

Hypercarbons in polyhedral structures

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Though carbon is mostly tetravalent and tetracoordinated, there are several examples where the coordination number exceeds four. Structural varieties that exhibit hypercarbons in polyhedral structures such as polyhedral carboranes, sandwich complexes, encapsulated polyhedral structures and novel planar aromatic systems with atoms embedded in the middle are reviewed here. The structural variety anticipated with hypercoordinate carbon among carboranes is large as there are many modes of condensation that could lead to large number of new patterns. The relative stabilities of positional isomers of polyhedral carboranes, sandwich structures, and endohedral carboranes are briefly described. The *mno* rule accounts for the variety of structural patterns. Wheel-shaped and planar hypercoordinated molecules are recent theoretical developments in this area.

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1. Introduction

Carbon is traditionally tetravalent and follows the octet rule. In saturated compounds of carbon tetra valency leads to tetra coordination. When the number of atoms or groups attached to carbon in a molecule exceeds four, that carbon is termed as hypercoordinate carbon, abbreviated as hypercarbon.¹ Often



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the number of valence electrons around carbon in the hypercoordinate carbon molecule does not exceed eight. When it does so, hypercarbon is also hypervalent.

Hypercoordinate carbon appears in a variety of contexts. The transition state in the S_N2 reaction is a familiar example. Obviously, this violates the basic octet rule. On the other hand the transition state for the S_E2 reaction has a hypercarbon which follows the octet rule. The prototype, CH_5^+ , and its derivatives follow the octet rule and have a hypercarbon.^{1,2} Non-classical carbonium ions³ that occupied the attention of many chemists during the latter quarter of last century have one hypercarbon. The hyper carbon compounds such as carbocations,¹ metal alkyls^{1,4} and transition metal carbido-complexes^{1,5} where bonding around a single carbon atom is primarily different from normal have been reviewed previously. These and the related structures with metal substituents such as CLi_5^+ , CLi_6 etc. will not be discussed here.

Another entree point to hypercarbon is through the removal of electrons from two dimensional aromatic compounds, such as cyclooctatetraene dication, tropylium cation, benzene and cyclopentadienyl anion (Fig. 1, box). The deficiency of electron forces molecules to adopt structures where the available electrons can be shared in a more efficient way through clustering of the atoms. This increases the coordination number and leads to pyramidal and polyhedral structures with hypercoordinated carbon atoms. Neutral structures isoelectronic to the highly charged carbocations are obtained by replacing the appropriate number of carbon atoms by boron atoms (Fig. 1, box). In a similar fashion, we can begin from the electron deficient boranes. The extreme deficiency of electrons in polyhedral boranes is often overcome by negative charges. Neutral structures known as carboranes result when the negative charge is compensated by replacing one or more boron atoms by carbon atoms. Thus carboranes must be the most common family of compounds which exhibit hypercarbons. Depending on the nature of the molecular skeleton, these are grouped under various names. Polyhedral structures where all vertices are occupied (e.g. **7**, **8**, **9**, **10**, **15**, **19**, **21**) are described as *closo*. Structures with one vertex missing (e.g. **4**, **5**, **6**, **11**, **16**) are termed *nido*. *Arachno* describes polyhedral structures where two vertices are missing. These structural and electronic structure relationships have evolved over the years from the works of Hoffmann,⁶ Mingos,⁷ Rudolph,⁸ William⁹, Jemmis and Schleyer¹⁰ and especially Wade.^{11,12} While some of the structures are known experimentally as all-carbon species, the isoelectronic deltahedral carboranes and related structures developed by Wade provide the largest set of molecules with hypercarbon.^{9,11-14} We build up on this well accepted approach to polyhedral molecules to include condensed and encapsulated structures expanding to constitute Fig. 1.

Several structures in Fig. 1, taken separately, appear to be very different from each other. This review attempts to bring out the relationship between these apparently unrelated structures. The charge, bonding, modes of fusion and topology of all these structures can be understood from the *mno* rule,¹⁵ an extension of Wade's rules.¹⁶ The Hückel $(4n + 2)\pi$ electron rule for two-dimensional aromatic compounds and the Wade's rules are special cases of the *mno* rule. Representative

molecular formulas available from the literature either from experimental studies or calculated to be minima are given below the structures in Fig. 1. To distinguish from the experimentally known structures, theoretically calculated structures are represented in bold italics. Molecules that fall under different structural variety are represented by numbers. The molecules derived from a given structural type are distinguished by adding letters after the number. (Thus **7a** is $1,5-C_2B_3H_5$, **7b** is $1,2-C_2B_3H_5$, **7c** is $2,3-C_2B_3H_5$, **7d** is $C_3B_2H_5^+$ and so on). Different types of arrows are used to indicate the nature of the relationship that exists between adjacent molecules. The double line arrows connect clusters with the same number of electron pairs for cluster bonding similar to the Rudolph diagram shown in the box.⁸ The relationship between *closo*-, *nido*-, *arachno*- and endohedral cluster geometries are emphasized here. The double sided arrows connect clusters with the same number of atoms and different number of electron pairs for cluster bonding. Single line arrows indicate the condensation between two cluster geometries or sandwiching. Larger *closo*-polyhedral structures are obtained by dimerizing the pyramidal structures represented by **4**, **5** and **6**. For example, dimerization of structure **6** leads to fourteen vertex structure **19** and dimerization of **5** leads to the icosahedral structure **21**. The dimerization of **4** leads to the ten vertex *closo*-structure. Carboranes based on these are known experimentally. In view of the general similarity of these to the icosahedral carboranes, these are not separately discussed. Condensation is also possible for **7**, **8**, **9** and larger carboranes in several ways. Let us consider **9**. Several modes of condensation such as single atom sharing, edge sharing, face sharing and four vertex sharing are possible for polyhedral structures. Here, we have shown the representative edge sharing and single vertex condensation of structure **9** leading to **10** and **15** respectively. Removal of vertices from **10** one at a time similar to the Rudolph diagram^{8,13} results in various *nido*- and *arachno*- condensed species and finally to condensed planar molecules, **14**. The relationship between **1** and **14** are obvious. The condensed structures between benzenoid aromatics and carboranes are another class of compounds exhibiting hypercarbons (**27**).¹⁷ Formally, these may be constructed from the corresponding condensed *closo*-polyhedral structures. There are several experimentally known edge shared *nido*- and *arachno*- structures which contain one or more hypercarbons.^{9,11-14}

The condensation of two pentagonal bipyramidal structures (**9**) by single vertex sharing gives **15**. Removal of vertices one at a time from **15**, as in the Rudolph diagram (Fig. 1), eventually leads to the metallocenes, **18**. Well-known triple (**18**) and tetra decker complexes are schematically constructed in this fashion and these have two and three single vertex sharing atoms respectively.¹⁸ If the central atom in **15** is small, it is possible to imagine an appropriate electron count to bring up the upper and lower pentagonal pyramids together to form an icosahedron, encapsulating the central atom (**20**).¹⁹ Encapsulated structures derived from dodecahedrane²⁰ are other examples of hypercarbon compounds. Some of the well-known transition metal carbido-complexes may also be considered as encapsulated structures formally derived from the corresponding deltahedral metallocarbonyl clusters. These have been reviewed

