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A carboranylpentaphenylbenzene

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Abstract—1-(*o*-Carboran-9-yl)-2,3,4,5,6-pentaphenylbenzene (**1**) was prepared by the Diels–Alder reaction of 9-phenylethynyl-*o*-carborane and tetraphenylcyclopentadienone at 300 °C. An X-ray crystal structure of **1** shows that the steric demands of the carborane induce a significant stretching of the aryl carbon–boron bond as well as a variety of distortions of the central benzene ring, the *ortho* phenyl groups, and the carborane cage.
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During a recent study of poly(*tert*-butyl)polyphenyl-naphthalenes,[1] we carried out several lengthy searches of the Cambridge Structural Database[2] (CSD) for crowded arenes with substituents more sterically demanding than phenyl groups. As one might expect, tertiary alkyl and bulky silyl groups are among the most common large substituents, but a surprising (to us) omission is the absence of the icosohedral boranes in sterically demanding environments. For example, there are several dozen structures of mono-, di-, and triarylcarboranes, but only three of these have substituents on the arene larger than hydrogen at the positions *ortho* to the carborane, and even these are limited to the smaller halogens.[3,4] Carboranes are interesting bulky groups because of their great stability and the presence of five atoms, rather than three, bonded to the site of attachment. We therefore decided to prepare the carboranylpentaphenylbenzene **1** in order to examine a carborane in a very crowded environment. In this arylcarborane, both *ortho* substituents on the arene are phenyl groups, and these are further buttressed by the three remote phenyls. There is clearly insufficient space on the periphery of a planar benzene ring to accommodate these substituents, but what degree of distortion would be observed in **1**?

The synthesis of **1** proved to be straightforward. Iodination and alkynylation of *o*-carborane (**2**) by the
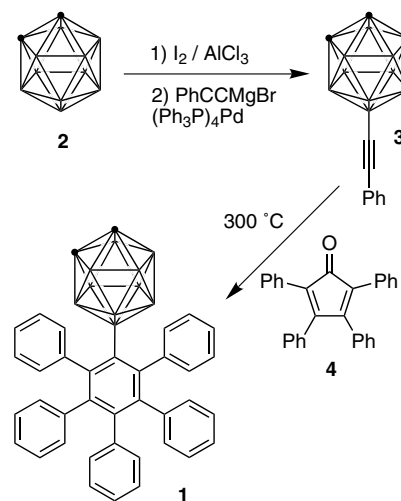
methods of Andrews et al.[5] and Zakharkin et al.[6] gave the known 9-(phenylethynyl)carborane (**3**) in 52% overall yield. This material was then mixed with a threefold excess of tetraphenylcyclopentadienone (**4**) in a Pyrex screw-capped tube, and the solid mixture was heated at 300 °C for 2 h. After cooling, the residue was dissolved in dichloromethane, and methanol was added to precipitate crude compound **1**. Preparative TLC (silica gel GF; 2:1 hexanes–benzene) gave pure **1** in 85% yield.[7] Single crystals of **1** were obtained by the slow evaporation of solutions in dichloromethane–methanol.

The molecular structure[8] of compound **1** is illustrated in Figure 1 (with the crystallographic numbering scheme

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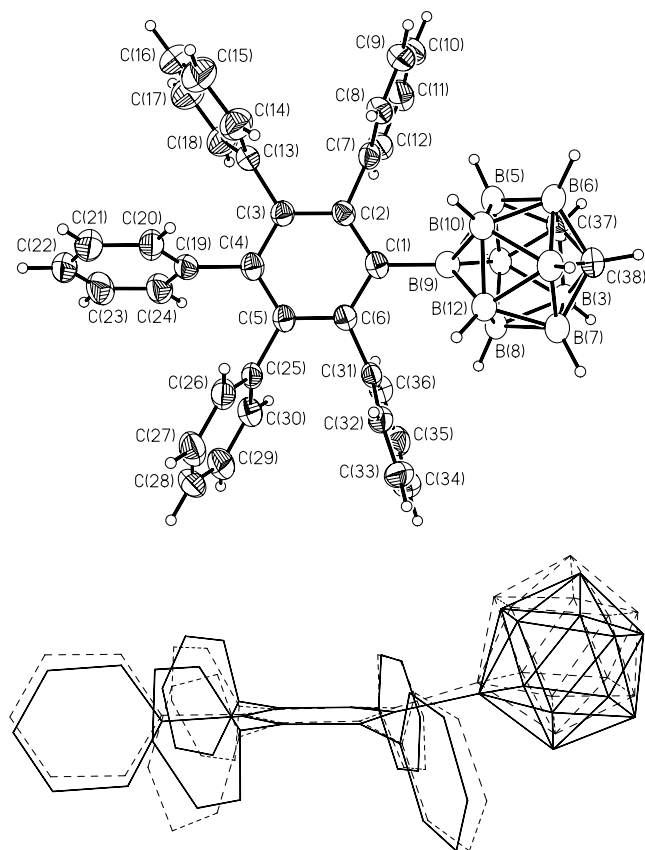
Figure 1. Top: molecular structure of compound **1**; thermal ellipsoids have been drawn at the 50% probability level. Bottom: Overlay of the experimental (solid lines) and B3LYP/6-31G(d) calculated (dashed lines) structures of compound **1**; hydrogen atoms have been omitted for clarity.

