

Boranes, Boron: the Amazing Element, and Applications

ACCOUNTS OF CHEMICAL RESEARCH

VOLUME 6

NUMBER 8

AUGUST, 1973

Three-Center Bonds in Electron-Deficient Compounds. The Localized Molecular Orbital Approach

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Received December 18, 1972

Having more valence atomic orbitals than valence electrons, electron-deficient compounds present ambiguities in the use of the paired electron bond. Molecular orbitals, at least of stable neutral compounds, are filled usually with a substantial energy gap to the lowest unoccupied excited orbital. However, molecular orbitals based upon the molecular symmetry group are delocalized. Moreover, they are not readily transferable to chemically closely related molecules.

Here, we seek a middle ground: nearly transferable multicenter bonds. We derive localized molecular orbitals (LMO's) objectively from accurate self-consistent field (SCF) molecular orbital (MO) theory. We explore the limits of transferability of these LMO's in the boranes, carboranes, and their related ionic species. Finally, we only begin to ask how these LMO's restrict the compositions, geometries, and reaction pathways in this area of chemistry.

Localized Molecular Orbitals

Recent studies have considerably narrowed the gaps between resonance descriptions of these molecules^{1,2} and molecular orbital results.^{3,4} Extended Hückel theory, developed in this laboratory,^{4,5} has been related^{6,7,8} to rigorously defined SCF theory^{9,10} of complex molecules. Leaving aside the severe limitations of SCF theory when electron correlation¹¹ is important, we note that it yields good approximations to electron density and to properties derived from one-electron operators,¹²⁻¹⁴ like the dipole moment and nmr shielding constants.

Here, we start with symmetry MO's. Their conversion to localized chemical bonds is achieved by mixing MO's of different symmetries. For example, con-

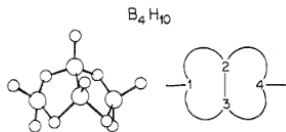


Figure 3. Geometrical and localized valence structure of B_4H_{10} . One terminal hydrogen is omitted from each boron (or, later, carbon) atom. The extra terminal H is indicated by a straight line, and the bridge hydrogen by a curved line.

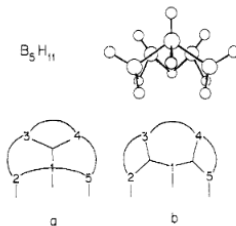


Figure 4. B_5H_{11} . Structure a, with an open three-center B(2)-B(1)-B(5) bond, is not favored by the localization, which yields central three-center bonds idealized in structure b.

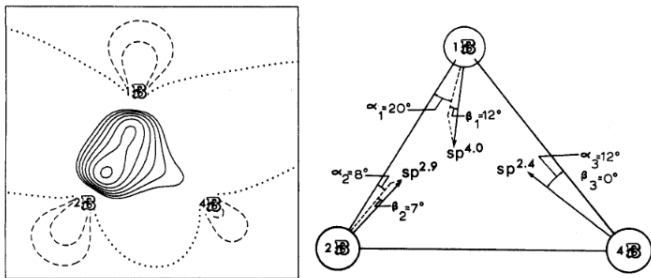
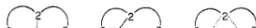


Figure 5. (a) One of the two localized three-center orbitals in the boron framework of B_6H_{11} . The electron density is obtained by squaring this function. (b) Hybrids resulting from the localization procedure.



Figure 6. B_6H_{10} , which localizes uniquely.



3D Aromaticity of Closo Polyhedral Borane Anions

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Journal of the American Chemical Society / 100:11 / May 24, 1978

Such a localized orbital can be imagined to exist in every triangular face of $B_nH_n^{2-}$. In the present approach, the adjacent localized orbitals in the same $B_nH_n^{2-}$ ion are assumed to interact with each other, as in the case of p_π orbitals of carbon atoms in an unsaturated hydrocarbon. This assumption leads to a delocalized MO energy scheme of the $B_nH_n^{2-}$ ion. Each MO of $B_nH_n^{2-}$ can hence be expressed as a linear combination of the three-center BBB bonding orbitals. This three-center bond formalism actually leads to the same pattern of MO energy levels as does the LCAO method.¹²

On this basis, the MO calculation can be carried out in a manner entirely analogous to the original Hückel method for treating conjugated hydrocarbons, setting up an $N \times N$ matrix A , where N is the number of triangular faces of a polyhedral borane considered. The n th column and n th row of the matrix are each put into a 1:1 correspondence with the n th face of the polyhedron. Diagonal matrix elements are given the value α (Hückel Coulomb integral), and off-diagonal matrix elements, which correspond to faces with an edge in common, the value β (Hückel resonance integral). All other matrix elements are set equal to zero.