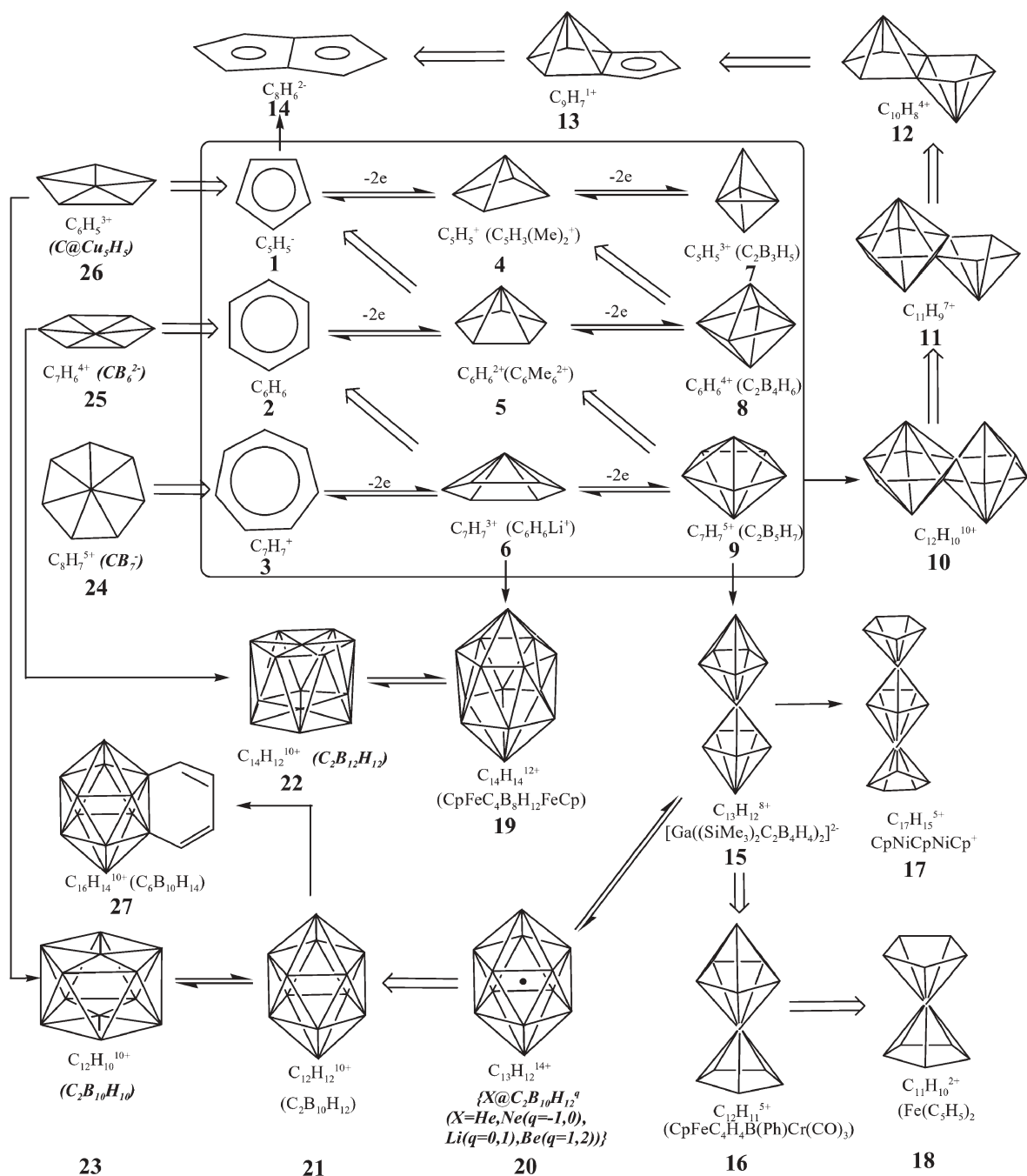


Fig. 1 Schematic representation of the family of structures with hypercarbon. The electronic structural relationship between the *closo*-, *nido*- and *arachno*- structures shown within the box has been analyzed previously. Condensation of each of these structures following the *mno* rule leads to further examples of hypercarbon. The double line arrows (e.g. 1–4) connect clusters with the same number of electron pairs for cluster bonding. The double sided arrows (e.g. 1–5) connect clusters with the same number of atoms and different numbers of electron pairs for cluster bonding. Single line arrows (e.g. 9–10, 9–15) indicate the condensation between two cluster geometries or sandwiching. Representative examples from experimentally known structures and theoretically calculated structures (in bold italics) are given in parentheses.

recently and are not included here.^{1,4} Compression of two opposite vertices of the twelve vertex (21) and fourteen vertex structures (19) to the five and six membered rings results in wheel shaped molecule 23 and 22 respectively which have been studied by Schleyer *et al.* recently.²¹ Fragmentation of these molecules perpendicular to the principal axis results in 26 and 25. A more direct approach to

these disk-like structures is the addition of atoms to the centre of 1, 2, and 3 as reported recently.^{22,23} It should be emphasized that the minimum energy structures *CB₇⁻* and *CB₆²⁻* calculated for the structural type 24 and 25 do not have hydrogens at any vertex.²¹ This review focuses on the structural relationship in molecules with hypercarbons represented in Fig. 1.

2. Pyramidal carbocations and polyhedral carboranes.

The three dimensional carbocation structures shown inside the box in the upper part of the Fig. 1 have been discussed many times in the literature and are the starting point of discussions here as well.^{1,8–12} The three two-dimensional aromatic compounds **1**, **2** and **3** follow the Hückel $(4n + 2)\pi$ electron rule and have no hypercarbons. Hückel's rule had a far reaching effect in two-dimensional aromaticity and is applicable to condensed benzenoid aromatics such as naphthalene, azulenes *etc.* In these molecules, the HOMO and LUMO are generally doubly degenerate. The removal of electrons from these aromatic molecules makes them unstable. It is logical to anticipate that as we remove electrons, the atoms cluster together to share the available electrons in a more efficient way. Thus the flat structures become pyramidal first, making the apical carbon atom hypercoordinate (**1**→**4**, **2**→**5**, **3**→**6**). Several derivatives of these are known.^{9,11–14} Neutral structures where one or more carbon atoms are replaced by boron and other electropositive atoms are available in the literature.^{9,11–14}

