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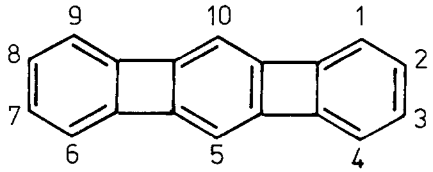
BENZO[3,4]CYCLOBUTA[1,2-b]BIPHENYLENE, THE LINEAR SESQUIBIPHENYLENE

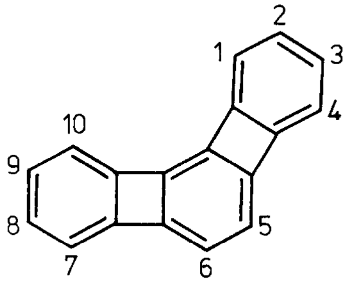
J.W. Barton* and D.J. Rowe
School of Chemistry, The University, Bristol BS8 1TS, England

Syntheses of the benzodicinnolines (3) and (4), and their vacuum thermolysis to give the title compound (1), are reported.

The effects which arise from the fusion of small, strained rings[1,2] and of potentially antiaromatic rings[3] to benzenoid systems have been the subjects of much recent interest. The benzo[3,4]cyclobuta[1,2]biphenylenes (1) and (2) are particularly relevant to this as they contain both types of structural feature.



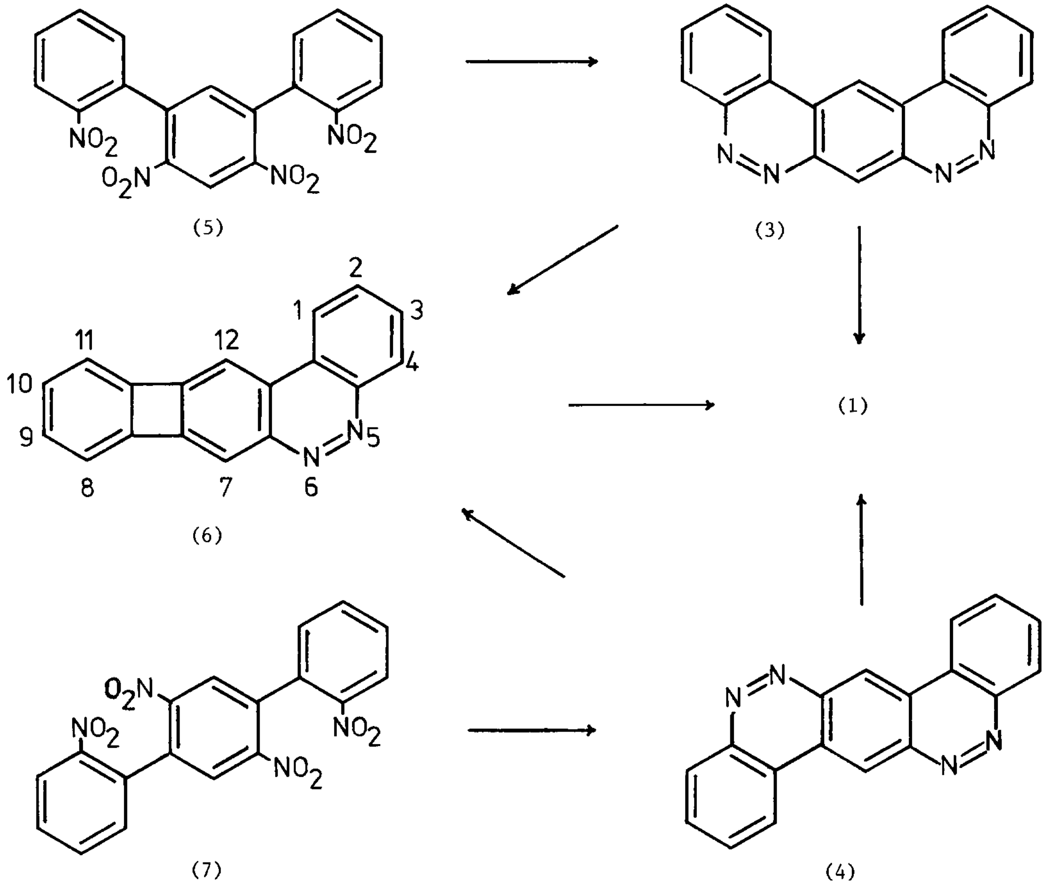
(1)



(2)

The linear isomer (1), for which no Kekulé structure can be drawn without a formal double bond in a four-membered ring, has been predicted by Hückel molecular orbital theory[4] to be less stable than the angular isomer (2), although this has been disputed on the basis of a graph theoretical approach.[5] Previously, we reported the formation of (2) by thermal extrusion of nitrogen from a benzodicinnoline precursor,[6] the present paper describes syntheses and properties of the linear isomer (1). There are two possible dicinnoline precursors, (3) and (4), which could extrude nitrogen to give the linear sesquibiphenylene; we find that both of these give (1) on vacuum thermolysis.