A secular equation of this polyhedral borane is then expressed as

Table I. Resonance Energies of Polyhedral Boranes

Species	Molecular shape	Number of faces	Resonance energy (β)	Number of valence structures ^a
B_4H_4	I	4	0.000	1
$B_5H_5^{2-}$	II	6	0.000	2
$B_6H_6^{2-}$	III ^b	8	0.844	32
$B_7H_7^{2-}$	IV ^c	10	0.938	20
$B_8H_8^{2-}$	V ^c	12	0.798	8 ^h
$B_9H_9^{2-}$	VI ^d	14	0.813	16
$B_{10}H_{10}^{2-}$	VII ^e	16	1.145	72
$B_{11}H_{11}^{2-}$	VIII ^f	18	1.000	16 ^h
$B_{12}H_{12}^{2-}$	IX ^g	20	1.763	132 ^h

^a Reference 18. ^b R. Schaeffer, D. Johnson, and G. S. Smith, *Inorg. Chem.*, **4**, 917 (1965). ^c F. Klanberg, D. R. Eaton, L. J. Guggenberger, and E. L. Muetterties, *ibid.*, **6**, 1271 (1967). ^d L. J. Guggenberger, *ibid.*, **7**, 2260 (1968). ^e R. D. Dobrott and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 1779 (1962). ^f F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, **5**, 1955 (1966). ^g J. A. Wunderlich and W. N. Lipscomb, *J. Am. Chem. Soc.*, **82**, 4427 (1960). ^h R. N. Camp, I. R. Epstein, and W. N. Lipscomb, unpublished work.

Boron Clusters come of Age

Russell N. Grimes *J. Chem. Educ.* 2004, 81 657.

- The stable existence of the neutral and polyhedral boranes helped force a revolution in the way chemists think about covalent bonding
- Additionally, there are diverse areas of application exploiting their remarkable properties
- Icosahedral $B_{12}H_{12}^{2-}$ is water soluble and heat resistant: salts survive temperatures above 810 °C without decomposition
- $B_{12}H_{12}^{2-}$ is arguably the most stable molecule in all of chemistry
- Its chemical inertness leads to very low toxicity in humans and suitability for medical applications

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Boron-11 NMR

<http://dx.doi.org/10.1021/ed054p469>

- ^{11}B signals are more intense than those for ^{10}B due to greater natural abundance
- ^{11}B has a larger nuclear magnetic moment than ^{10}B
- NMR signal-to-noise increases with increasing nuclear magnetic moment
- Nuclear spin I in units of $h/2\pi$ of ^{11}B is $3/2$ while that of ^{10}B is 3
- The larger nuclear quadrupole moment of ^{10}B gives it spectra that are not as sharp as for ^{11}B

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- In a uniform magnetic field, H , a given nucleus can assume any one of $2I + 1$ orientations relative to the applied field
- Each orientation corresponds to an energy
- $E = -\gamma hH \frac{M}{2\pi}$
- $M = I, I - 1, I - 2, \dots, -I$
- A proton coupled to a ^{11}B nucleus “sees” four different fields, all equally probable
- The ^1H NMR spectrum of a proton coupled to a ^{11}B nucleus is a quartet with all four peaks of equal intensity