The studies of Stohrer and Hoffmann based on B_5H_9 led to the preferable square pyramidal structure for $(CH)_5^+$ which can be considered as a half sandwich structure, **4**, (Fig. 1).⁶ Though $(CH)_5^+$ itself is not experimentally known so far, $(C_5H_3(Me)_2)^+$ has been characterized by 1H and ^{13}C NMR spectroscopy.²⁴ These molecules are aromatic and their stability can be explained by six interstitial electron rule.¹⁰ The electronic structure of these pyramidal molecules can be understood from interaction diagrams between caps and rings (Fig. 2). Here the two fragments, cyclobutadiene and CH^+ are brought together so that C_{4v} symmetry is maintained. The main frontier orbitals involved in the formation of the pyramidal structure are the lowest three delocalized π molecular orbitals of cyclobutadiene and the two p- and one sp- hybrid orbitals of the CH group. A symmetrical nondegenerate bonding molecular orbital and two degenerate bonding molecular orbitals result from this interaction. The carbon atom of the CH cap is obviously hypercoordinated. If there are six electrons as in $C_4H_4 + CH^+$ to fill the three molecular orbitals, the system must be stable. An interaction

of any cyclic polymer with a cap would lead to the one plus two pattern of molecular orbitals, resulting in the six interstitial electron rule.¹⁰ The extra stability of pyramidal structures with six interstitial electrons, such as $C_5H_5^+$, $C_6(Me)_6^{2+}$ (Fig. 2a), C_5H_5Li , C_5H_5X (BeH, BeCH₃, BeCCH, BeBr, BeCl, BeBH₄, BeCp) and $(CCH_3)_5BI^+$ are well-known. There are theoretical studies on C_6H_6 isomers with hypercoordinated carbon.^{25,26}

Removal of another two electrons from the pyramidal structures leads to the *closo*-polyhedral structures, (**4**→**7**, **5**→**8**, **6**→**9**) where atoms are brought further closer to each other. Excessive charge prevents the existence of the all-carbon species. However these are familiar in the world of polyhedral boranes.^{9,11–14} Replacement of three, four and five carbon atoms from **7**, **8** and **9** by boron atoms lead to well known polyhedral carboranes, each with several hypercarbons. Their connections to two-dimensional aromatic systems are obvious (Fig. 1). An interaction diagram similar to Fig. 2a can be constructed from *closo*-structures by bringing cyclic polyenes and two caps from the either side (Fig. 2b). *closo*-Carboranes corresponding to **7**, **8** and **9** belong to this category.

This six-electron requirement is independent of the number of rings and caps present in the borane skeleton. A similar pattern can be observed even if the number of atoms in the ring is changed. This approach effectively explains the origin of aromaticity in polyhedral boranes, if they can be conveniently split into rings and caps. It can also be understood by the successive removal of the capping vertexes from the borane as in the Rudolph diagram for the *closo*-, *nido*- and *arachno*-boranes. Thus the series **9**→**5**→**1**, **8**→**4** and **6**→**2** (Fig. 1) retains Wade's rules. Hence the three-dimensional aromatic systems such as *closo*- $B_6H_6^{2-}$ and $B_7H_7^{2-}$ directly related to two-dimensional aromatic systems such as $C_4H_4^{2-}$ and $C_5H_5^-$ (**1**).

While the beginning point in the above discussion is planar aromatics, the well-known Wade's skeletal electron pair rules begin with the *closo*-structures.^{11,16} According to this $n + 1$, $n + 2$ and $n + 3$ electron pairs (n = the number of vertices) are required for *closo*-, *nido*- and *arachno*-polyhedral structures to be stable. The sp hybrid orbital on the boron or carbon vertices that point towards the center of the cage form a unique bonding molecular orbital (BMO) and is called the 'radial'

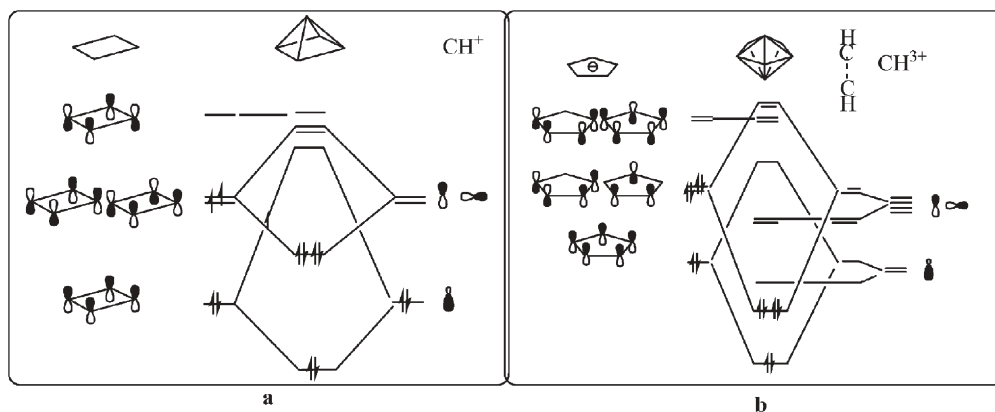


Fig. 2 Interaction diagram between (a) cyclobutadiene and CH^+ to give square pyramidal $C_5H_5^+$ and (b) cyclopentadienyl anion and two CH_3^+ to give pentagonal bipyramidal $C_7H_7^{5+}$. Isoelectronic and isostructural $C_2B_5H_7$ is well known.

orbital. The remaining two p-orbitals which are perpendicular to each other form $2n$ molecular orbitals, n bonding and n antibonding. This accounts for the $(n + 1)$ electron pair requirement for the *closo*-skeleton. The *nido*- and *arachno*-structural forms with one and two missing vertices respectively need one and two additional electron pairs than that required by the parent *closo*-system and correspond to the pyramidal and planar structures of Fig. 1. The double line arrows connect clusters with the same number of electron pairs for cluster bonding following the approach of Rudolph.⁸ It is indicated by $9 \rightarrow 5 \rightarrow 1$, $8 \rightarrow 4$ and $6 \rightarrow 2$ and shows the relationship between *closo*-, *nido*-, and *arachno*- cluster geometries. The stable isomers *nido*-carboranes based on pentagonal pyramid and square pyramid prefer carbon atoms in the ring, and not at the cap, so that the carbon atoms are only tetracoordinate. Corresponding *arachno*-structures of **7**, **8**, and **9** are planar aromatics.

Though there is no equivalent planar to pyramidal and to deltahedral transition possible to obtain $B_nH_n^{2-}$ ($n = 8-12$), it is instructive to visualize schematic dimerization of **4** to $C_2B_8H_{10}$, **5** to **21**, and **6** to **19**. Any of the resulting carboranes provide examples of structures with hypercarbon. $CpFeC_4B_8H_{12}FeCp$ and $CpCoC_2B_{10}H_{12}CoCp$ are examples of fourteen-vertex carboranes.²⁷ The perturbation caused by carbon in the borane cage affects both chemical and physical properties. Anionic $CB_{n-1}H_n^{-1}$ and neutral *closo*-carboranes ($C_2B_{n-2}H_n$; $n = 5-12$) are well-known in the literature and have many interesting applications.^{9,11-14,28}

Wade's rules prescribe the right electron count needed for a structural pattern. The presence of the carbon atoms leads to positional isomers. Their relative isomer stabilities is one of the intriguing aspects of polyhedral carboranes. Many experimental and theoretical studies have been made in order to assess the stability order of relatively rigid *closo*-structures with

hypercarbons.^{11,29-32} Three isomers of the icosahedral carborane $C_2B_{10}H_{12}$ are known (Fig. 3). Thermal isomerization and equilibrium studies established that **21a** (1,2-isomer (*ortho*)) is the least stable one and isomerizes to the next stable **21b** (1,7-isomer (*meta*)) at 500 °C. This in turn goes to the most stable **21c** (1,12-isomer (*para*)) above 615 °C.³¹ Theoretical studies at various levels have confirmed this experimental trend.³²

