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Distorted benzene bearing two bulky substituents on adjacent positions: structure of 1,2-bis(1,2-dicarba-*closo*-dodecaboran-1-yl)benzene

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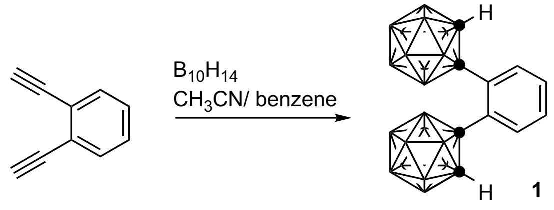
Abstract—Synthesis and structural analysis of 1,2-bis(*o*-carboranyl)benzene were performed to examine the steric effects of the two extremely bulky *o*-carborane cages at adjacent positions on the planarity of the benzene ring. X-ray crystallographic analysis supported by DFT calculations revealed that the benzene ring is significantly deformed by the bulky *o*-carboranyl groups.

Highly strained compounds in which substituents are forced into close proximity by the molecular geometry are of interest in structural chemistry. In particular, distortion of the benzene ring is of great interest and importance for better understanding of aromaticity and its role in the stabilization of organic molecules. Studies in this area include the preparation of 1,2,3,5-tetra-*t*-butylbenzene,[1] dimethyl 3,4,5,6-tetra-*t*-butylphthalate,[2] hexakis(trimethyl-germyl)benzene,[3] and hexakis(trimethylsilyl)benzene.[4] In the crystal structures of the latter hexasubstituted benzenes, the benzene ring is distorted to a chair form with the average C_{benz}–C_{benz}–C_{benz}–C_{benz} torsional angles of 6.8° and 8.5°, respectively. Even disubstituted benzene derivatives with sufficiently large groups in the *ortho* positions show significant distortion of the ring. For instance, in 1,2-di-(1-adamantyl)benzene the C_{benz}–C_{benz}(Ad)–C_{benz}(Ad)–C_{benz} torsional angle is 7.1°.[5] To test the extent of benzene ring distortion by two *ortho* substituents, we focused on dicarba-*closo*-dodecaborane (carborane) as an extremely bulky group.

The carboranes are icosahedral boron clusters with unusual electronic structure[6] and properties,[7] which offer remarkable thermal and chemical stability, a hydrophobic surface,[8] and nearly spherical geometry. Considering the size and the topology, carboranes are expected to be more effective substituents for imposing distortion on the benzene ring than adamantane. In this letter, we report the preparation and structure of 1,2-bis(*o*-carboranyl)benzene (**1**), and show that it has the most distorted benzene ring bearing only two substituents studied to date.[9]

The preparation of 1,2-bis(*o*-carboran-1-yl)benzene (**1**), shown in Scheme 1, utilizes a general reaction of decaborane(14) with an acetylenic compound in the presence of



Scheme 1.

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Lewis bases.[6] Thus, reaction of 1,2-diethynylbenzene[10] with decaborane(14) in acetonitrile–benzene under reflux for three days afforded 1,2-bis(*o*-carboran-1-yl)benzene (**1**) in 10% yield.[11] The procedure using Et_2S as a Lewis base instead of acetonitrile did not work in the preparation of **1**, even though it has been demonstrated to be effective for the synthesis of 1,2-diaryl-*o*-carboranes[12] and aryl derivatives containing more than one carborane substituent.[13]

The ^1H NMR spectrum of **1** is unremarkable, except for a 0.25 ppm downfield shift of aromatic protons *ortho* to the electron-withdrawing carboranyl groups. The signals of the aromatic protons of **1** appear at 7.75 and 7.34 ppm, while the protons of 1-phenyl-*o*-carborane (**2**)[14] appear at 7.50 (*ortho*), 7.34 (*meta*), and 7.38 (*para*) ppm. However, X-ray crystallographic analysis revealed that the benzene ring in **1** is significantly deformed by the bulky *o*-carboranyl groups, as shown in Figure 1.[15]

Analysis of the molecular geometry of **1** (Fig. 2)[16] shows that the C(1)–C(2) bond in benzene is elongated by about 0.04 Å while the opposite C(4)–C(5) bond is contracted by about 0.02 Å relative to the normal value of 1.39 Å found in the solid state structure of benzene.[17] Similar alternation of the C–C bond lengths in the benzene ring was reported for the diadamantyl analog.[18] The C(1A(cage A))–C(1)–C(2) and C(1)–C(2)–C(1B(cage B)) angles are expanded by about 11° and 13°, respectively, and the two carboranyl substituents are forced out of plane to form the C_{Carb}–C(1)–C(2)–C_{Carb} dihedral angle of 26.7° (Fig. 2c and d). At the same time, the benzene ring is twisted and the C(3)–C(2)–C(1)–C(6) angle is 12.6° (Fig. 2c and d). The corresponding values reported for 1,2-diadamantanylbenzene are 16.6° for the C_{Ad}–C(1) and C(2)–C_{Ad}, and 7.1° for C(3)–C(2)–C(1)–C(6), respectively.[5,18]

This observed deviation from the ideal geometry of the benzene ring implies that considerable strain is imposed on for the sp^2-hybridized carbon atoms in **1**. Using a homodesmotic reaction shown in Scheme 2 and SCF energies for each molecule,[19,20] the total strain energy (SE) in **1** was estimated to be 31 kcal/mol. To assess the contribution to the SE from the distorted benzene