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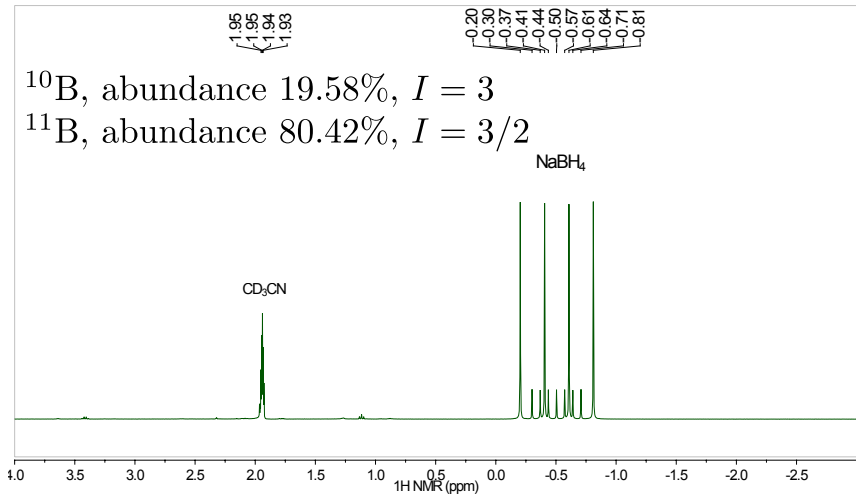
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Borohydride Ion $[\text{BH}_4]^-$ has T_d Symmetry



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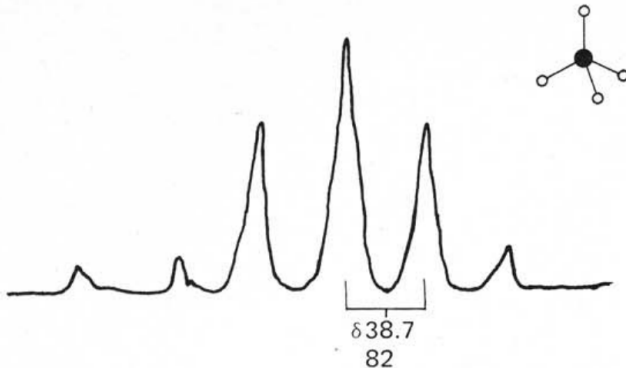


Figure 1. 6 MHz ^{11}B nmr spectrum of NaBH_4 in H_2O . Ref. (3) and (13).

Boron-11 NMR

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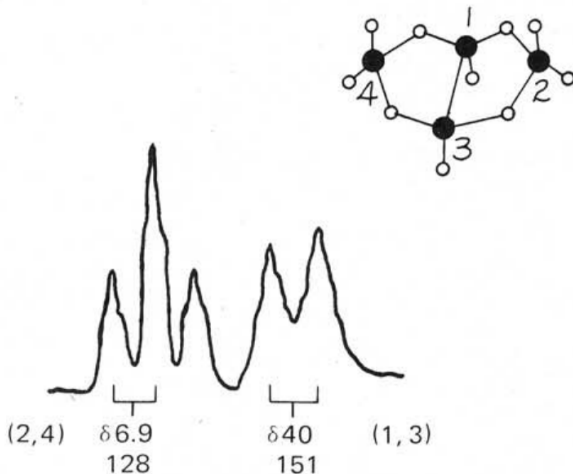


Figure 2. 12.8 MHz ^{11}B nmr spectrum of neat B_4H_{10} . Ref. (3) and (15).

Boron-11 NMR

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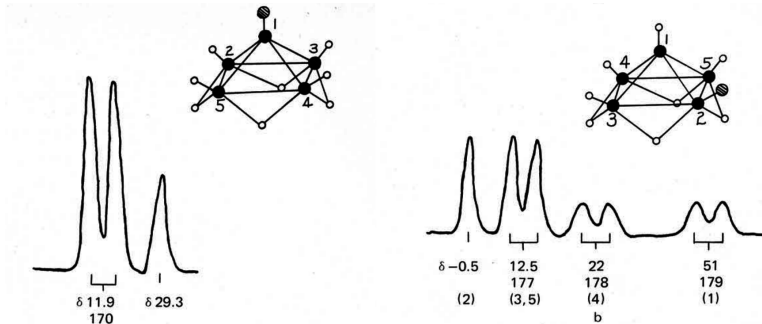


Figure 4 (a) 32.1 MHz ^{11}B nmr spectrum of 1- CIB_5H_8 . Ref. (22). (b) 32.1 MHz ^{11}B nmr spectrum of 2- CIB_5H_8 . Ref. (23).