Many empirical suggestion have been put forward to account for the relative stability of various isomers.^{27,33,34} According to the William's rule,³³ carbon prefers to be at lower connectivity site, and they will take nonadjacent position. Gimarc's topological charge rule³⁴ predicts the location of carbon atoms based on the perturbations caused on the homogeneous system by a foreign atom. The charge generated by this perturbation at various locations in the molecule decides the next preferred position for another incoming atom. In other words, the electronegative heteroatoms prefer sites with the highest negative charge. According to the ring-cap compatibility rule,²⁷ the most stable isomer will be the one where the size of the ring matches the capping group for maximum overlap for the interaction as described in Fig. 2 (Fig. 4). This allows the selection of a ring of a particular size for a given cap and *vice versa*. The BH group has more diffuse orbitals than the CH group. BH would therefore prefer a larger ring than that preferred by the CH.

The overlap of BH caps with borocycles will decrease in the order of the ring size as $5 > 4 \gg 3 \sim 6$. Similarly for CH with less diffuse orbitals, the order is $4 > 3 > 5 \gg 6$. In **7**, the axial position above and below the three membered ring will be more appropriate for a CH than a BH cap. Hence **7a** is most stable and **7c** is the least stable (Fig. 5). Theoretical studies at MP2/6-31G* level of theory³⁰ shows that **7a** is more stable than **7b** and **7c** by 35.3 and 57.1 kcal mol⁻¹ respectively. Only **7a** is synthesized.³⁰ Similarly **8a** is more stable than **8b** by

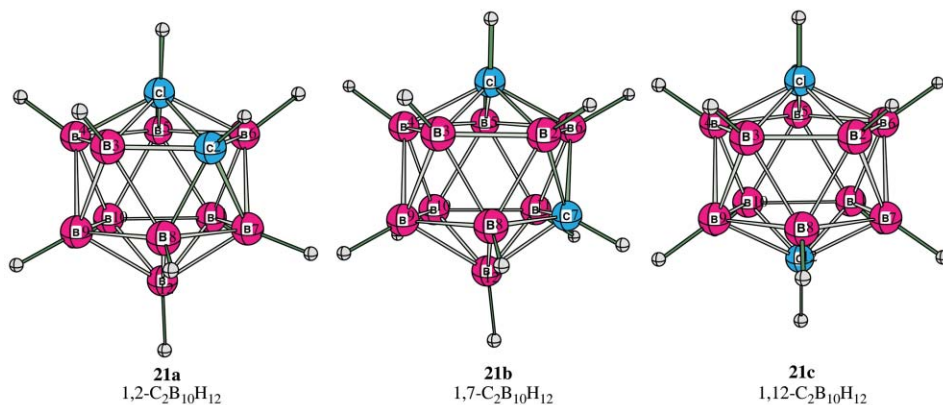


Fig. 3 Structural isomers of icosahedral dicarborane, $C_2B_{10}H_{12}$.

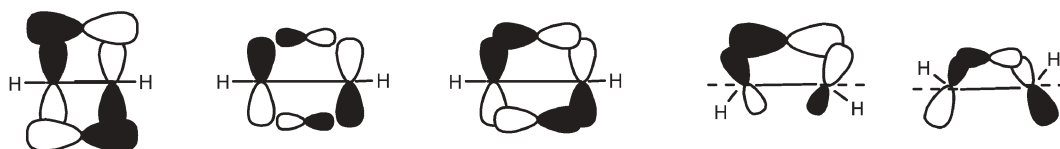


Fig. 4 Diagrammatic presentation of the ring-cap compatibility.

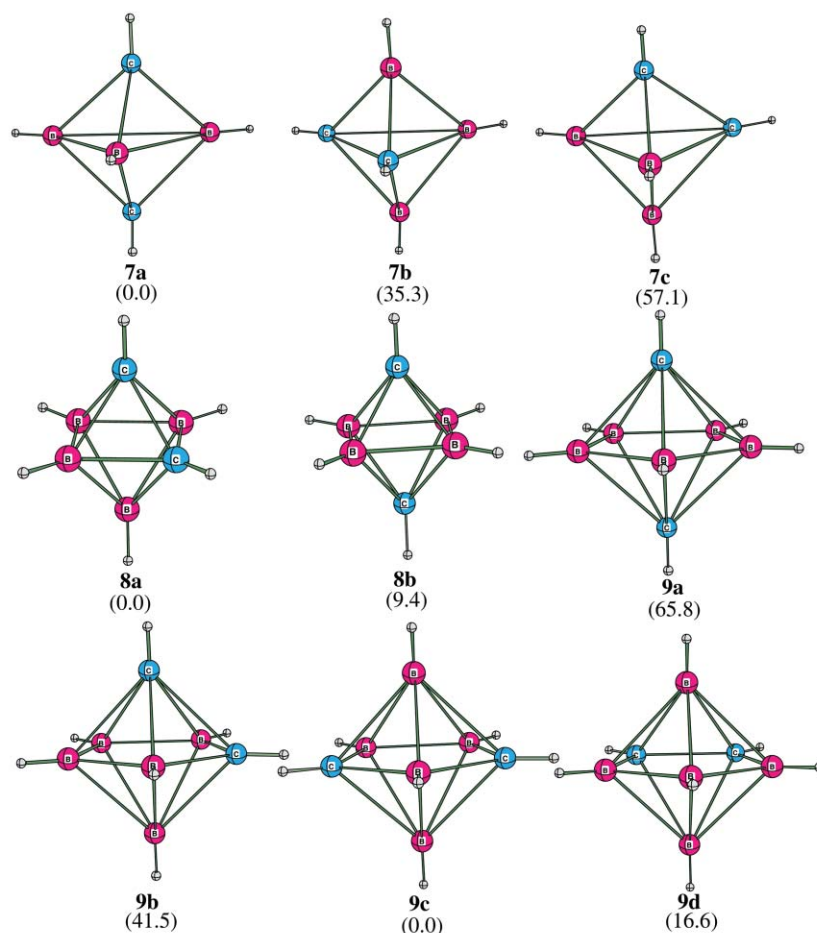


Fig. 5 Structural isomers of **7** ($C_2B_3H_5$), **8** ($C_2B_4H_6$) and **9** ($C_2B_5H_7$) of *closo*-dicarbaborane. Relative energies in kcal mol^{-1} are shown in the parenthesis at MP2/6-31G* level of theory.

$9.4 \text{ kcal mol}^{-1}$. According to overlap criterion five membered borocycles prefer BH rather than CH as caps. Hence **9a** is the least stable isomer of the four possibilities. When one CH cap is exchanged with a BH group from the ring as in **9b**, the system becomes more stable. Hence the most stable isomers are **9c** and **9d**. The greater stability of **9c** over **9d** may be explained by the concept of bond separation energy or by the difference in bond energies. Hence, the stability order is **9c** > **9d** > **9b** > **9a**. The calculated energies are in accordance with this (Fig. 5).

