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Carboranophanes

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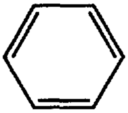
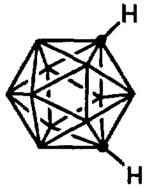
Abstract: *m*-Carboranes bridged by a single all-carbon chain or a carbon and sulfur bridge are synthesized from 1,7-bis(mercapto)-*m*-carborane by an alkylation-oxidation-pyrolysis route.

The analogy between the two-dimensional benzenes and the three-dimensional carboranes has often been made.[1] One of the most intriguing chapters of benzene chemistry has involved the cyclophanes in which the 1,4- or 1,3-positions of one or more benzene rings are bridged. In the singly bridged [*n*]cyclophanes, short chains spanning the ring induce bending of the benzene ring. In the smaller [*n*]cyclophanes distortion from planarity is severe, and stability sharply reduced.[2] As noted by Cram,[3] and Kane, *et al.*,[2b] the early syntheses of [*n*]cyclophanes used conventional synthetic techniques (acyloin condensations, S_N2 displacements, for example) to generate compounds to which further conventional ring-contraction procedures could be applied to make really interesting molecules. Here we report what we hope will be a similar beginning to an expanding chemistry of "carboranophanes" in which non-adjacent vertices of carboranes are spanned.



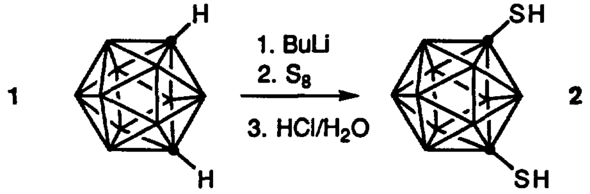
Benzene, the archetypal two-dimensional aromatic molecule

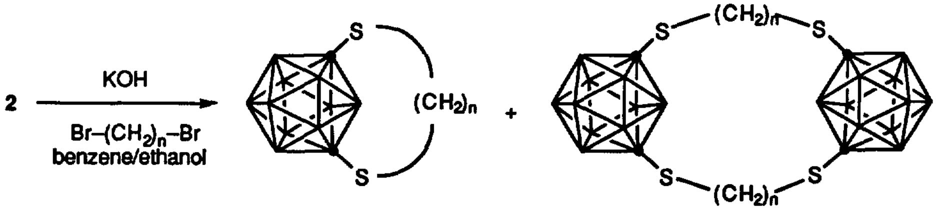


meta-carborane, a three-dimensional aromatic molecule. The dots mark the carbons; the remaining vertices are B-H groups.

There are already many carboranes known in which adjacent atoms are bridged by atoms or chains. Fascinating though many of these molecules are,[4] they are not carboranophanes. They bear the same relation to the carboranophanes as tetralins and dihydroanthracenes do to the cyclophanes. Until the rings become very small, such molecules are unlikely to experience substantial strain. There is, in fact, a single example of a complex carboranophane already known, an exquisite three-fold array of alternating *meta*-substituted benzenes and *meta*-carboranes constructed by Wade and his group.[5] Our method leads to simpler molecules, in which a single cage is bridged by a carbon and sulfur or an all-carbon bridge.

We started with *m*-carborane, **1**, in which the carbons are in a 1,3-relationship to each other. This compound was converted into the known dithiol, **2**, by straightforward procedures.[6] Solutions of KOH in ethanol and of **2** and the 1,n-dibromoalkane in benzene were added simultaneously to refluxing ethanol. This led to the three [*n*]carboranophanes **3-5**, along with much larger amounts of the more complicated [*n.n*]carboranophanes **6-8**. Identification was by the usual examination of spectra, and single crystal X-ray diffraction of **4** and **7**.





