Carboranes: Introduction, Structure, and Bonding

1. Introduction

Carboranes are a unique class of **polyhedral boron–carbon–hydrogen clusters** that exhibit remarkable stability, distinctive three-dimensional aromaticity, and versatile applications in chemistry, medicine, and materials science. They belong to the broader family of **boranes** (boron–hydrogen compounds), but in carboranes, some boron atoms are replaced by carbon atoms. This incorporation of carbon alters the electronic, structural, and chemical properties, making carboranes exceptionally important in both theoretical and applied chemistry.

The name *carborane* is derived from **carbon + borane**, reflecting their hybrid nature. They are usually expressed with the general formula $C_2B_{10}H_{12}$, though variations with different numbers of carbon atoms and cage sizes are also well known.

Carboranes are often regarded as **electron-deficient clusters**, and their stability can be rationalized using **Wade's rules**, which relate the number of skeletal electron pairs to the geometry of the cluster. These rules show how clusters adopt **closo (closed), nido (nest-like), arachno (spider-like)**, and **hypho (open)** structures depending on electron count.

Their discovery in the **1950s** initiated a revolution in cluster chemistry. The synthesis of *ortho-carborane* (o-$C_2B_{10}H_{12}$) in 1963 at the Olin Mathieson Chemical Corporation opened new avenues in organometallic chemistry, medicinal chemistry (especially **boron neutron capture therapy, BNCT**), catalysis, and polymer science.

2. General Features of Carboranes

1. **Cluster Nature:**
    - Polyhedral, cage-like molecules.
    - Exhibit high symmetry and compact geometry.
2. **Bonding:**
    - Delocalized, multi-center two-electron bonds (unlike classical two-center two-electron covalent bonds).
    - This bonding leads to *three-dimensional aromaticity*.
3. **Thermal and Chemical Stability:**
    - Remarkable resistance to heat (stable up to 400–600 °C).
    - Resistant to oxidation, reduction, and attack by acids/bases.

4. **Isomerism:**
    - Carboranes can have isomers depending on the relative positions of carbon atoms within the cluster.
    - Example: *ortho, meta,* and *para* isomers of $\mathbf{C_2B_{10}H_{12}}$.
5. **Applications:**
    - Boron neutron capture therapy (BNCT).
    - Lubricants, polymers, ceramics.
    - Ligands in coordination chemistry.
    - Drug delivery and medicinal chemistry.

3. Classification of Carboranes

Carboranes can be classified according to:

(a) Geometry and Electron Count (Wade's Rules):

- **Closo-carboranes**: Closed polyhedral clusters with *n* skeletal atoms and *n+1* skeletal electron pairs.
  Example: $\mathbf{C_2B_{10}H_{12}}$ (icosahedral).
- **Nido-carboranes**: Nest-like structures with *n+2* skeletal electron pairs.
  Example: $\mathbf{C_2B_9H_{11}^-}$.
- **Arachno-carboranes**: Spider-like structures, more open than nido, with *n+3* skeletal electron pairs.
  Example: $\mathbf{C_2B_8H_{12}^{2-}}$.
- **Hypho-carboranes**: Very open structures with *n+4* skeletal electron pairs.

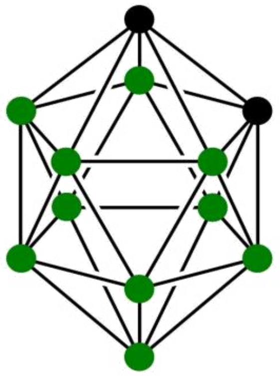
(b) Number of Carbon Atoms:

- **Monocarboranes** (one carbon atom).
- **Dicarboranes** (two carbon atoms, e.g., $C_2B_{10}H_{12}$).
- **Higher carboranes** (more than two carbon atoms in the cluster).

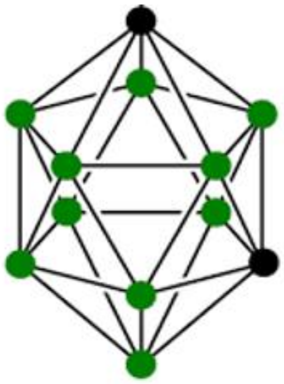
4. Important Examples of Carboranes

(i) Ortho-Carborane (o-$C_2B_{10}H_{12}$)

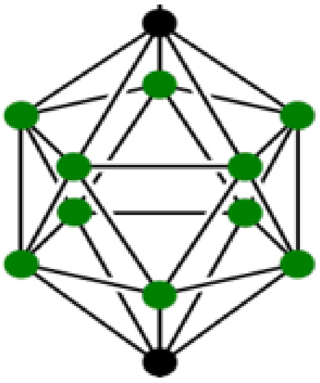
- Structure: Icosahedral cluster, with **two adjacent carbon atoms** at neighboring vertices.
- Formula: $\mathbf{C_2B_{10}H_{12}}$.
- Stability: Extremely stable, with decomposition above ~500 °C.
- **Figure 1:** Icosahedron with adjacent carbon atoms at positions 1 and 2.