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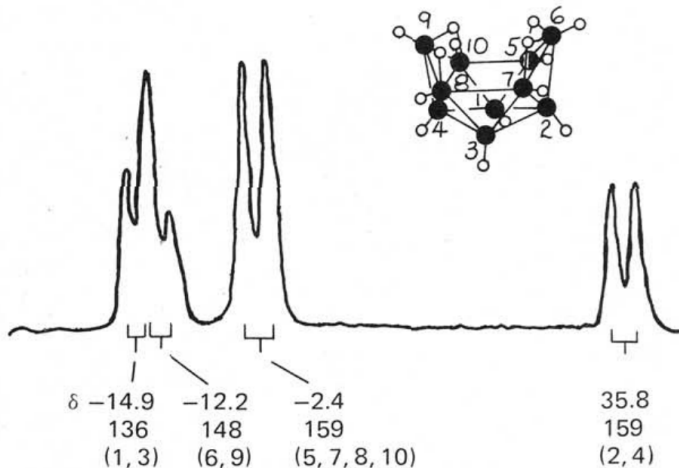


Figure 8. 64.2 MHz ^{11}B nmr spectrum of $\text{B}_{10}\text{H}_{14}$ in CS_2 solution. Ref. (4) and (25c).

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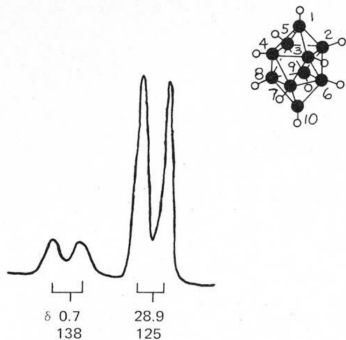


Figure 9. ^{11}B nmr spectrum of $\text{B}_{10}\text{H}_{10}^{2-}$ as $(\text{Et}_3\text{NH})_2\text{B}_{10}\text{H}_{10}$ in CH_3CN . Ref. (28b).

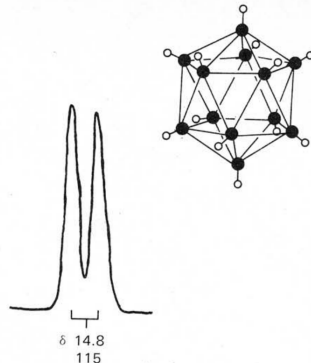
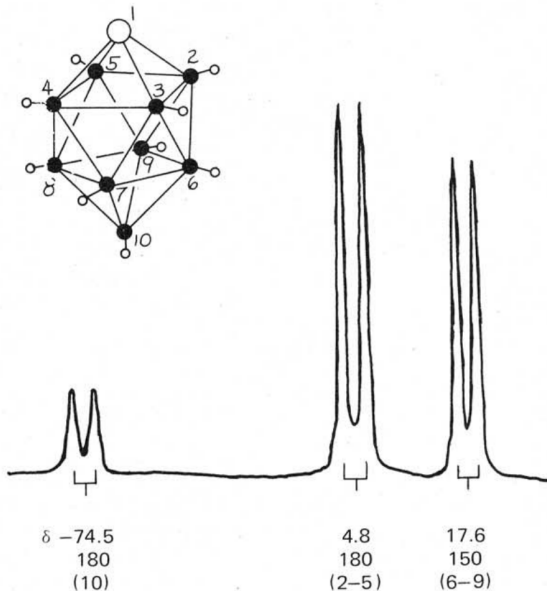


Figure 10. ^{11}B nmr spectrum of $\text{B}_{12}\text{H}_{12}^{2-}$ ion as $(\text{Et}_3\text{NH})_2\text{B}_{12}\text{H}_{12}$ in CH_3CN . Ref. (32).

