Carborods

Icosahedral carborane modules can be linked with each other by direct C–C bond formation, through a linking moiety such as alkylene, alkenylene, alkynylene and arylene groups, or a metal center such as Hg. The intermodular linkage can be made at a carbon vertex or at a boron vertex of the carborane cage. The functionalization of the C–H vertices of carborane is easily accomplished via metallation. Electrophilic substitution reactions at the B–H vertices of the aromatic carborane modules are comparable to those observed with aryl groups. If the modular components are linked in a cyclic array the macromolecular construct is identified as a carboracycle, but if they are linked in a rigid linear assembly the resulting oligomer is called a carborod.

The following graphic represents a survey of representative linear rigid rods based on carboranes which were synthesized by the Hawthorne group in the order in which they appeared in the chemical literature.

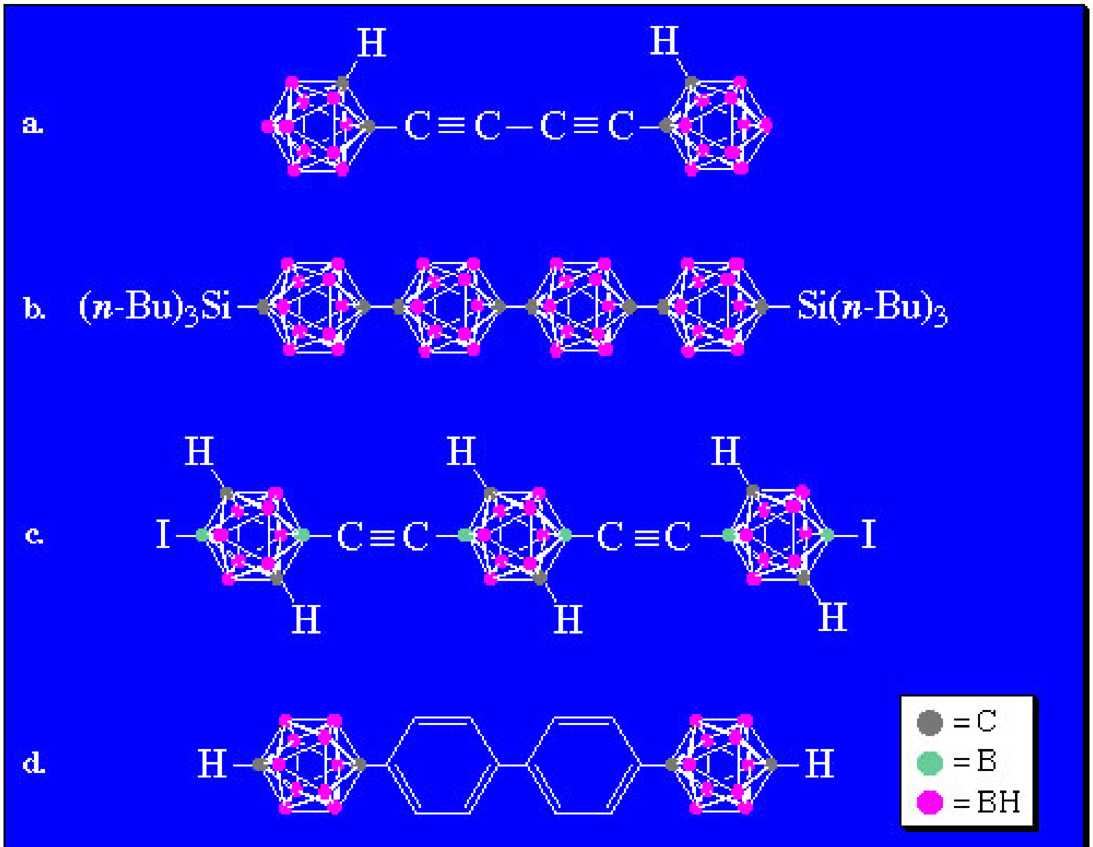
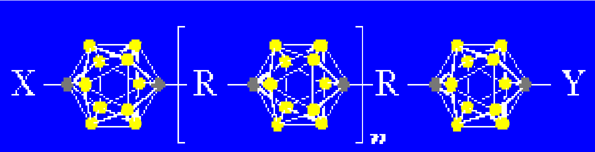


Figure 1. Representative examples of the variety of carborods which have been synthesized.

Carborods are thick compared to known rigid-rod molecules such as [n]staffanes, [n]rodanes, and [n]cubanes. Their van der Waals diameter is approximately 7 Å. The high symmetry of the carborane cage results in uniformly filled space around the longitudinal axis of the carborod, thus providing a cylindrical shape. The lengths of carborods are commonly integral multiples of about 4.5 Å (the average length of the carborane, plus the incremental distance for the linker and endcap). In this manner, the span of a carborod can be tailored to match individual applications. The tetramer (17.2 Å long) depicted in Figure 1b is the longest *para*-carborod to be structurally characterized by X-ray diffraction.