Recently, Welch *et al.* successfully synthesized the missing thirteen-vertex *closo*-monocarbaborane $CB_{12}H_{13}^-$, where carbon is hexacoordinate.³⁵ There are endless possibilities of hypercoordinate carbon in *nido*- and *arachno*-structural varieties based on larger polyhedra. The charges in these structures are often alleviated by adding hydrogens. Most of the carbon atoms in these carborane skeletons are hypercoordinate.

We have investigated theoretically the stability of relatively unexplored carbon-rich cationic *closo*-tricarboranes, the new candidates in this category.³⁶ The results on $C_3B_{n-3}H_n^{I+}$, ($n = 5, 6, 7, 10, 12$), point out the feasibility of synthesis of several of them (Fig. 6).

There are many positional isomers possible and their stability could be explained by the ring-cap compatibility rule

as described earlier. The positive charge of the isomers of $C_3B_{n-3}H_n^{I+}$ is distributed throughout the cage, making them suitable candidates as weakly electrophilic cations. Only *nido*- and *arachno*- variants are known experimentally with three or more carbon atoms so far. Some of the familiar examples are the pentagonal pyramidal $C_4B_2H_6$ and $C_3B_3H_7$.^{5,37} The compatibility of fragment molecular orbitals in overlap holds true here as well. The carbon atoms in the pentagonal pyramidal $C_4B_2H_6$ prefer to be a part of the five membered ring, so that the boron atom with more diffuse orbitals interacts with the five membered ring (Fig. 4). Thus, $C_4B_2H_6$ does not have a hypercoordinate carbon.

The variety of hypercarbon environment enlarges with further substitution of boron vertices by metal and other hetero atoms. Metallocarboranes are a distinctive class of compounds where one of the vertices is replaced by a transition metal with or without ligands, which is distinct from metallocarboranes, which have metal atoms as substituents occupying *exo*-sites attached to carborane cages.³⁸

The structure of carboranes discussed so far has *exo*-bonds on all the vertices excluding the shared vertices. Another variation in hypercarbon chemistry of carboranes came from its comparison to benzyne. The benzyne equivalents of such

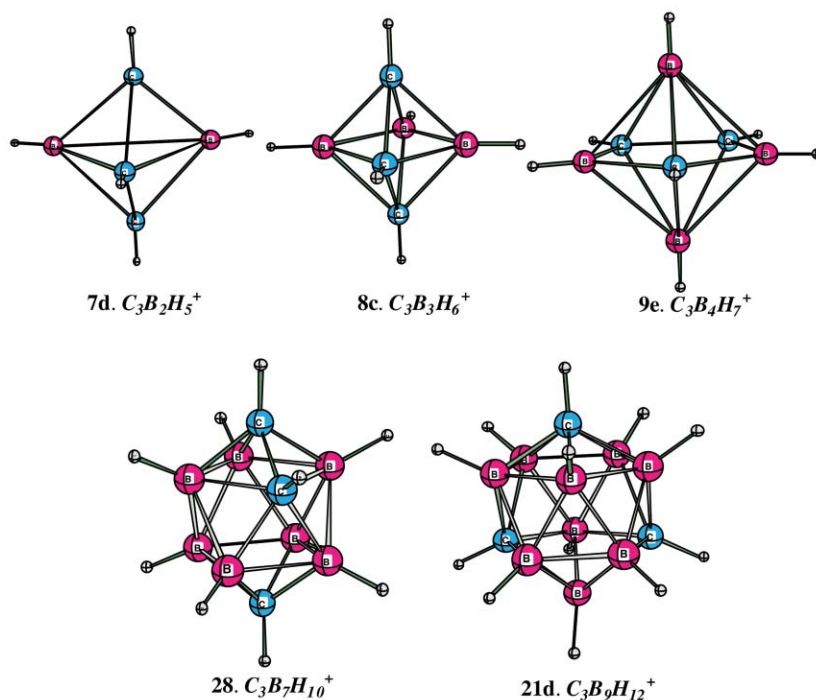


Fig. 6 The most stable structures calculated in each structural variety of $C_3B_{n-3}H_n^+$ ($n = 5, 6, 7, 10, 12$).

polyhedral carborane structures are found to be minima on their potential energy surface by first principles calculations.³⁹ The *ortho*, *meta* and *para* isomers of dicarborynes, $C_2B_{10}H_{10}$, are calculated to be minima (Fig. 7). Among these isomers, the *ortho*- isomer is synthesized and characterized.³⁹ Other structures are predicted to be stable. The *ortho*-isomer (**29**) is similar in reactivity to benzyne and undergoes cyclo additions and ene reactions with various unsaturated species such as dienes and acetylenes.³⁹ A theoretical investigation on various carborynes (5-, 6-, 7-, 10- and 12-vertex dicarba isomers) showed that there are isomers that are thermodynamically more favorable than benzyne. All these structures have hypercoordinated carbon atoms. The stability of these isomers depends upon the ring-cap compatibility rule mentioned earlier.²⁷

3. Condensed polyhedral carboranes

Condensed carboranes form another family of compounds exhibiting hypercarbons. There are four types of condensation possible in polyhedral systems namely single vertex, edge, face and four atoms sharing. The electron requirement of these compounds can be accounted by extending the Wade's rules. This is realized by introducing a new electron counting rule, with two additional variables m and o , the '*mno*' rule.¹⁵ According to this, the number of electron pairs needed for a stable condensed polyhedral structure is given by the sum of the number of cages (m), the number of vertices (n), and the number of single vertex shared atoms (o).¹⁵ Application of this rule to neo- $C_4B_{18}H_{22}$ (**30**) shows that twenty six electron pairs ($m = 2$, $n = 22$, $o = 0$ and the two for the two missing vertices)