Boron-11 NMR

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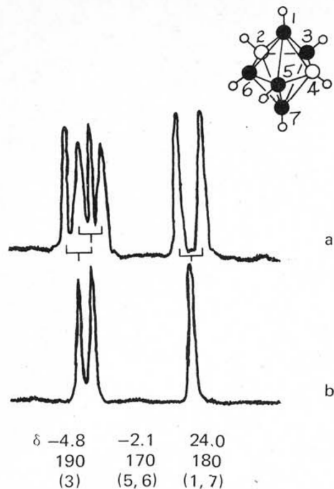


Figure 5. 28.8 MHz ^{11}B nmr spectra of $\text{C}_2\text{B}_5\text{H}_7$ in $(\text{C}_2\text{H}_5)_2\text{O}$ using Fourier transform techniques. (a) shows B-H coupling; (b) is the decoupled spectrum. Ref. (24).

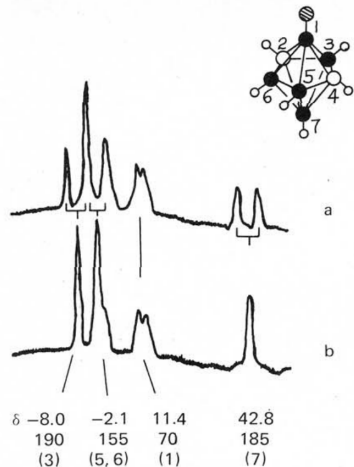


Figure 6. 28.8 MHz ^{11}B nmr spectra of 1- $\text{FC}_2\text{B}_5\text{H}_7$ in $(\text{C}_2\text{H}_5)\text{O}$ using Fourier transform techniques. (a) shows B-H coupling; (b) is the proton-decoupled spectrum. Ref. (24).

Elemental Boron

- Borax was known in antiquity and used to prepare glazes and hard borosilicate glasses
- Impure boron was obtained by H. Davy, 1808, and by J. L. Gay Lussac
- H. Moissan obtained pure boron in 1892 by reduction of B_2O_3 using Mg
- High purity boron and crystalline phases only obtained in the later 20th century
- The name “Boron” was proposed by Davy to indicate the source of the element and its similarity to carbon, i.e. *bor(ax + carb)on*

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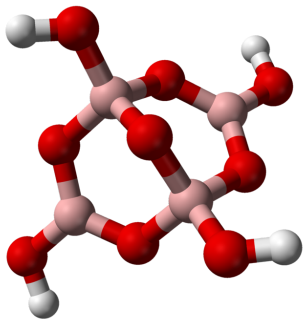
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Elemental Boron comes from Borax

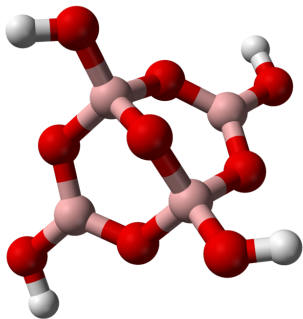
- Borax, the mineral, contains the tetraborate ion, $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$



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- Borax is formulated as $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$

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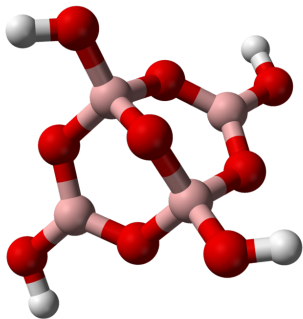
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- Boron is comparatively un abundant in the universe
- It occurs to the extent of about 9 ppm in crustal rocks, so rather less abundant than lithium (18 ppm), but similar to praseodymium and thorium
- Occurrence is invariably as borate minerals or borosilicates
- Commercially valuable deposits are rare, but can be vast as in California and Turkey
- Structural complexity of borate minerals is surpassed only by silicates
- Metal borides and allotropic modifications of boron also show great complexity and variety

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Crystalline Boron

- Structural complexity of boron arises from the way it seeks to solve the problem of having fewer electrons than atomic orbitals available for bonding
- Elements in this situation usually adopt metallic bonding
- Due to its small size and high ionization energy, B engages in covalent bonding
- The dominant structural unit is the B_{12} icosahedron, which also occurs in metal boride structures
- Fivefold rotation symmetry at individual boron atoms gives rise to inefficient packing of B_{12} icosahedra, giving regularly spaced voids to be occupied by metal or other atoms