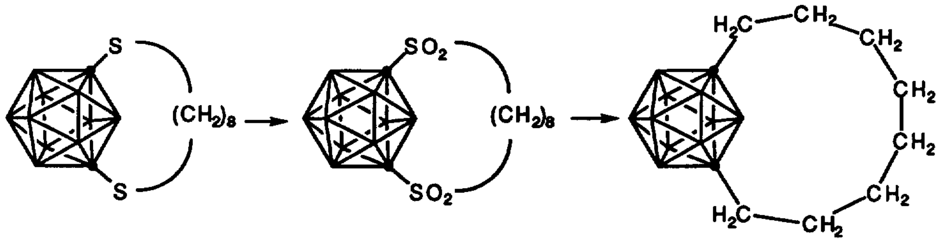
3, n = 8, mp 173.5-175 °C, 4%
4, n = 7, mp 174-176 °C, 2%
5, n = 6, mp 156-157 °C, 0.5%

6, n = 8, mp 178-181 °C, 44%
7, n = 7, mp 207.5-209 °C, 14%
8, n = 6, mp 234-236.5 °C, 9%

Here we quote spectral data for **4** and **7**, but the analyses for the other compounds were comparable. The molecular weights and elemental compositions were determined through precise mass spectrometry. The ^1H NMR spectra of the two compounds were very similar, each showing a triplet for the hydrogens adjacent to sulfur (**4**, δ 2.85 ppm, 2H, **7**, δ 2.78 ppm, 2H), a multiplet for the hydrogens β to sulfur (**4**, δ 2.05-1.87 ppm, 2H, **7**, δ 1.70-1.55 ppm, 2H), and multiplets at higher field for the other methylene groups (**4**, δ 1.7-1.6 ppm, 3H, **7**, δ 1.45-1.35 ppm, 3H). These last positions are difficult to determine with precision because of the underlying absorptions of the boron-attached hydrogens. The coupled ^{11}B NMR spectrum of **4** showed the expected 2:4:2:2 pattern of doublet borons. These signals collapsed on decoupling to singlets at δ –5.10, –9.87, –11.56, and –13.49 ppm, referenced to external boron trifluoride etherate. Compound **7** was less clean, showing three doublet signals in the coupled ^{11}B spectrum which collapsed on decoupling to singlets at δ –6.07, –10.81, and –12.77 ppm.

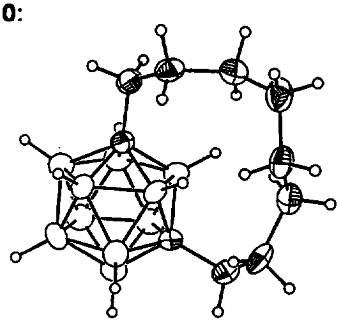
None of these data unequivocably distinguishes these compounds as *meta*-, not *ortho*-carboranes. Even though there seemed little doubt that the original meta relationship of the carbons would be preserved, the conversion of *ortho*- to *meta*-carboranes is well known at > 400 °C,[1] and it seemed just barely possible that strain induced by the bridge both lowered the activation energy for the rearrangement and reversed the normal thermodynamic preference for *meta*-carboranes over *ortho*-carboranes. Accordingly, we examined single crystals of **4** and **7** by X-ray diffraction. A colorless prism of **4** measuring 0.28 mm x 0.42 mm x 0.42 mm was analyzed with a Siemens P4 diffractometer equipped with graphite-monochromated Mo Ka radiation ($\lambda = 0.71073$ Å).[7] The structure was solved in the monoclinic space group $P2_1/n$ (No. 14) by direct methods,[8] and refined by full-matrix least-squares.[9] Although only a preliminary X-ray evaluation was made of the structure of **7**, like **4**, it is clearly still a *meta*-carborane.

Carboranophane **3** could be oxidized to disulfone **9**. Pyrolysis of **9** at 500 °C, led to a single compound **10** of the formula $C_{10}B_{10}H_{26}$ as judged by mass spectrometry. Once again, the structure was confirmed by X-ray diffraction. A colorless arrowhead-shaped fragment roughly 0.05 mm x 0.12 mm x 0.48 mm was analyzed in the same fashion as were **4** and **7**. The structure was solved in the orthorhombic space group Pbca (No. 61) by direct methods (Figure).[8]



9 **10**

Figure: The Structure of **10**:



As can be seen from the ^{1}H NMR spectra of all these carboranophanes, no upfield shifts for the hydrogens on the bridge are observed. By contrast, in [8]paracyclophane, a molecule very roughly comparable to **5**, there is a signal as high as δ 0.19 ppm.[10] In carboranes, the frontier orbitals are directed inwards, and no effects analogous to those produced by ring currents in benzene-based cyclophanes are to be expected. It would be quite another story were an NMR-active nucleus to be located inside the cage.[11]

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