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BENZO[3,4]CYCLOBUTA[1,2-a]BIPHENYLENE, A NEW BIPHENYLENE SYSTEM

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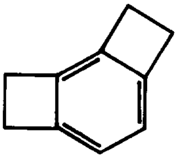
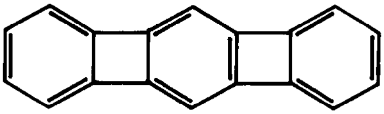
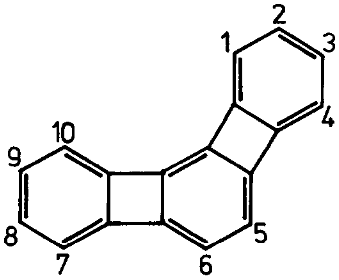
Current interest in strained systems resulting from the fusion of more than one small, strained ring onto a benzene nucleus has led to the recent synthesis of molecules such as 1,2,5,6-tetrahydrodicyclobuta[a,c]benzene (1).[1]


(1)

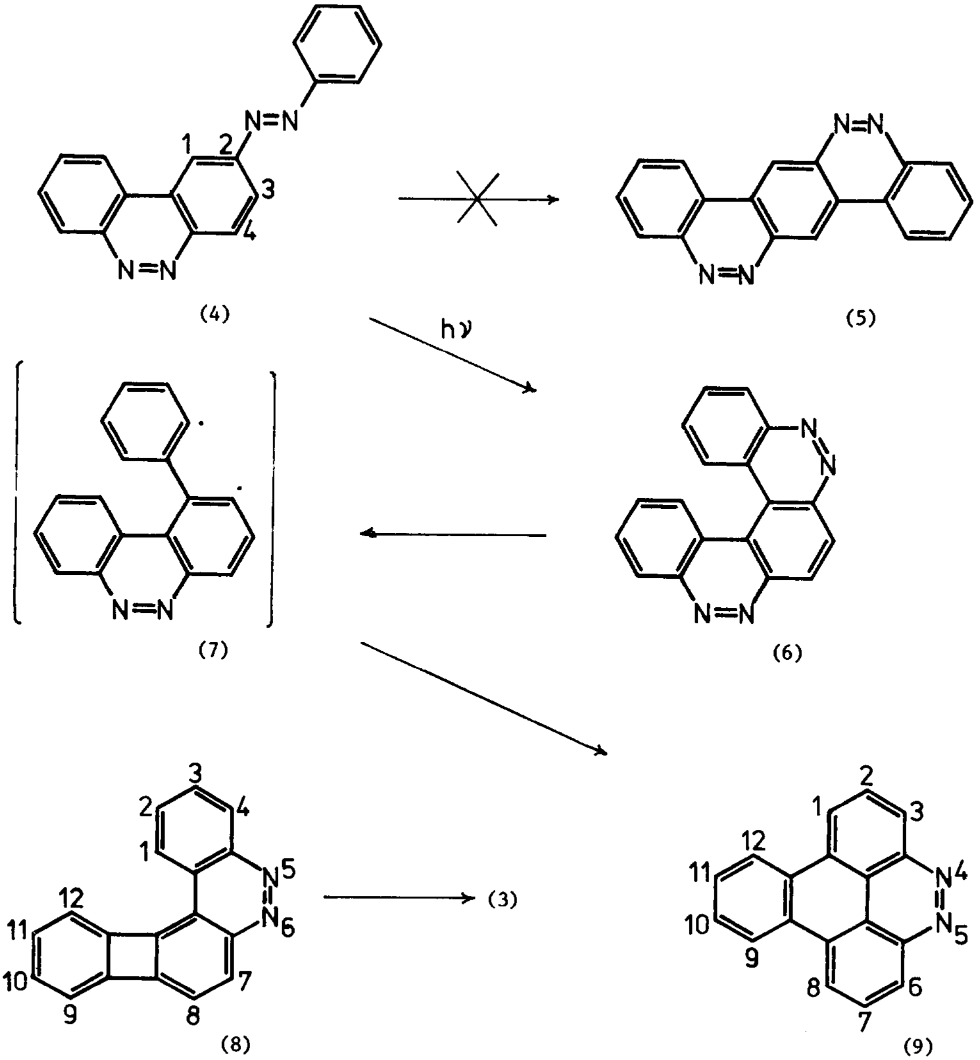

(2)



(3)

The so-called sesquibiphenylenes (2) and (3) are of interest in this respect and also in the fact that both four-membered rings in them are potentially antiaromatic; on the basis of molecular orbital calculations the linear isomer (2) is expected to have higher bond orders in the four-membered rings and a marginally lower delocalisation energy,[2] although the validity of this treatment has recently been questioned.[3] The present paper describes the preparation of the angular isomer, benzo[3,4]cyclobuta[1,2-a]biphenylene (3) by thermal extrusion of nitrogen from benzo[1,2-c:4,3-c']dicinnoline (6), using methods similar to those employed recently for the synthesis of aza-analogues of biphenylene.[4]