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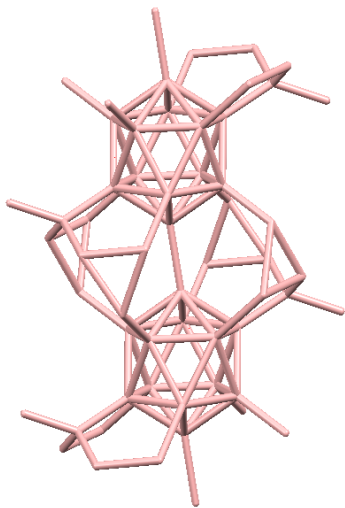
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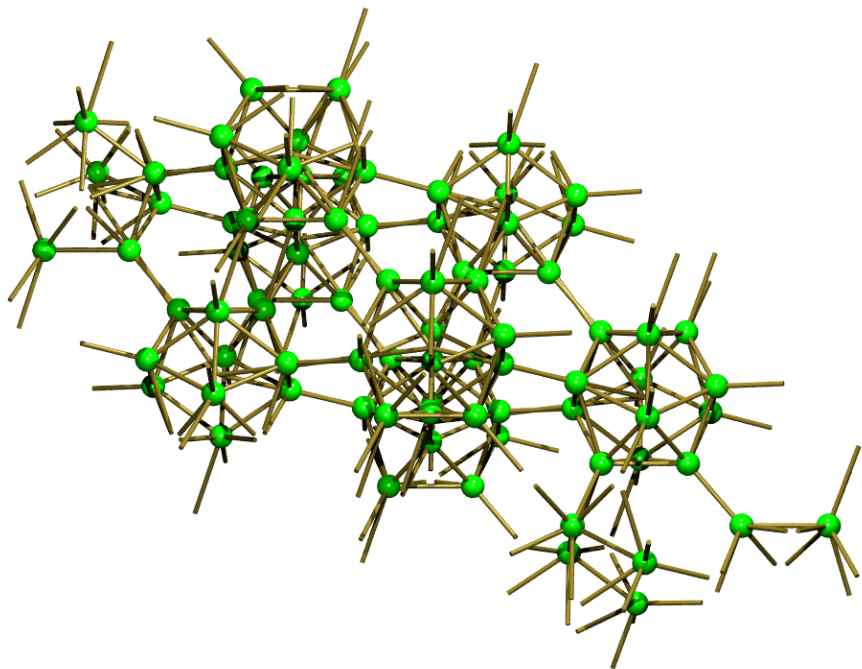
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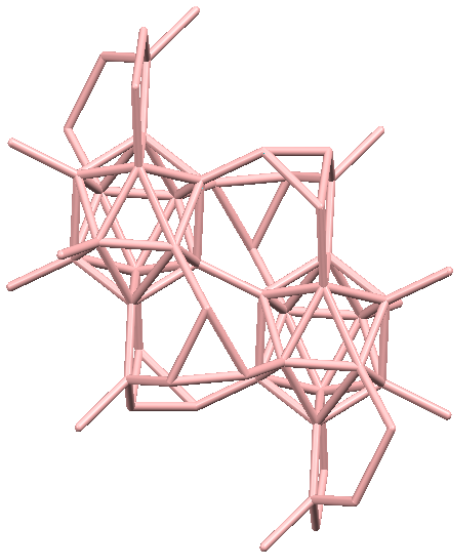
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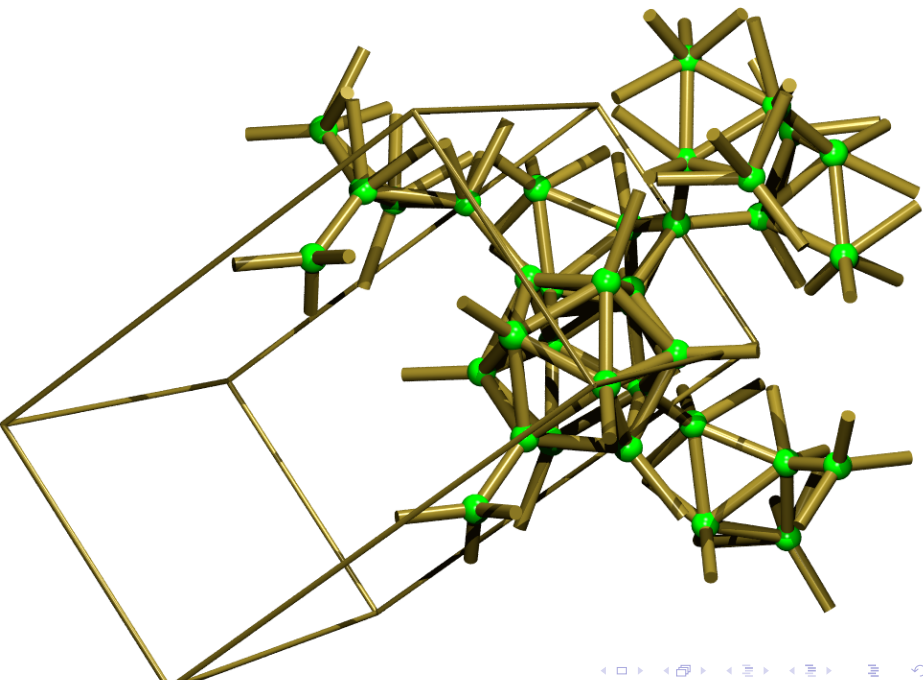
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Rhombohedral Boron









