

Synthesis of a Trisazahexaradialene and X-Ray Crystal Structure of a Derivative

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Summary The triamine (**4**), obtained by reaction of hexakisbromomethylbenzene with benzylamine, has been structurally elucidated by X-ray crystallography; reaction of (**4**) with *m*-chloroperbenzoic acid and sub-

sequently with a mixture of acetic anhydride and triethylamine yields *NN'N''*-tribenzylbenzo[1,2-*c*:3,4-*c'*:5,6-*c''*]tripyrrole (**3**), the first example of the trisazahexaradialene ring system.

MOLECULES of the hexaradialene type (**1**), which possess an array of six exocyclic double bonds around the central ring, have attracted considerable recent attention.¹⁻³ In contrast, comparatively little work has appeared concerning structurally related systems of type (**2**) which embody three five-membered heterocyclic rings.⁴ We now report the synthesis of the highly reactive tripyrrole (**3**) which possesses the novel trisazahexaradialene ring system.

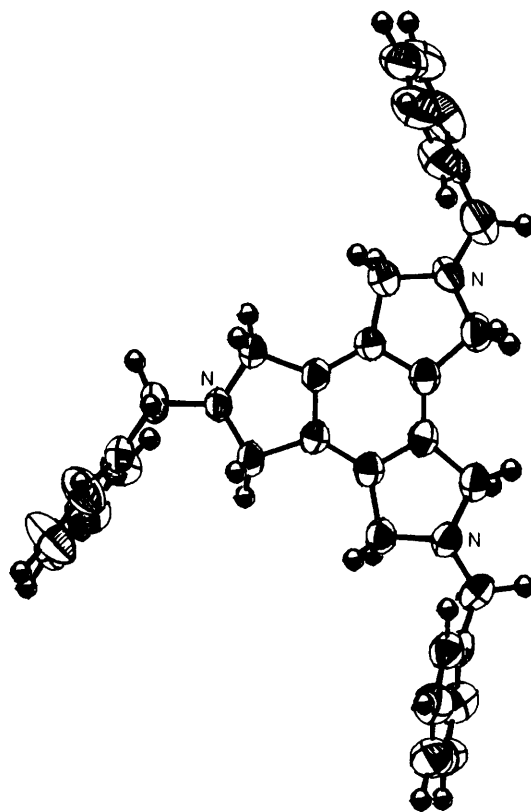
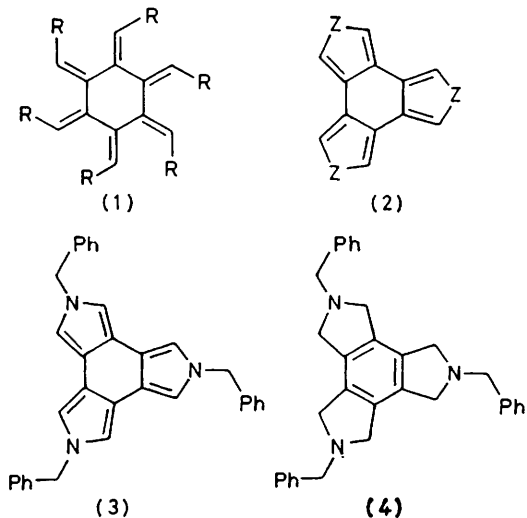


FIGURE. A view of the triamine (**4**) in the crystal, looking directly on to the plane of the central benzene ring. The hydrogen atoms have been given an arbitrary isotropic temperature factor for clarity.

In the course of investigating the reaction of hexakisbromomethylbenzene, $C_6(CH_2Br)_6$ with amines,⁵ we have found that reflux in nitromethane with an excess of benzylamine under Ar allows isolation† of the triamine (**4**), m.p. 201–202 °C (sealed tube) in moderate yield. Structure (**4**) was assigned on the basis of spectroscopic evidence: ¹H n.m.r. $\tau(CDCl_3)$, 6.23 (12H, s), 6.14 (6H, s), and 2.68 (15H, m); ¹³C n.m.r. (δ_c in $CDCl_3$), 57.3(t), 60.2(t), 127.0(d), 128.3(d), 128.6(d), 132.9(s), and 139.1(s) p.p.m.; and gave a satisfactory high-resolution mass spectrum.