A crossed Ullmann reaction between 1-chloro-2-nitrobenzene and 1,3-dichloro-4,6-dinitrobenzene gave, after chromatography, 2,4',6',2"-tetranitro-1,1':3',1"-terphenyl (5) (27%) as buff crystals, m.p. 211-2°C. Catalytic hydrogenation of (5) in 0.5% ethanolic sodium hydroxide



in the presence of palladium oxide gave a solution which, on exposure to the air, deposited benzo[1,2-c:5,4-c']dicinnoline (3) (71%) as yellow-brown crystals m.p. > 360°C; m/z (%): 282 (100), M^+; 254 (4), $M^+ - N_2$; 226 (43), $M^+ - 2N_2$. Passage of this compound through a 1-metre silica tube at 800°C, 0.04 Torr gave, after flash chromatography over silica gel in dichloromethane/hexane, benzo[3,4]cyclobuta[1,2-b]biphenylene (1) (11%) as orange crystals, m.p. 260°C decomp. (sublimes above 200°C); m/z (%): 226 (100), M^+; 224 (26); λ_{max} nm (cyclohexane) 276 (log ε 4.54), 285 (4.69), 409 (3.83), 435 (4.12). The complex of (1) with 2,4,7-trinitro-9-fluorenone was obtained as very deep red needles m.p. 217-8.5°C. Further elution of the chromatogram with dichloromethane/ethyl acetate gave the intermediate product, biphenyleno[2,3-c]cinnoline (6) (36%), as bright yellow crystals, m.p. 261-3°C; m/z (%): 254 (100), M^+; 226 (44), $M^+ - N_2$; ^1H NMR ($CDCl_3$) δ ppm: 8.55 (multiplet H_4), 8.28(multiplet H_1), 7.79(multiplet $H_{2,3}$), 7.73(singlet H_7), 7.67(singlet H_{12}), 7.04(multiplet H_{8-11}).

In a similar sequence an Ullmann reaction between 1-chloro-2-nitrobenzene and 1,4-dichloro-2,5-dinitrobenzene gave, after chromatography, 2,2',5',2"-tetranitro-1,1':4',1"-terphenyl (7) (9%) as off-white needles, m.p. 264-5°C. This was cyclised as described above to give benzo [1,2-c:4,5-c']dicinnoline (4)[7] (41%) as greenish-yellow microcrystals m.p. > 360°C; m/z (%): 282 (100), M^+; 254 (8), $M^+ - N_2$; 226 (48), $M^+ - 2N_2$. Thermolysis of (4) as described for isomer (3) gave the sesquibiphenylene (1) (6%) together with (6) (31%). Thermolysis of the intermediate biphenyleno[2,3-c]cinnoline (6) under these conditions gave (1) (19%) with 61% recovery of the starting material.

NMR Data for Benzo[3,4]cyclobuta[1,2]biphenylenes (1) and (2)

		Ring position				
		1-	2-	3-	4-	5-
(1)	^1H	6.42	6.63	6.63	6.42	6.24
	^{13}C	115.307	127.724	127.724	115.307	110.464
(2)	^1H	6.95	6.95	6.95	6.95	6.15
	^{13}C	119.091 or 118.122	128.684 or 128.137	128.137 or 128.684	118.122 or 119.091	113.966
Δ (1),(2)	^1H	-0.53	-0.32	-0.32	-0.53	+0.09
	^{13}C	-3.874 or -2.815	-0.960 or -0.413	-0.413 or -0.960	-2.815 or -3.784	-3.502

Spectra were measured on solutions in $CDCl_3$; δ (ppm) values downfield of TMS = 0.000. Signals were assigned by analogy with those for biphenylene[8,9] and for (2).[6]

Benzo[3,4]cyclobuta[1,2-b]biphenylene (1) is more deeply coloured than the angular isomer (2). It appears to be moderately stable in the solid state but is light-sensitive in solution; solutions are bleached on exposure to daylight and thin layer chromatography results in extensive decomposition. The ultra-violet spectrum of (1) shows a close similarity of form to that of biphenylene, but subject to a large bathochromic shift. In view of its instability to light the log ε values quoted for (1) are not considered to be of high accuracy. The table shows NMR data for (1) in comparison with those for (2). ^1H NMR shows an AA'XX' system and a singlet in the ratio 2:2:1. The ^{13}C NMR spectrum shows the expected three signals of proton-bearing carbon atoms in the ratio of 2:2:1, but the quaternary carbon atoms were not detectable with the small amounts of material available. The upfield shifts of all signals of (1) relative to those of (2) [except in the case of the protons of the central rings, where the situation is complicated by proximity effects in (2)] may be attributed to a reduction of the aromatic deshielding effects due to increased opposing paramagnetic ring currents in the four-membered rings of (1). This is to be expected if (1) has higher bond orders, i.e. increased cyclobutadiene character, in the four-membered rings and is in keeping with the Hückel molecular orbital evaluation of the structures.[4]

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