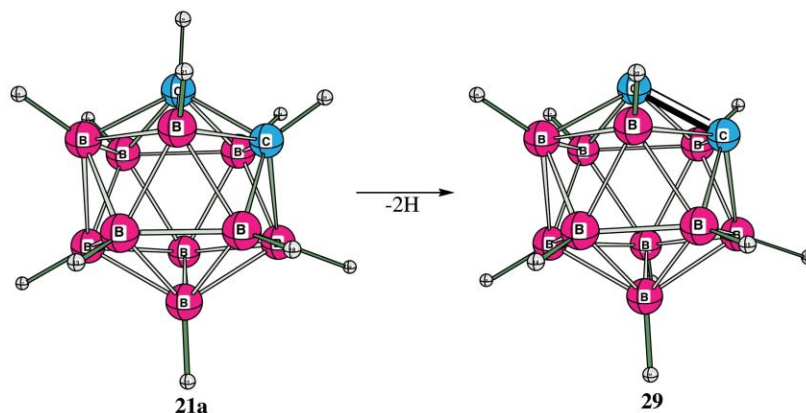
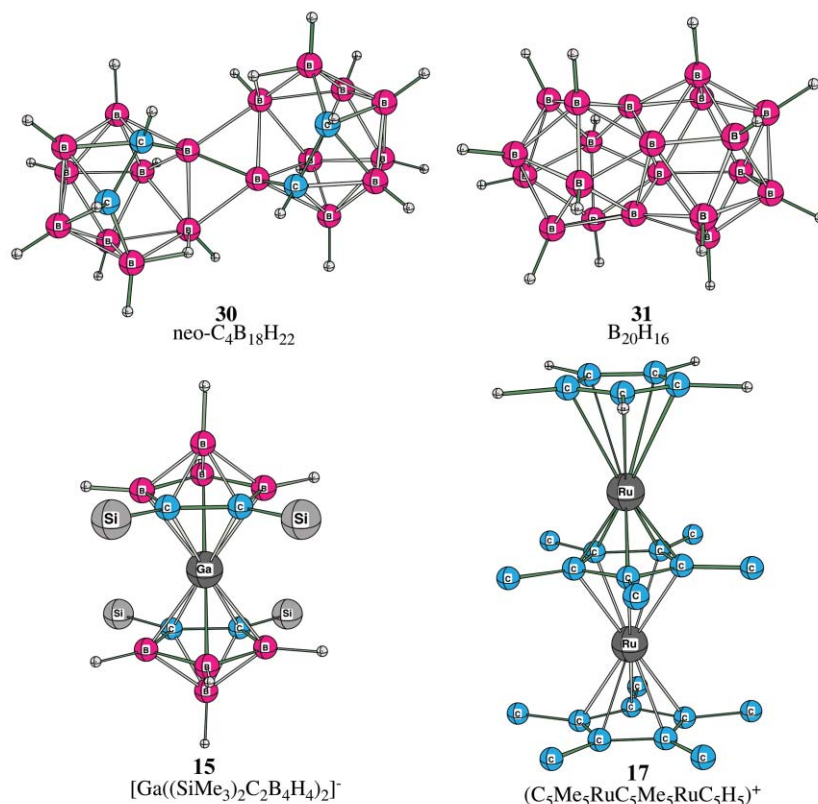


Fig. 7 Schematic diagram of *ortho*-dicarboryne and corresponding dicarboryne.

are needed for the stability. This electron requirement is satiated by sixteen electron pairs from sixteen BH vertices, six electron pairs from four CH vertices, three electron pairs from the two shared boron atoms (since shared atom gives all its electrons) and one electron pair from the two bridging hydrogen atoms. *closo*-Condensed carboranes are not reported so far.

The twenty vertex $B_{20}H_{16}$ (**31**) obtained by sharing four atoms between two icosahedra is known experimentally and follows the *mno* rule. A carborane with this structure, for example, $CB_{19}H_{16}$ will require a positive charge. This is not yet known. We have studied recently the energetics of the isomers of $CB_{19}H_{16}^+$.⁴⁰ There are four possible isomers *viz.* $1-CB_{19}H_{16}^+$, $2-CB_{19}H_{16}^+$, $3-CB_{19}H_{16}^+$, and $4-CB_{19}H_{16}^+$. Out of these, $1-CB_{19}H_{16}^+$ is the most stable and the $4-CB_{19}H_{16}^+$ is the least. Their stability could be explained by the ring-cap compatibility rule as described earlier. $1-CB_{19}H_{16}^+$, $2-CB_{19}H_{16}^+$ and $3-CB_{19}H_{16}^+$ have hexacoordinated carbon atoms and $4-CB_{19}H_{16}^+$ has a heptacoordinated carbon atom. Condensation of **9** by edge sharing gives **10**. The double line arrows between condensed systems $10 \rightarrow 11 \rightarrow 12 \rightarrow 13 \rightarrow 14$ have implications similar to those in the Rudolph diagram. These are characterized by the same number of electron pairs for cluster bonding. *nido*- and *arachno*-condensed species are experimentally known both as molecular and polymeric structures.¹⁵ The condensed structure consisting of two *nido*- C_2B_9 units joined by forming *exo* bonds, $C_4B_{18}H_{22}$ (**30**), and its isomer *iso*- $C_4B_{18}H_{22}$, where *closo*-dicarba and *nido*-dicarba units are fused by 2c-2e bonds are two early experimental examples.

Structures **15**, **16**, **17** and **18** are schematic representation of single vertex sharing system. The specific example for **15** is $[Ga((SiMe_3)_2C_2B_4H_4)_2]^-$.¹⁵ According to the *mno* rule, sixteen electrons pairs ($m = 2$, $n = 13$, $o = 1$) are needed for **15**. Eight electron pairs from the eight BH vertices, six electron pairs from the four $CSiMe_3$ vertices and three electron pairs from shared gallium (since the shared atom gives all its valence electrons) make it only 15.5 electron pairs. Therefore, the structure requires one additional electron to be stable. Hence it is a monoanion. Triple decker (**17**) and tetra decker sandwich complexes are important classes of hypercarbon compounds obtained by removing two capping groups.^{18,41} A variety of rings such as C_5H_5 , C_6H_6 , $C_2B_2SR_4$, $C_4B_3R_5$, and $C_3B_2R_5$ and a range of transition metals are found in triple decker sandwich complexes.^{18,41} The geometry of these rings varies considerably with metals and the number of valence electron present in the system. $[(C_5H_5)Ru(C_5(Me)_5)Ru(C_5(Me)_5)]^+$ (**17**),¹⁸ is an example of triple decker sandwich complexes and has five hypercarbon atoms. According to the *mno* rule, the skeletal electron pair requirement for this structure is twenty four ($m = 3$, $n = 17$, $o = 2$ and two electron pair for missing vertex). The fifteen CH groups contribute 22.5 electron pairs and the two Ru atoms contribute one electron pair each for skeletal bonding. The total electron pair for the skeletal bonding is 24.5. Hence the molecule is monocation. There are several isoelectronic and isostructural metallacarboranes characterized experimentally.¹⁵ There are a series of experimentally known tetra decker sandwich complexes.^{18,41} In these complexes the two terminal metallocene units slip away from the central metal by differing amounts when the electron count



differs from what is estimated from the *mno* rule. Larger multidecker sandwiches and one dimensional stacks with hypercarbons, *e.g.* $(C_3B_2R_5Ni)_n$ and $(C_3B_2R_5Rh)_n$ are also known experimentally.^{18,41}

Condensation is also possible between the polyhedral structures and benzenoid aromatics. The obvious mode of mixed condensation between benzenoid aromatics and polyhedral boranes is by two atoms sharing (edge-sharing). Benzocbororane, $C_6B_{10}H_{14}$ (**27**, Fig. 1) and related structures are experimentally characterized.^{17,42} The benzene ring in **27** does not possess substantial π -delocalization.⁴³ According to the *mno* rule, twenty electrons pairs ($m = 2$, $n = 16$, $o = 0$ and the two for the two missing vertices) are needed for **27**. The twelve BH vertices contribute twelve electron pairs, four CH vertices contribute six electron pairs and the two shared carbon atoms contribute four electron pairs (since shared atom gives all its valence electrons). The total number of electron pairs contributed for cluster bonding is twenty, so that **27** is neutral.