As part of an investigation into the synthesis of possible benzodicinnoline precursors of (2) and (3) we re-examined the photocyclisation of 2-phenylazobenzo[c]cinnoline (4) in sulphuric acid, previously reported as giving benzo[1,2-c:4,5-c']dicinnoline (5), the structure being assigned on the basis of its U.V. spectrum and the fact that cyclisation was expected to take place at the less sterically-hindered position 3-.[5] However, other characteristics of this compound, e.g. a strong C—H out of plane bending band at 839 cm^{-1} in the I.R. spectrum, were more in keeping with its having the alternative structure (6), and this was confirmed by the products obtained when it was subjected to vacuum thermolysis.



Passage of this compound through a 1-metre silica tube at 800° C, 0.04 Torr gave, after preparative T.L.C. on silica gel in benzene/hexane, benzo[3,4]cyclobuta[1,2-a]biphenylene (3) (9.5%), as pale yellow needles, m.p. 175-177° C; M$^+$ 226, λ_{max} (EtOH) 218.5 (log$_\varepsilon$ 4.64), 231 (4.48), 271.5 (4.66), 276 (4.62), 284 (4.85), 301 (4.34), 308 (4.42, 316

(4.80), 354 (3.59), 374 (3.62) and 394 nm (3.50). The ^{1}H N.M.R. spectrum shows an ABCD pattern signal at τ 3.08 (H_{1-4} and H_{7-10}) together with a sharp singlet at τ 3.87 ($H_{5,6}$). The striking feature of this spectrum is the resonance of H_5 and H_6 at such high field, the deshielding effect of the central benzene ring being opposed by the paramagnetic effects of the four-membered rings.[6] The ^{13}C N.M.R. spectrum shows five strong signals of equal intensity at -113.966 ($C_{5,6}$), -118.122 ($C_{1,10}$ or $C_{4,7}$), -119.091 ($C_{4,7}$ or $C_{1,10}$), -128.137 ($C_{2,9}$ or $C_{3,8}$), and -128.687 ($C_{3,8}$ or $C_{2,9}$) p.p.m., thus confirming the assigned structure (3); the highly symmetrical linear isomer (2) should show only three signals from proton-substituted carbon atoms. The signals due to the carbon atoms of the four-membered rings were too weak to identify with the small amounts of material available.

The intermediate product, biphenylene[2,1-c]cinnoline (8), resulting from extrusion of one molecule of nitrogen from (6), was next eluted from the chromatogram as an orange solid (13.7%), m.p. 174-176° C; M^+ 254; λ_{max} (EtOH) 212 ($\log_\varepsilon$ 4.58), 231 (4.46), 264 (4.26), 285 (4.44), 294 (4.49), 321 (4.37), 331 nm (4.40). The ^{1}H N.M.R. spectrum showed signals characteristic of an areno[c]cinnoline at τ 1.4 (multiplet H_4), τ 1.78 (doublet H_7), τ 2.17 (multiplet H_{1-3}), τ 2.81 (doublet H_8), $J_{7,8}$ = 7.8 cps. and of a biphenylene at τ 3.28 (ABCD multiplet H_{9-12}).

Further elution of the chromatogram gave starting material (6.6%) and a yellow compound (6.5%), m.p. 276-277° C, which, from the symmetry of its ^{1}H and ^{13}C N.M.R. spectra, is thought to be phenanthro[1,10,9-cde]cinnoline (9); M^+ 254; λ_{max} (EtOH) 208 ($\log_\varepsilon$ 3.70), 214 (3.76), 231.5 (3.62), 252 (3.84), 259 (3.83), 273 (3.99), 292 (3.21), 303 (3.27), 310.5 (3.23), and 361 nm (3.10); ^{1}H N.M.R. τ 1.06 (doublet of doublets $H_{1,3,6,8}$), τ 1.33 (doublet of doublets $H_{9,12}$), τ 1.74 (doublet of doublets $H_{2,7}$) and τ 2.27 (quartet $H_{10,11}$); $J_{9,10} = J_{11,12}$ = 6.4 cps; $J_{9,11} = J_{10,12}$ = 3.5 cps; $J_{1,2} = J_{2,3} = J_{6,7} = J_{7,8}$ = 8.0 cps; $J_{1,3} = J_{6,8}$ = 3.25 cps. The ^{13}C N.M.R. spectrum shows only four resonances of proton-substituted carbon atoms; these were assigned as follows by comparison with the spectra of benzo[c]cinnoline and of triphenylene:[7] -128.603 ($C_{10,11}$), -128.373 ($C_{2,3,6,7}$), -124.217 ($C_{9,12}$), -123.751 ($C_{1,8}$). Formation of this isomer of (8) presumably involves rearrangement of the diradical intermediate (7) prior to ring closure.

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