1,2-$C_2{}^{10}B_{10}H_{12}$



1,7-$C_2B_{10}H_{11}$



1,12-$C_2B_{10}H_{10}$

(ii) Meta-Carborane (m-$C_2B_{10}H_{12}$)

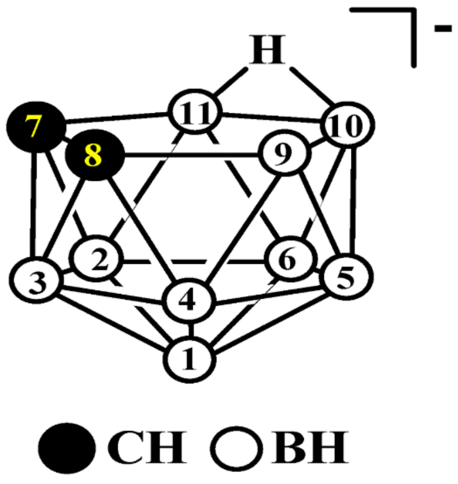
- Structure: Icosahedral, with **two carbon atoms separated by one boron atom**.
- **Figure 2:** Icosahedron with carbons at positions 1 and 7.
- Slightly less stable than ortho-isomer.

(iii) Para-Carborane (p-$C_2B_{10}H_{12}$)

- Structure: Icosahedral, **carbons opposite each other** in the cage.
- **Figure 3:** Icosahedron with carbons at opposite vertices (1 and 12).
- Symmetrically most stable form.

(iv) Nido-Carboranes

- Derived by removal of one vertex from a closo-carborane.
- Example: **$[C_2B_9H_{12}]^-$**, derived from $C_2B_{10}H_{12}$ by removing one vertex.
- Structure resembles a **nest** with one open face.
- **Figure 4:** Draw an 11-vertex polyhedron missing one apex, with two carbons present.



(v) Arachno-Carboranes

- More open, derived by removal of two vertices.
- Example: $[\mathbf{C_2B_8H_{12}}]^{2-}$.
- Structure: Like a “spider” with an open framework.
- **Figure 5:** Polyhedron missing two connected vertices.

5. Bonding in Carboranes

Carborane bonding is unusual, relying on **multi-center bonding** rather than localized covalent bonds.

1. **3-center 2-electron bonds (3c–2e):**
    - Essential to explain cluster stability.
    - Example: In B–H–B bridges of boranes and carboranes.
2. **Delocalization:**
    - Electrons delocalize over the entire cage, similar to aromaticity in benzene.
    - But unlike benzene’s **planar 2D aromaticity**, carboranes exhibit **3D aromaticity**.
3. **Application of Wade’s Rules:**
    - For $\mathbf{C_2B_{10}H_{12}}$ **(12 skeletal atoms)** → 13 skeletal electron pairs → *closo* structure (icosahedron).

6. Three-Dimensional Aromaticity

Carboranes are often described as **3D aromatic molecules** because:

- They follow **Hückel-like electron delocalization**, but in three dimensions.
- Delocalized bonding stabilizes the cage.
- This property explains their extraordinary **thermodynamic and chemical stability**.\

7. Synthesis of Carboranes

Typical synthetic routes involve:

1. **Reaction of Acetylenes with Boranes:**
    - Example: Decaborane ($B_{10}H_{14}$) + Acetylene → $C_2B_{10}H_{12}$ (ortho-Carboranes).

2. **Thermal Rearrangement:**
   - Ortho-Carboranes can thermally rearrange to meta- and para-isomers at elevated temperature.
3. **Metal-Catalysed Methods:**
   - Transition-metal catalysts help in selective functionalization.

8. Applications of Carboranes

1. **Medicine:**
   - **Boron Neutron Capture Therapy (BNCT):** Carboranes act as boron carriers, selectively targeting tumor cells.
   - Used in drug design due to their stability and hydrophobic character.
2. **Materials Science:**
   - High-temperature lubricants.
   - Components in heat-resistant polymers and ceramics.
3. **Organometallic Chemistry:**
   - Carborane ligands (e.g., dicarbollide anion) stabilize unusual oxidation states in metal complexes.
   - Used in catalysis and electronic materials.
4. **Nanotechnology:**
   - Building blocks for nanoscale clusters and supramolecular assemblies.

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9. Figures (Suggested Diagrams to Draw)

1. **Figure 1:** Icosahedral o-$C_2B_{10}H_{12}$ (adjacent carbons).
2. **Figure 2:** Icosahedral m-$C_2B_{10}H_{12}$ (carbons separated).
3. **Figure 3:** Icosahedral p-$C_2B_{10}H_{12}$ (opposite carbons).
4. **Figure 4:** Nido- Carboranes cage with one vertex missing.
5. **Figure 5:** Arachno-Carboranes cage with two vertices missing.
6. **Figure 6:** Schematic of 3D aromaticity (electron delocalization over cage).

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10. Conclusion

Carboranes represent a fascinating intersection of **inorganic and organic chemistry**, embodying unique structures, bonding, and stability that defy classical bonding theories. Their **polyhedral cage structures**, rationalized by **Wade’s rules**, exhibit **three-dimensional aromaticity**, making them thermally and chemically robust.

The discovery of Carboranes has expanded horizons in cluster chemistry, organometallics, materials science, and medicine. The versatility of their **substitution chemistry** and **isomerism** continues to inspire new applications—from **anticancer therapy (BNCT)** to **advanced materials and nanotechnology**.

Thus, Carboranes are not only of academic interest in understanding unconventional bonding but also of immense practical importance, ensuring their continued study in modern chemistry.