4. Endohedral structures

The single atom bridged structure such as **15** are discussed previously as sandwich of two pentagonal pyramids with a skeletal electron pair requirement of sixteen ($m = 2$, $n = 13$, $o = 1$). Here the bridging atom is relatively large. If the bridging atom that links the two pentagonal pyramids is small, there will be strong nonbonding interactions between the two polyhedra. This is in tune with the nonexistence of the sandwich complexes involving boron skeleton alone. If the two pentagonal pyramids are brought together to form an icosahedron encapsulating the central atom, the skeletal electronic pair requirement will reduce to thirteen ($m = 1$, $n = 12$, $o = 0$) (Fig. 8). The orbitals of the encapsulated atom stabilize the molecular orbitals of the icosahedral borane and do not bring any additional stabilized orbitals. Thus there is a

difference of three electron pairs between the requirements of these two structures.

To our knowledge, no endohedral complex of polyhedral borane (**20**) has been reported experimentally, even though recent theoretical studies have shown that several of them are minima on their potential energy surfaces.¹⁹ Though $C@B_{12}H_{12}^{2+}$ itself is not a minimum, the presence of an encapsulated boron atom inside a polyhedral arrangement of β -rhombohedral boron has encouraged further studies in this direction.⁴⁴

The structure and the stability of endohedral carboranes, $X@CB_{11}H_{12}^q$ and $X@C_2B_{10}H_{12}^q$ ($X = He, Ne$ ($q = -1, 0$), Li ($q = 0, 1$), Be ($q = 1, 2$)) and endohedral hydrocarbon cage like $X@C_4H_4$, $X@C_8H_8$, $X@C_8H_{14}$, $X@C_{10}H_{16}$, $X@C_{12}H_{12}$ and $X@C_{16}H_{16}$ ($X = H^+, H, He, Ne, Ar, Li^{0,1+}, Be^{0,1+,2+}, Na^{0,1+}, Mg^{0,1+,2+}$) have been studied.¹⁹ Since the encapsulation makes the system strained, the encapsulation in the smaller cages makes the resulting endohedral species even more unfavorable.

Three-dimensional structures with central carbon atom are also known experimentally with the fullerenes and even with the classical strained hydrocarbon, dodecahedron ($C_{20}H_{20}$, I_h).⁴⁵ Theoretical studies on the structure and stability of $X@C_{20}H_{20}$ ($X = H, He, Ne, Li^{0/+}, Be^{0/+2+}, Na^{0/+}, Mg^{0/+2+}$) have been reported (**32**, Fig. 9).²⁰ The C–H bonds are found to be longer in $Li@C_{20}H_{20}$, $Na@C_{20}H_{20}$ and $Mg@C_{20}H_{20}$ than in $Li^+@C_{20}H_{20}$, $Na^+@C_{20}H_{20}$ and $Mg^{2+}@C_{20}H_{20}$ respectively. The LUMO of the parent dodecahedron is C–H antibonding and C–C bonding (Fig. 9). Thus, the additional electrons contributed by the central atom occupy this empty orbital, elongating the C–H bonds and shortening the C–C bonds.

5. Planar molecules

Is it possible to design planar hypercoordinate carbon atom? Schleyer and coworkers have studied theoretically a variety of such structures with planar penta, hexa or hepta coordinated

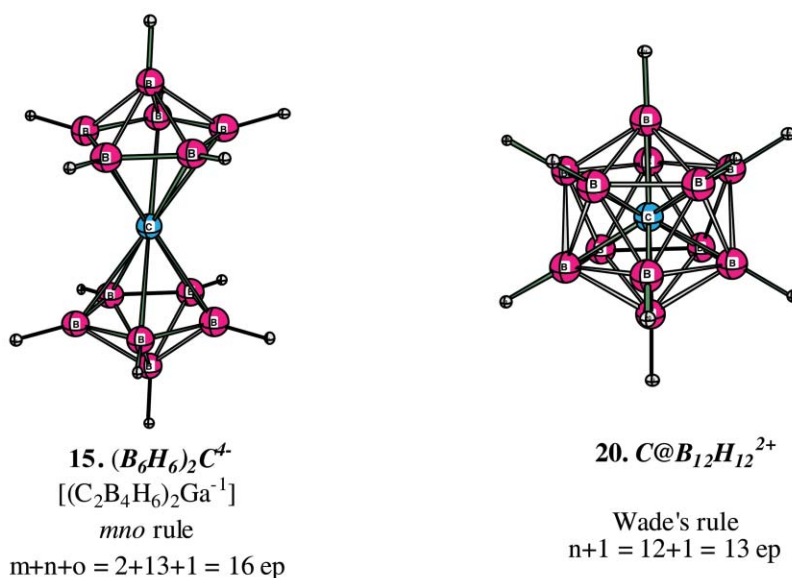


Fig. 8 Schematic representation of the relation between a condensed vertex-sharing polyhedra and an encapsulated polyhedron. Experimental known structure is shown in square brackets. Electronic requirement by *mno* rule and Wade's rule is given below each structure.

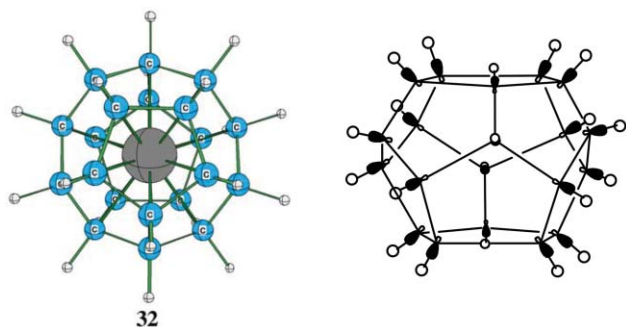


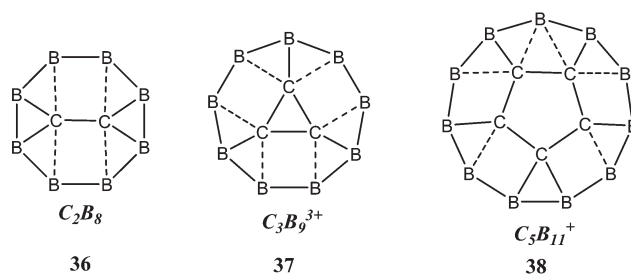
Fig. 9 $X@C_{20}H_{20}$ ($X = H, He, Ne, Li^{0/+}, Be^{0/+2}, Na^{0/+}, Mg^{0/+2}$) and LUMO of the $C_{20}H_{20}$.

carbon atoms.^{22,23} If a carbon is added at the centre of **1**, **2** and **3**, hypercoordinated **26**, **25** and **24** result. As an approximation, these molecules can be considered as encapsulated *arachno*-systems. These studies were triggered by the nucleus independent chemical shift (NICS) values, a measure of aromaticity, calculated by placing a ghost atom at the center of the ring. If the cyclic electron delocalization is retained, an atom at the centre could be made a part of the aromatic structure provided the ring is large enough. The calculations pointed out that naked hexagonal rings of CB_6^{2-} (**25a**) and various positional isomers of C_3B_4 (**25b–25d**, Fig. 10) are minima on their potential energy surfaces. The stability of these structures with 6π electrons is explained in terms of their delocalized π molecular orbitals. The highest occupied molecular orbital (HOMO) is the degenerate set (e_{1g}) similar to benzene and the third occupied π -level (a_{2u}) is stabilized by the favorable interaction with the p-orbitals of the central carbon atom (Fig. 11). However these structures are expected to be highly reactive for the following reason. Let us consider CB_6^{2-} which has twenty four valence electrons. Six electrons are involved in π delocalization. There are only eighteen electrons remaining for the six B–B bonds and to fill the exohedral sp-hybrid orbitals on the boron atoms. This would

leave several low-lying vacant orbitals in the sigma plane. In the absence of exohedral hydrogen atoms, it is not possible to predict the exact number of electrons that boron contribute to skeletal bonding, making it difficult to apply the *mno* rule.