Crystal data: (**4**), $C_{33}H_{33}N_3$, monoclinic, space group Cc , $a = 39.521(6)$, $b = 5.538(1)$, $c = 26.701(6)$ Å, $\beta = 115.92(2)^\circ$, $Z = 8$. Cell dimensions and intensity data were obtained with an Enraf-Nonius CAD-4 diffractometer using monochromated Mo- K_α radiation. The structure was solved by direct methods and refined to $R = 0.050$ for 1201 reflections with $I > 2.5\sigma(I)$. In the final cycles of least-squares refinement the hydrogen atoms were included in their theoretical positions with an overall temperature factor whilst all other atoms were refined anisotropically.‡

† Other identified products, for example, hexakis(benzylaminomethyl)benzene, m.p. 181–183 °C, will be described in a full paper, along with details of isolation procedures and other cosolvents employed.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation or this communication.

The Figure shows a view of the molecular structure of (**4**) looking directly on to the central planar benzene ring. The three five-membered rings are non-planar, and two nitrogen atoms lie above the mean plane of central benzene ring, with displacements of 0.30 and 0.34 Å, while the remaining nitrogen atom is displaced 0.49 Å below this plane.

Conversion of (**4**) into (**3**), a process involving the removal of six hydrogen atoms from (**4**), was achieved by an extension of the elegant method of Kreher and Seubert⁶ for the easy transformation of isoindolines into isoindoles. Thus, employing CD_2Cl_2 (or $CDCl_3$) as solvent to allow ¹H n.m.r. monitoring, addition of a slight excess of *m*-chloroperbenzoic acid to a cooled (*ca.* –10 °C), degassed solution of (**4**) caused disappearance of the starting material and formation of a mixture of tris-*N*-oxides which was not isolated: direct treatment with an excess of Ac_2O-Et_3N (1:1, v/v) led, after appropriate work-up, to isolation of (**3**), m.p. 226–227 °C (decomp., sealed tube). The structure of (**3**) was substantiated spectroscopically: ¹H n.m.r.

(CD₂Cl₂), 4.89 (6H, s), 3.09 (6H, s), and 2.77 (15H, m); ¹³C n.m.r. (δ_c in CDCl₃) 53.5 (t), 112.5 (d), 115.6 (s), 126.9 (d), 127.3 (d), 128.5 (d), and 138.5 (s) p.p.m.; *m/e* 465.22031. C₃₃H₂₇N₃ requires *m/e* 465.22049. Minor impurities in samples of (3) can be eliminated by formation of a stable charge-transfer adduct with 1,3,5-trinitrobenzene; ratio *ca.* 1:1 by ¹H n.m.r. spectroscopy.

The tripyrrole (3), formally a heterocyclic analogue of triphenylene, merits a detailed theoretical investigation of

the distribution of its 18 π-electrons.⁷ Interestingly, unlike the corresponding trithiophen (2, Z=S),^{4a} (3) reacts readily with dienophiles and the nature of the products is currently under investigation.

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¹ For syntheses of the parent (1, R = H) see: A. J. Barkovich, E. S. Strauss, and K. P. C. Vollhardt, *J. Amer. Chem. Soc.*, 1977, **99**, 8321; P. Schiess and M. Heitzmann, *Helv. Chim. Acta*, 1978, **61**, 844; L. G. Harruff, M. Brown, and V. Boekelheide, *J. Amer. Chem. Soc.*, 1978, **100**, 1893.

² H. Hopff and A. K. Wick, *Helv. Chim. Acta*, 1961, **46**, 380; W. Marsh and J. D. Dunitz, *ibid.*, 1975, **58**, 707.

³ H. Hopff and A. Gati, *Helv. Chim. Acta*, 1965, **48**, 1289.

⁴ (a) For a very recent synthesis of a trisithiahexaradialene, (2, Z = S), see H. Hart and M. Sasaoka, *J. Amer. Chem. Soc.*, 1978, **100**, 4326; (b) a possible synthetic route for the preparation of (2, Z = NMe) has been proposed: J. Ciric, S. L. Lawton, G. T. Kokotailo, and G. W. Griffin, *J. Amer. Chem. Soc.*, 1978, **100**, 2173.

⁵ Cf. A. D. U. Hardy, D. D. MacNicol, and D. R. Wilson, *J.C.S. Chem. Comm.*, 1977, 525.

⁶ R. Kreher and J. Seubert, *Angew. Chem. Internat. Edn.*, 1964, **3**, 639; 1966, **5**, 967.

⁷ Cf. E. Chacko, J. Bornstein, and D. J. Sardella, *J. Amer. Chem. Soc.*, 1977, **99**, 8248.