In the past 10 years, there has been a dramatic increase in both the syntheses and applications of rigid rod molecules which can be used as building blocks or modules to create supramolecular arrays. Carborod-based supramolecular structures have been demonstrated to be useful as building blocks for molecular scaffolding and supramolecular constructs, polymers for high temperature applications and semi-permeable membranes, self-assembled monolayers and Langmuir-Blodgett films, neutron shielding materials, ceramic precursors, and as materials for non-linear optics.

The *para*-carborods are only sparingly soluble. Thus, one major goal of carborod chemistry is to increase their solubilities by substituting the B–H vertices of the molecular cage units with solubilizing substituents. This can be accomplished by using camouflaged carboranes, like per-*B*-methylated *para*-carborane, which will provide excellent solubility in hydrophobic hydrocarbon solvents. In principle, per-*B*-hydroxylated *para*-carborane could be utilized to synthesize a hydrophilic rod. Figure 2 shows a universal *para*-carborod to demonstrate/summarize the research activities that are currently in progress. The investigations include the variation of the terminal substituents (X, Y), the type of linkage (R), the substituents at the B–H vertices of the cage (R’), and the isomeric carborane used (*ortho-*, *meta-*, *or para-*) in modular construction. In this manner, the dimensions, solubility, and function of the resulting carborod may be tuned to fulfill a particular purpose.



(a) $n = 0$, $X = H$, Y = polar group

(b) $n = 0 - \infty$, $X = Y = H$

(c) $n = 0 - \infty$, $X = Y = L_mM$

● = C ○ = BR'
R = $-C\equiv C-$, arylene
R' = alkyl, alkoxy, or OH

Figure 2. A generalized representation of a series of *para*-carborods.

If Y in **2a** represents a polar group such as –COOH or $-SiCl_3$ the dimeric rod is suited for the generation of an ordered monolayer on water or silica. Polymeric rods resembling **2b** represent potential candidates for liquid-crystal applications. Molecules of type **2c** which are terminally substituted with metal centers in different oxidation states may serve as molecular wires allowing the metal centers to communicate electronically. Furthermore, cross-coupling the three isomeric icosahedral carboranes via suitable linkers will lead to mixed, three-dimensional carborod-like constructs (e.g. “carboboxes”). This endeavor, if successful, could provide a large advance toward a real molecular “tinker toy” construction set based upon aromatic organoborane components.

Selected References:

Kenneth P. Callahan and M. Frederick Hawthorne, "Organometallic Reactions of 1-Ethynyl-1,2-carborane,” *J. Am. Chem. Soc.*, *95*, 4574, (**1973**).

Xiaoguang Yang, Wei Jiang, Carolyn B. Knobler and M. Frederick Hawthorne, "Rigid-Rod Molecules: Carborods. Synthesis of Tetrameric *p*-Carboranes and the Crystal Structure of Bis(tri-*n*-Butylsilyl)-Tetra-*p*-Carboranes,” *J. Am. Chem. Soc.*, *114*, 9719, (**1992**).

Wei Jiang, Carolyn B. Knobler, Mark D. Mortimer, and M. Frederick Hawthorne, "A Camouflaged Icosahedral Carborane: Dodecamethyl-1,12-dicarba-*closo*-dodecarborane(12) and Related Compounds," *Angew. Chem.*, *34*, 1332, (**1995**).

Wei Jiang, David E. Harwell, Mark D. Mortimer, Carolyn B. Knobler and M. Frederick Hawthorne, "Palladium-Catalyzed Coupling of Ethynylated *p*-Carborane Derivatives: Synthesis and Structural Characterization of Modular Ethynylated *p*-Carborane Molecules," *Inorg. Chem.*, *35*, 4355, (**1996**).

Laura J. Yeager, Fusayo Saeki, Kenneth Shelly, M. Frederick Hawthorne and Robin L. Garrell, "A New Class of Self Assembled Monolayers: *closo*-$B_{12}H_{11}S^{3-}$ on Gold," *J. Am. Chem. Soc.*, *120*, 9961, (**1998**).

Toralf Peymann, Axel Herzog, Carolyn B. Knobler, and M. Frederick Hawthorne, "Aromatic Polyhedral Hydroxyborates: Bridging Boron Oxides and Boron Hydrides," *Angew. Chem. Int. Ed.*, *38* (8), 1061, (**1999)**.

Axel Herzog, Andreas Maderna, George N. Harakas, Carolyn B. Knobler and M. Frederick Hawthorne, "A Camouflaged *Nido*-Carborane Anion: Facile Synthesis of Octa-*B*-methyl-1,2-dicarba-*closo*-dodecaborane(12) and Its Deboration Reaction," *Chem. Eur. J.*, *5*, 1212, **(1999)**.