Boron Carbide

J. Am. Ceram. Soc., 94 [11] 3605–3628 (2011) DOI: 10.1111/j.1551-2916.2011.04865.x

- Boron carbide has a unique combination of properties that make it a material of choice for a wide range of engineering applications
- Boron carbide is used in refractory applications due to its high melting point and thermal stability
- It is used as abrasive powders and coatings due to its extreme abrasion resistance
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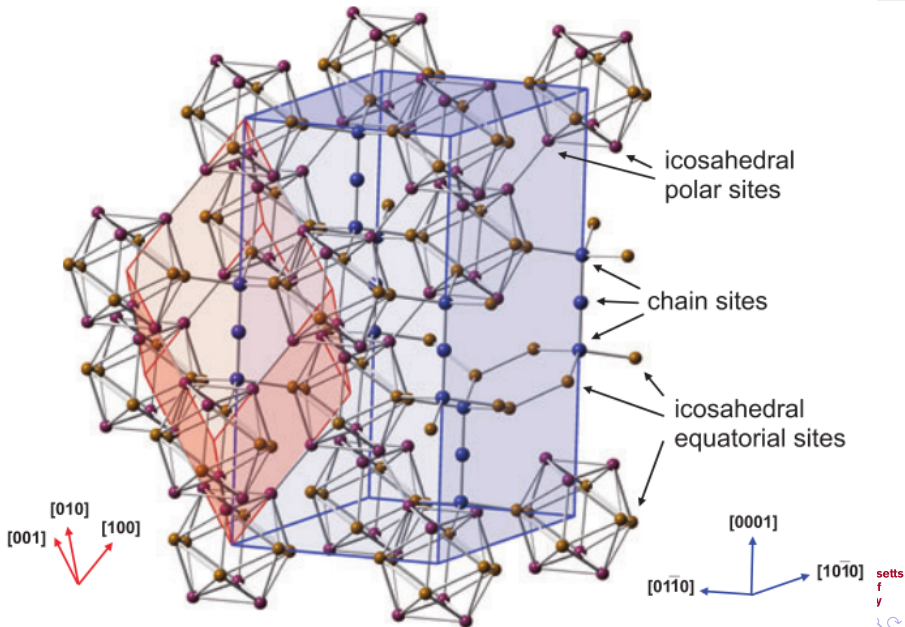
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Boron Carbide Lattice Structure



Vercor Materials LLC

THEORETICALLY DENSE, COMPLEX-SHAPED BORON CARBIDE FOR ARMOR



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Vol. 86 No. 10 October 2009 Journal of Chemical Education, 1131–1131

