cm^3. After the residue had cooled the crude product was filtered off and recrystallised from EtOH (50 cm^3) to give the title compound (3.1 g, 35%), m.p. 158–159 °C (lit.,[30] m.p. 159–160 °C).

2,6-*Dibromo*-1,5-*dinitronaphthalene*—2,6-Dibromonaphthalene (12.0 g) was added in portions over 5 min to HNO_3 (*d* 1.5; 100 cm^3) at −30 °C. The resulting greyish suspension was stirred in the range −30 to −25 °C for 1 h, during which time it thickened gradually, and was then poured onto ice. The off-white precipitate was filtered off, suspended in water (100 cm^3), and the suspension boiled until NO_2 evolution ceased. The resulting buff solid was filtered off, dried and recrystallised from $CHCl_3$ (150 cm^3) to give the *title compound* (14.7 g, 93%) as pale yellow needles which turned pink on exposure to light, m.p. 303–304 °C (slow decomp. > 270 °C) (Found: C, 31.8; H, 1.1; Br, 42.8; N, 7.5. $C_{10}H_4Br_2N_2O_4$ requires C, 31.9; H, 1.1; Br, 42.6; N, 7.4%); δ_H 7.68 (2 H, d, 3-, 7-H, $J_{3,4}$ 8.77) and 7.87 (2 H, d, 4-, 8-H); δ_C 124.6 (C-3, -7) and 133.2 (C-4, -8); *m*/*z* 376 (M^+, 6%) and 330 ($M^+ - NO_2$, 100).

1,5-*Dinitro*-2,6-*bis*(2′-*nitrophenyl*)*naphthalene* **5**.—A mixture of 2,6-dibromo-1,5-dinitronaphthalene (0.40 g), 1-bromo-2-nitrobenzene (1.60 g), 4-(dimethylamino)pyridine (1.30 g), copper bronze (1.00 g) and copper(II) sulfate (5 mg) in MeCN was refluxed with stirring for 30 min. The resulting brown suspension was diluted with Et_2O, filtered and evaporated under reduced pressure. The product was slurred with hot, light petroleum (b.p. 80–100 °C) and the supernatant (containing 2,2′-dinitrobiphenyl) discarded. The residue (0.52 g) was recrystallised from toluene (15 cm^3) to give the *tetranitro compound* **5** (0.48 g, 98%), buff crystals, m.p. 302–303 °C (rapid decomp. > 280 °C) (Found: C, 57.3; H, 2.4; N, 12.1. $C_{22}H_{12}N_4O_8$ requires C, 57.4; H, 2.6; N, 12.2%); δ_H 7.41 (2 H, m, 6′-, 6″-H), 7.62 (2 H, d, 3-, 7-H, $J_{3,4}$ 8.75), 7.73 (4 H, m, 4′-, 4″-, 5′-, 5″-H), 8.08 (2 H, d, 4-, 8-H) and 8.30 (2 H, m, 3′-, 3″-H); *m*/*z* 414 ($M^+ - NO_2$, 98%), 386 ($M^+ - 2NO_2$, 100) and 198 (31).

[5,6]*Phenanthrolino*[4,3-c][5,6]*phenanthroline* **6**.—A suspension of the tetranitro derivative **5** (0.5 g), sodium methoxide (1.25 g) and palladium oxide (50 mg) in EtOH was hydrogenated at room temperature and atmospheric pressure. After

5 h, uptake had ceased (*ca.* 220 cm^3 H_2 in total) and the resulting brown mixture was stirred in the presence of air for a further 2 h. Filtration, followed by sublimation of the residue gave the *phenanthrolinophenanthroline* **6** (43 mg, 12%) as a greenish yellow solid, m.p. > 360 °C (sublimes > 300 °C) (Found: C, 79.3; H, 3.5; N, 16.7. $C_{22}H_{12}N_4$ requires C, 79.5; H, 3.6; N, 16.9%); *m/z* 332 (M^+, 100%), 304 ($M^+ - N_2$, 9), 276 ($M^+ - 2N_2$, 12) and 274 ($M^+ - 2N_2H$, 11).

Flash Vacuum Thermolysis of the Phenanthrolinophenanthroline **6**.—(*a*) A sample of compound **6** (45 mg) was sublimed over a period of 3 h at 300 °C and 0.002 mmHg through a pyrolysis tube maintained at 800 °C, and the products were condensed into a liquid nitrogen trap. The pyrolysate was suspended in $CHCl_3$ (5 cm^3), and the phenanthroline **6** filtered off (25 mg); the filtrate was then subjected to column chromatography on silica using $CHCl_3$ as the eluent. This gave *biphenyleno*[1,2-c]-[5,6]*phenanthroline* **7** (8 mg, 19%, 44% based on consumed phenanthroline **6**), yellow–orange crystals, m.p. 277–279 °C (Found: M^+, 304.1018. $C_{22}H_{12}N_2$ requires *M*, 304.1000); δ_H, see text; *m/z* 304 (M^+, 100%) and 276 ($M^+ - N_2$, 18). (*b*) Pyrolysis of the phenanthrolinophenanthroline **6** (40 mg) under the conditions described above at 850 °C, followed by flash chromatography of the pyrolysate on silica using dichloromethane as the eluent, gave *biphenyleno*[2,1-a]*biphenylene* **2** (2.7 mg, 8%), deep red crystals, m.p. > 200 °C (sublimation accompanied by slow decomp. > 150 °C) (Found: M^+, 276.0932. $C_{22}H_{12}$ requires *M*, 276.0939); $\delta_H(CDCl_3)$ see text; $\delta_H(C_6D_6)$ 6.37 (4 H, m, 1-, 4-, 7-, 10-H), 6.55 (4 H, m, 2-, 3-, 8-, 9-H), 6.64 (2 H, d, 6-, 12-H) and 6.93 (2 H, d, 5-, 11-H); δ_C 115.4, 116.0, 118.4 (C-1, -4, -6, -7, -10, -12, unassigned), 124.4 (C-5, -11), 127.7 and 127.9 (C-2, -3, -8, -9, unassigned); *m/z* 276 (M^+, 100%) and 138 (M^{2+}, 17). This was followed by the mono-extrusion product **7** (3 mg, 8%), identical with the sample prepared above. (*c*) Pyrolysis of the phenanthroline **6** (55 mg) under the conditions described above at 900 °C, followed by flash chromatography as described in (*b*), gave the hydrocarbon **2** (1.8 mg, 4%), identical with that isolated above. After a solution of compound **2** in C_6D_6 solution had been stored for 24 h, its ^1H NMR spectrum indicated that complete decomposition had occurred, apparently by formation of a mixture of dimers: the spectrum exhibited two overlapping AB systems centred at δ 3.8 (J_{AB} 6.96) and a series of complex multiplets in the range δ 6.2–7.6. Although the structures of these products have not been further investigated owing to the small amounts of **2** available, a mass spectrum of the sample showed peaks at *m/z* 552 (12%) and 276 (100).

