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FORMATION OF A TRIBENZO[12]ANNULENE BY THERMOLYSIS OF A BENZOTRICINNOLINE. A UNIQUE [2 + 2 + 2]BENZENE - ACETYLENE CYCLOREVERSION?

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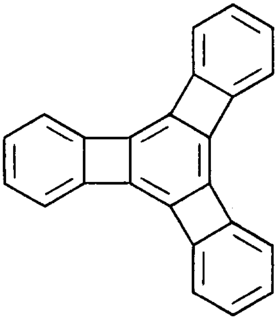
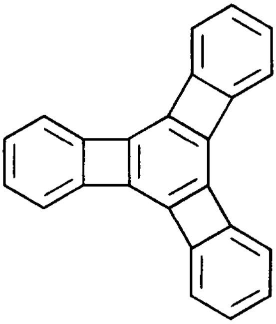
Abstract: The synthesis of benzotricinnoline (3) is described; vacuum thermolysis of this compound gives, *inter alia*, the annulene 5,6,11,12,17,18-hexadehydrotribenzo[a,e,i]cyclododecene (6).

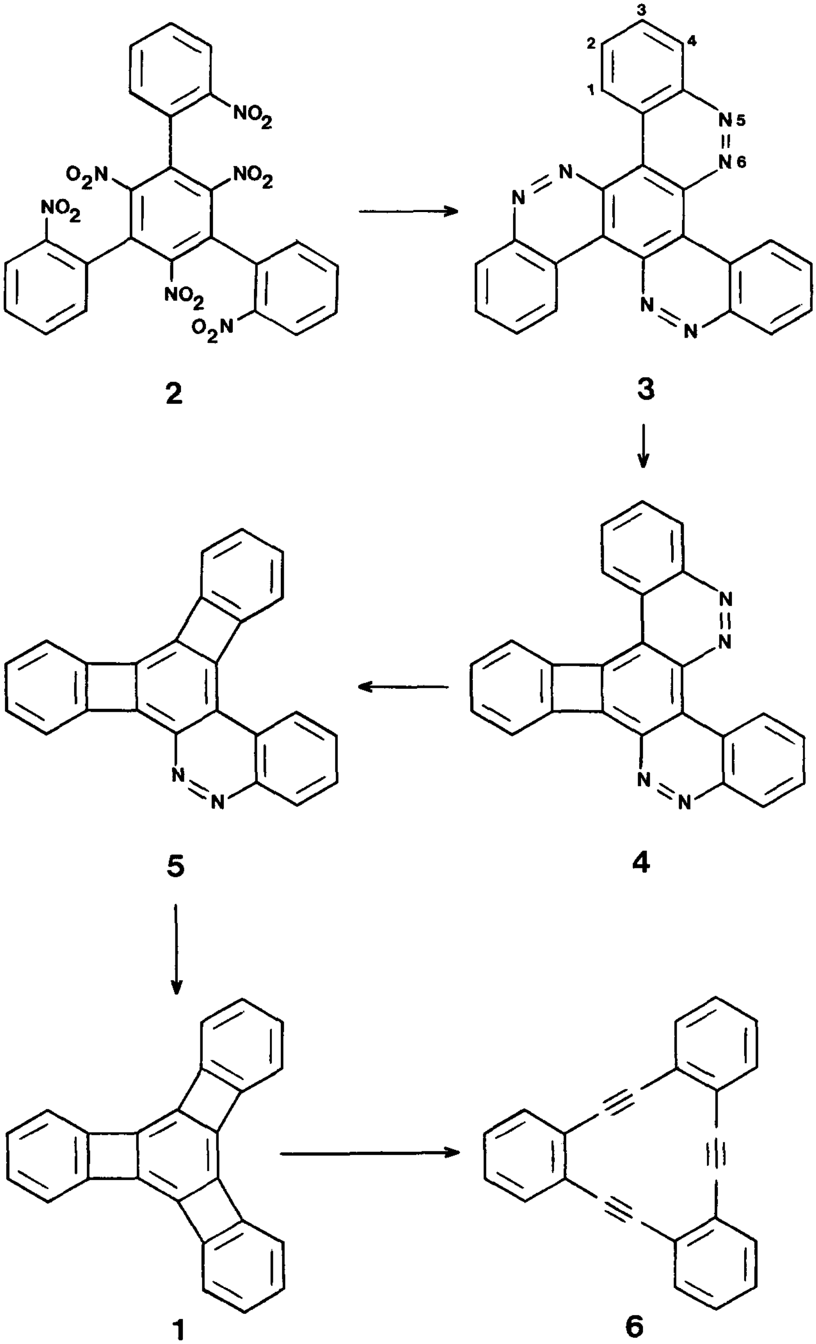
Papers from these laboratories have reported syntheses of the angular and linear benzocyclobutabiphenylenes, the 'sesquibiphenylenes', by thermal extrusion of nitrogen from benzodicinnoline precursors.[1,2] Only in the case of the angular 'sesquibiphenylene' does the possibility exist for the further annelation of a second benzocyclobutene moiety to the central six-membered ring, the present communication describes an attempt to extend our general method to the preparation of the ultimate member of this series, dibenzo[3,4:3',4']dicyclobuta[1,2-a:1',2'-c]biphenylene (1).