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- Became leader of exploratory research group at the Army's Redstone Arsenal, 1950s
- Mission was exploration of borane chemistry to be applied to Cold War rocket motors
- Ph.D. work was in physical organic chemistry; BF_3 was the only boron reagent he had used!
- Decaborane, $\text{B}_{10}\text{H}_{14}$, was available from a jet engine fuel program, so investigated its characteristics in well-known organic reactions
- Exploratory work revealed the borane analogs of aromatic hydrocarbons, $\text{B}_n\text{H}_n^{2-}$ with closed polyhedral structures



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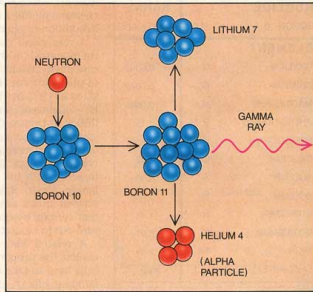
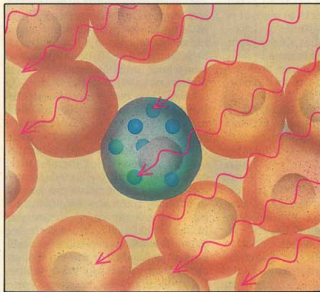
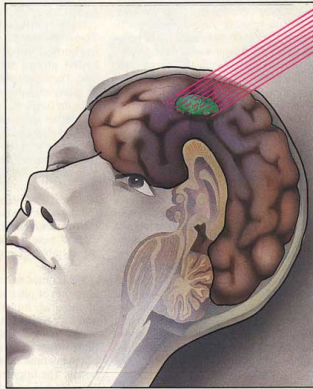
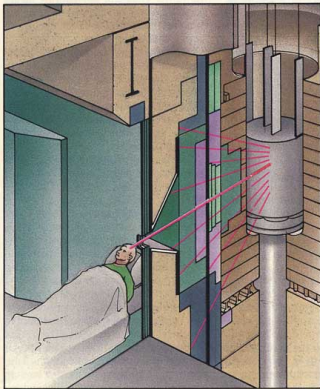
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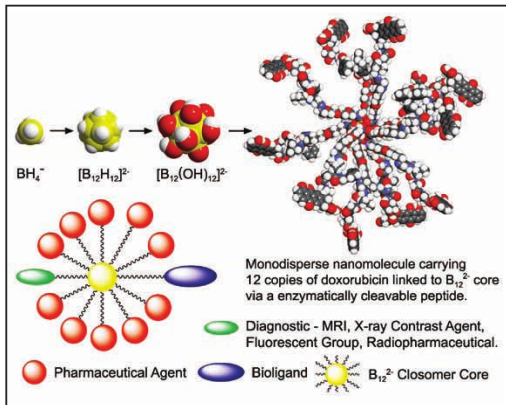


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heterocyclic, and organometallic organic compounds. The first boranes had been discovered in Germany by Alfred Stock in the early 1900s (B_2H_6 , B_4H_{10} , B_5H_9 , etc.) and these relatively unstable species corresponded to the aliphatic hydrocarbons.

Exploratory work revealed the borane analogs of aromatic hydrocarbons, which proved to be a complete family of $B_nH_n^{2-}$ dianions with $n = 6$ to 12 inclusive and having closed polyhedral structures. Like the aromatic hydrocarbons, these species were very stable and the icosahedral $B_{12}H_{12}^{2-}$ ion is probably the most

Figure 1. Starting with $B_{12}(OH)_{12}^{2-}$ as a core, the Hawthorne group creates nanoparticles capable of carrying various payload molecules—an imaging contrast agent, a biomolecule for tumor or organ targeting, or a drug—for potential all-in-one life-saving therapy, as shown schematically. In one example, they have created a potential anticancer agent by attaching 12 copies of doxorubicin to the B_{12} core via enzymatically cleavable peptides. Courtesy of Fred Hawthorne.



The Strongest Brønsted Acid

- What is the strongest acid?
- Can a simple Brønsted acid be prepared that can protonate an alkane at room temperature?
- Can that acid be free of the complicating effects of added Lewis acids that are typical of common superacid mixtures?
- The carborane superacid $\text{H}(\text{CHB}_{11}\text{F}_{11})$ is that acid

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DOI: 10.1002/anie.201308586

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