2,7-*Dibromo*-1,8-*dinitronaphthalene*.—A reaction between 2,7-dibromonaphthalene (5.0 g) and HNO_3 (*d* 1.5; 60 cm^3) under the conditions described for 2,6-dibromonaphthalene above gave, after boiling, filtration and drying, the crude dinitro derivative (6.1 g). This was recrystallised from toluene (75 cm^3) to give the *title compound* (4.8 g, 73%), pale yellow crystals, m.p. 260–261 °C (Found: C, 31.9; H, 1.0; Br, 42.6; N, 7.5. $C_{10}H_4Br_2N_2O_4$ requires C, 31.9; H, 1.1; Br, 42.6; N, 7.4%; δ_H 7.88 (2 H, d, 3-, 6-H, J_{34} 8.88) and 7.94 (2 H, d, 4-, 5-H); δ_C 131.8 and 132.1 (C-3 to -6, unassigned); *m/z* 376 (M^+, 33%), 330 ($M^+ - NO_2$, 100), and 124 (24).

1,8-*Dinitro*-2,7-*bis*(2′-*nitrophenyl*)*naphthalene*.—A mixture of 2,7-dibromo-1,8-dinitronaphthalene (0.50 g), 1-bromo-2-nitrobenzene (1.00 g), 4-dimethylaminopyridine (1.40 g) and copper bronze (1.00 g) in MeCN (10 cm^3) was refluxed with stirring for 1 h. After work-up and petroleum extraction as described for compound **5**, the residue (0.15 g) was recrystallised from toluene (3 cm^3) to give the *title compound* (90 mg, 15%) as colourless crystals, decomp. > 230 °C (Found: C, 57.6; H, 2.7; N, 12.1. $C_{22}H_{12}N_4O_8$ requires C, 57.4; H, 2.6; N, 12.2%); δ_H 7.31–7.69 (6 H, m, 4′–6′-, 4″–6″-H), 7.60 (2 H, d, 3-, 6-H, $J_{3,4}$ 8.54), 8.18 (2 H, d, 4-, 5-H) and 8.33 (2 H, m, 3′-, 3″-H); *m/z* 460 (M^+, 4%), 414 ($M^+ - NO_2$, 100) and 386 (27).

1,1,2,2-*Tetrabromo*[3,4,5,6-$^2H_4$]-1,2-*dihydrobenzocyclobutene* **8**.—A solution of 1,2-dibromo[1,2,3,4,5,6-$^2H_6$]1,2-dihydrobenzocyclobutene (0.5 g) and bromine (1.0 g) in carbon tetrachloride (50 cm^3) was refluxed over a 200 W bulb for 12 h. The solution was cooled and evaporated and the solid product was recrystallised (EtOH) to give the *title compound* (0.65 g, 82%) as colourless crystals, m.p. 117–118 °C (Found: C, 22.6; H, 1.8; Br, 75.5. $C_8D_4Br_4$ requires C, 22.6; H, 1.9; Br, 75.5%); δ_C 65.3 (C-1, -2), 121.8 (C-3, -6), 133.7 (C-4, -5) and 143.1 (C-1a, -6a); *m/z* 424 (M^+, 16%), 345 and 343 (M^+ – Br, 44) and 266 (M^+ – 2Br, 100).

[8,9,10,11-$^2H_4$]*Biphenyleno*[2,3-a]*biphenylene* **9**. Activated zinc[31] (*ca.* 1 g) was added in one portion to a solution of 1,2-bis(dibromomethyl)biphenylene (100 mg) and the dihydrobenzocyclobutene **8** (85 mg) in THF (3 cm^3). The crude product was worked up by the method previously described for the parent hydrocarbon **3**,[3] to give the *title compound* (18 mg, 32%), m.p. 175–177 °C (Found: C, 94.1; H, 5.8. $C_{22}D_4H_8$ requires C, 94.3; H, 5.7%); δ_H 6.54 (1 H, m, 4-H), 6.62 (1 H, m, 1-H), 6.66 (1 H, d, $J_{5,6}$, 7.32, 5-H), 6.67 (1 H, s, 7-H), 6.68 (2 H, m, 2-, 3-H), 6.70 (1 H, s, 12-H) and 6.92 (1 H, d, 6-H); δ_C 110.0, 116.0, 116.5, 119.4, 119.7, 127.8, 127.9 and 129.6 (C-1–7, -12, unassigned); *m/z* 280 (M^+, 100%), 279 (33) and 140 (M^{2+}, 12).

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