used in this discussion). In order to accommodate the extra bulk of the carborane, the central benzene ring is significantly distorted from planarity, the flanking phenyls are bent back from the carborane, and the *ipso* atoms of the carborane [B(9)] and the two flanking phenyl groups [C(7) and C(31)] are strongly displaced from the mean plane of the central benzene ring. Specifically, the angles C(3)–C(2)–C(7) and C(5)–C(6)–C(31) are narrowed to 115.1(2)° and 114.5(2)°, respectively, B(9) lies 0.345(5) Å above the mean plane of the central aromatic ring, and C(7) and C(31) lie 0.233(4) Å and 0.199(4) Å, respectively, below it. Most interesting, the B(9)–C(1) bond is significantly stretched, with a bond distance of 1.624(4) Å, compared to an average distance of 1.578(9) Å for 14 similar boron–carbon bonds in good quality, well ordered structures of aryl carboranes in the CSD. Indeed, the entire carborane cage appears to be stretched: the B(9)–C(38) distance in **1** is 3.298(4) Å, but 12 similar distances in aryl carboranes in the CSD average only 3.232(12) Å.

Figure 1 also shows an overlay of the B3LYP/6-31G(d)-optimized[11] structure of **1** with its X-ray structure. The conformations of the solid-state and calculated gas-phase structures are similar, with the out-of-plane deflections of the central ring's substituents being

slightly greater than for the X-ray structure. The calculation also reproduces the stretching of the B(9)–C(1) bond (1.632 Å) and the carborane cage [B(9)–C(38) = 3.305 Å] (the corresponding distances in the B3LYP/6-31G(d)-optimized structure of simple 9-phenylcarborane are 1.584 Å and 3.254 Å).

There is only one structure in the CSD in which a common bulky substituent is placed in an environment similar to that of the carborane in **1**: 1,3,5-tris(trimethylsilyl)-2,4,6-triphenylbenzene.[12] This molecule, at least, shows significantly less distortion of the central benzene ring and its substituents than is observed in compound **1**. Despite the distortion in **1**, it is extremely stable, surviving even the severe conditions of its synthesis (300 °C, 2 h, no solvent) without much, if any, decomposition. It will be interesting to see if a benzene ring bearing two *ortho o*-carboranes can be prepared; such a molecule would be exceptionally distorted from a 'normal' geometry.

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7. For **1**: mp 344–345 °C. ^{1}H NMR (CDCl$_3$) δ 1.15–2.55 (v br m, 9H), 3.08 (s, 1H), 3.31 (s, 1H), 6.66–6.79 (m, 15H), 7.00 (m, 6H), 7.09 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 52.3, 52.9, 124.8, 125.0, 126.0, 126.2, 126.3, 126.5, 131.2, 131.6, 133.6, 139.9, 140.5, 141.1, 141.6, 143.6, 147.0 (17 of 18 expected resonances); MS, *m/z* 601 (M$^+$ [^{10}B^{11}B$_9$], 100), 600 (M$^+$ [^{10}B$_2$^{11}B$_8$], 96); IR (KBr) ν_{max} 3076, 3056, 3021, 2924, 2600 (s, BH), 1599, 1493, 1441, 1384, 1072, 1026 cm^{-1}; exact mass 600.3826, calcd for C$_{38}$H$_{36}$^{10}B$_2$^{11}B$_8$ 600.3820.
8. Crystal data for **1**: C$_{38}$H$_{36}$B$_{10}$; orthorhombic, space group *Pna*2$_1$ (No 33); *a* = 20.7930 (9) Å, *b* = 23.4956 (10) Å, *c* = 6.7873 (2) Å, *V* = 3315.9 (2) Å^3, *Z* = 4. A colorless blade (0.52 mm × 0.10 mm × 0.08 mm) was used for data collection using Mo Kα radiation on a Nonius KappaCCD diffractometer at 200 K. A total of 23,287 reflections (θ_{max} = 27.44°) were reduced to 7369 unique reflections by using the program DENZO-SMN.^{9} The structure was solved by direct methods and it was refined by using Siemens SHELXTL.^{10} All nonhydrogen atoms

were refined anisotropically, and all but two hydrogens were included with a riding model [C–H = 0.95 Å, B–H = 1.12 Å, $U(H) = 1.2U(C)$ or $1.2U(B)$]. The hydrogen coordinates of the C–H groups of the *o*-carborane, for which there is no riding model in SHELXTL, were refined. $R(F) = 0.0597$, $wR(F^2) = 0.1178$, and $S = 1.103$ for 4869 reflections with $I > 2\sigma(I)$, and $R(F) = 0.1063$, $wR(F^2) = 0.1404$, and $S = 1.054$ for 7369 unique reflections, 439 parameters, and 1 restraint. Crystallographic data (excluding structure factors) for this structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 224004. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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