1a


1b

This compound is of theoretical interest since the potential antiaromaticity of the fused four-membered rings should force the central ring to adopt a localised and reactive cyclohexatriene bond arrangement (1a). Little or no participation from the high-energy cyclobutadienoid contributor (1b) would be expected. Even in the case of benzo[3,4]cyclobuta[1,2-a]biphenylene, the angular 'sesquibiphenylene', spectroscopic evidence points to the existence of considerable bond-fixation in the central six-membered ring.[2]

A crossed Ullmann reaction of 1,3,5-tribromo-2,4,6-trinitrobenzene in an excess of 1-chloro-2-nitrobenzene gave 2,2',2'',4',6'-pentanitro-5'-(2-nitrophenyl)-1,1':3',1''-


NO2
O2N
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2
3
2
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1
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6

terphenyl (2) (60%) as off-white crystals, m.p. 340-342°C; m/z (%): 530 (M^+-NO_2, 83), 146 (100); ^{1}H NMR: 8.53 - 7.74 (multiplet).[3] Reduction of (2) with hydrazine hydrate/Raney nickel or by catalytic hydrogenation in 0.5% ethanolic sodium hydroxide over palladium oxide gave, on exposure of the reaction solutions to air, the highly insoluble benzo[1,2-c:3,4-c':5,6-c''] tricinnoline (3) (20%) as lemon-yellow crystals, m.p. >360°C (sublimes >340°C); m/z (%): 384 (M^+, 100), 356 (M^+-N_2, 8), 327 (22), 298 (12); ^{1}H NMR ($CDClBr_2$, 100°C): 10.90 (3H, m, $H_{1,7,13}$), 9.05 (3H, m, $H_{4,10,16}$), 8.25 (6H, m, $H_{2,3,8,9,14,15}$).[4] Thermolysis of (3) through a 1 metre silica tube at 780°C/0.005 Torr gave, after preparative TLC on silica in chloroform/hexane, 5,6,11,12,17,18-hexadehydrotribenzo[a,c,i]cyclododecene (6) (8%) as pale yellow crystals, m.p. 210-220°C (polymorphic) (lit. m.p. 219.5 - 220.5°C;[5] 210 - 218.5°C[6]); ^{13}C NMR: 131.9 (C_1), 128.5 (C_2), 122.1 (C_{4a}), 92.9 (C_5), followed by a colourless compound $C_{24}H_{14}N_2$ (7%), m.p. 289-290°C (sublimes >250°C); m/z (%): 330 (M^+, 100), 165 (M^{2+}, 35); ^{1}H NMR: 8.67 - 7.36 (m), the structure of which is under investigation. Further elution of the chromatogram with ethyl acetate separated a mono-extrusion product, probably biphenyleno [1,2-c:3,4-c']dicinnoline, (4) (10%) as red crystals, m.p. >360°C (sublimes >270°C); m/z (%): 356 (M^+, 100), 327 (26), 300 (M^+-$2N_2$, 76); ^{1}H NMR: 10.70 (1H, m), 9.70 (1H, m), 8.66 - 6.63 (10H, complex system of multiplets). Our failure to detect (5) amongst the reaction products is not surprising in view of the ready extrusion of the remaining nitrogen from (4), as evidenced by the mass spectrum.

We have no direct evidence to show at what stage opening of the central ring takes place, however, formation of (6) can best be rationalised by assuming the intermediate generation of (1) followed by a novel (symmetry-allowed[7]) [2 + 2 + 2]retrocyclisation of the benzene ring. Theoretical calculations predict such cycloreversions to be both kinetically and thermodynamically prohibitive[8] (examples of the thermodynamically favourable reverse process, [2 + 2 + 2]thermal cyclotrimerisation, still await discovery[9]). For biphenylene (1) the energy barrier to rearrangement may be reduced by a combination of the lack of aromatic stabilisation due to bond localisation and the significant strain in the central ring. Benzo[3,4]cyclobuta[1,2-a]biphenylene is stable to pyrolysis under similar conditions.

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