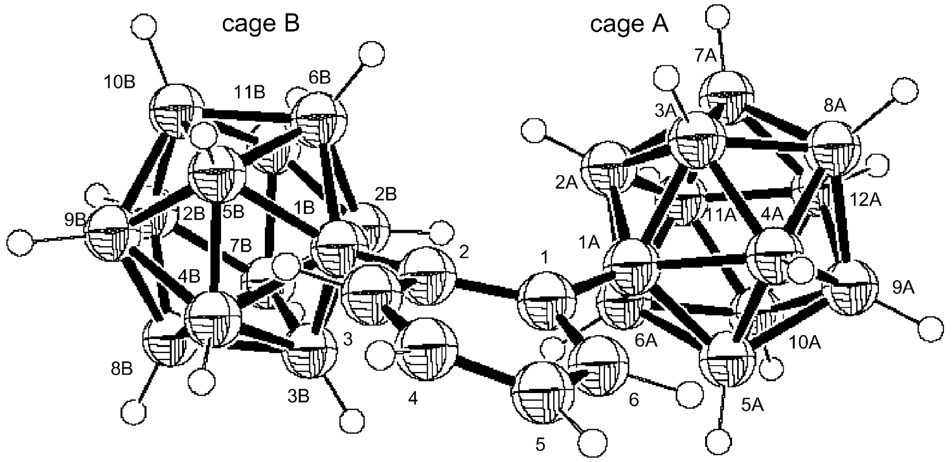
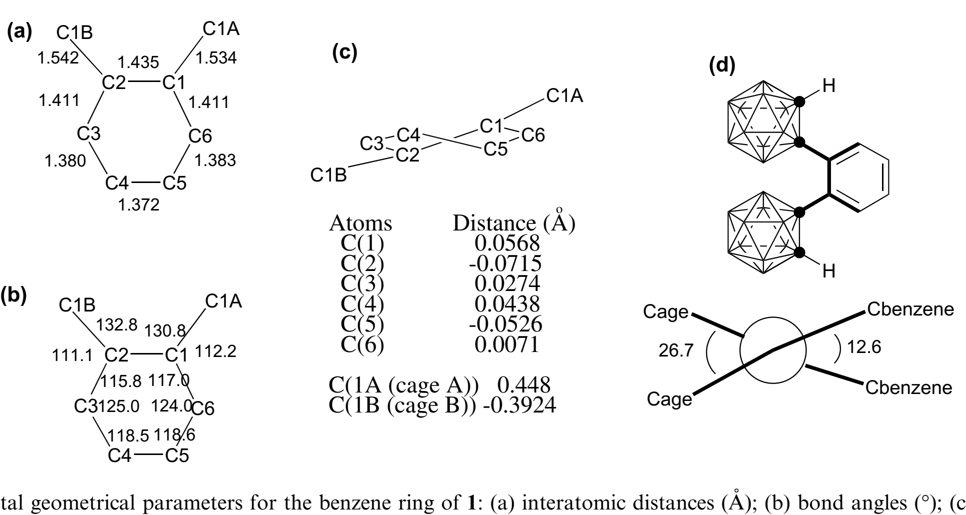
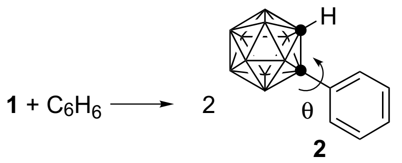


Figure 1. Thermal ellipsoid diagram for **1**.



Atoms	Distance (Å)
C(1)	0.0568
C(2)	-0.0715
C(3)	0.0274
C(4)	0.0438
C(5)	-0.0526
C(6)	0.0071
C(1A (cage A))	0.448
C(1B (cage B))	-0.3924

Figure 2. Experimental geometrical parameters for the benzene ring of **1**: (a) interatomic distances (Å); (b) bond angles (°); (c) deviation from the optimum plane (Å); (d) key dihedral angle values (°). The standard deviations are 0.003 Å and 0.2°.



Scheme 2.

ring, the SCF energy of benzene was obtained at the geometry calculated for **1**. The carboranyl groups were replaced with hydrogen atoms and all six C–H distances were optimized. A comparison with benzene at the D_{6h} symmetry shows that the distortion of the ring in **1** is worth 12 kcal/mol. Similar calculations for 1,2-diadamantyl-benzene show a total SE of 28 kcal/mol, out of which only 3 kcal/mol is associated with benzene ring distortion. These results indicate that the remaining 19 kcal/mol of SE of **1** is related to bond elongation in and steric interactions of the carboranyl units (see Fig. 1).

In general, the largest distortions of the carborane cages in **1** are observed in the vicinity of atom C(1A) connected to the benzene ring, and these deformations are significantly greater for cage A than for cage B. Thus, in the former cage the C(1A)–C(2A), C(1A)–B(4A), C(2A)–B(6A), C(2A)–B(7A), and C(2A)–B(11A) bonds are markedly elongated by 0.05–0.06 Å, while the B(3A)–B(4A) and B(3A)–B(7A) are contracted to a similar extent, relative to those in both crystallographic modifications of **2**.[21a,b] For comparison, the biggest changes in bond lengths in cage B of about 0.02–0.03 Å are observed for the expanded C(1B)–B(5B), C(2B)–B(7B), and C(2B)–B(11B), and contracted B(4B)–B(8B), B(4B)–B(9B) bonds relative to those in **2**. The remaining interatomic distances in the carborane cages are less affected by the steric congestion and typically are within 0.02 Å of those reported for **2**.

Other major factors contributing to the molecular SE of **1** are the C_{benz}–C_{Carb} bond lengths, which are expanded by about 0.02–0.04 Å relative to those in **2**, and the close C(2A)H$\cdots$HC(2B) non-bonding interatomic distance of 1.912 Å (Fig. 1), which corresponds to 80% of the van der Waals separation.[22]

The results demonstrate that 1,2-bis(*o*-carboran-1-yl)-benzene (**1**) has the most distorted benzene ring structurally characterized to date.

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