There are seventeen minima found on the potential energy surface of C_3B_4 , out of which thirteen are more favorable than the three isomers shown in Fig. 10. They are calculated to have appreciable barriers for rearrangement. These structures, therefore, may be realizable either in the gas-phase or in matrix isolation studies. Another favorable structure for hypercarbon is found in the heptacoordinated carbon compound, CB_7^- (**24**, Fig. 10).

Schleyer and coworkers further explored another class of compounds with planar penta coordinate carbon atom (ppC) theoretically.²² Three borocarbon units with ppC are introduced which can replace the $-(CH)_3-$ subunits in aromatic and antiaromatic hydrocarbons to construct this family of molecules called hyparenes (Fig. 10). These three borocarbon units $-C_3B_3-$, $-C_2B_4-$, and $-CB_5-$ contribute two, one and zero electrons respectively to the parent π -system. Thus, these units when introduced to a hydrocarbon, determine its aromatic character (**33–35**, Fig. 10). A C_3B_3 unit when introduced into naphthalene (**33**) makes it antiaromatic, whereas there is no change in the aromaticity when a CB_5 unit is added to naphthalene (**35**).



The Schleyer group also predicted local minima for higher boron rings holding more than one planar hypercoordinate carbon atom within. An eight membered ring, B₈ with two

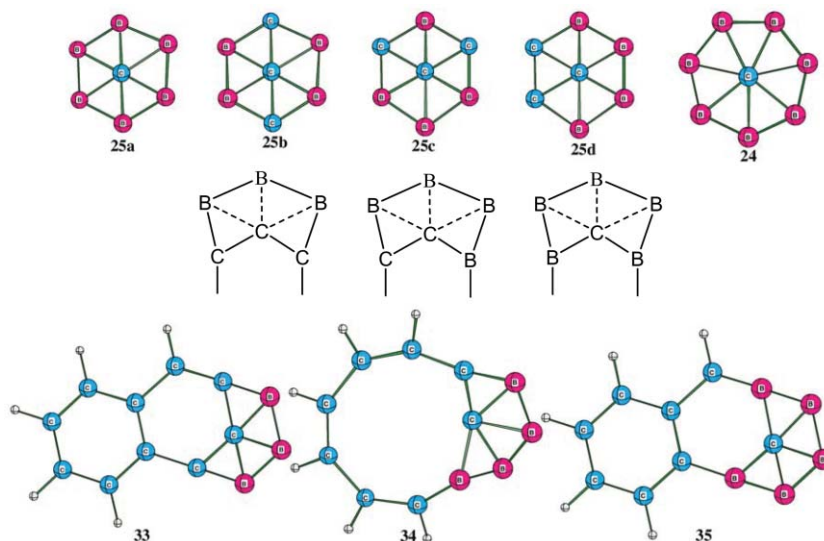


Fig. 10 The planar aromatic structures with hypercoordinate carbon atoms.

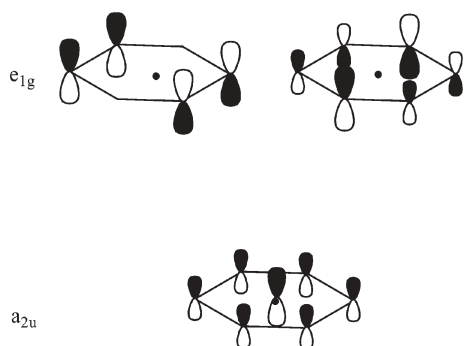


Fig. 11 π -Molecular orbitals of CB_7^- .

pentacoordinate carbon atoms (**36**), a nine membered ring B9 with three pentacoordinate carbon atoms (**37**) and an eleven membered ring with five carbon atoms (**38**),²³ are found to fulfil the geometric and electronic requirements. These molecules are calculated to be fluxional. There is computational evidence of D_{5h} planar pentacoordinate carbon in the centre of five membered Cu_5H_5 ring as well.⁴⁶

6. Wheel structures

Wheel type structures emerge when the planar structures, though not minima on their own, stack together by reducing the inter-ring distance.²¹ Stacking two of **26** or **25** give **23** and **22** respectively. A description of their electronic structure may

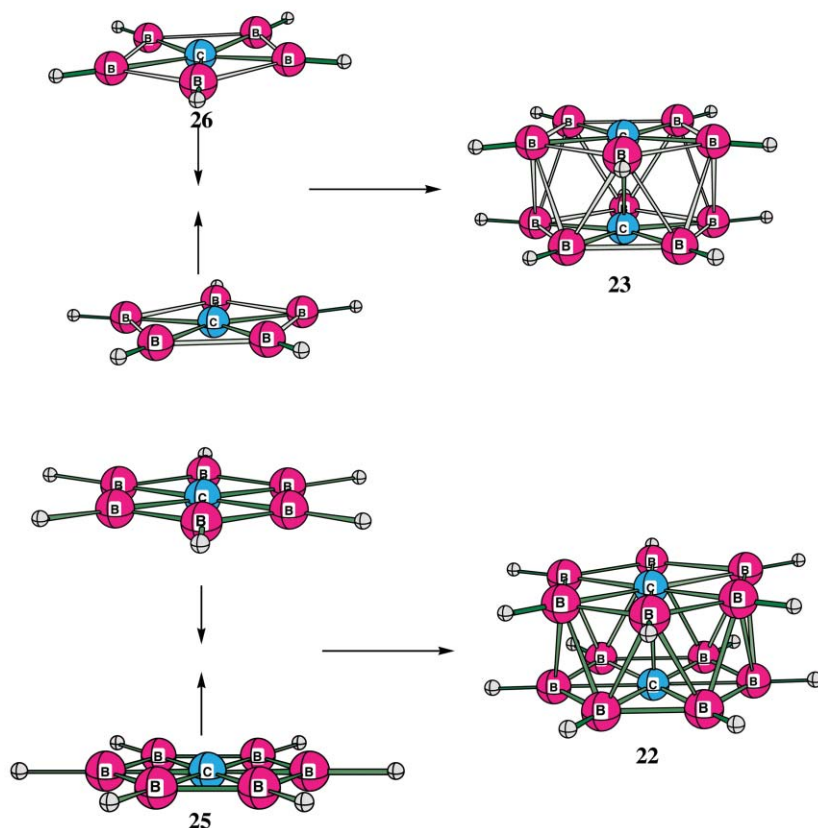


Fig. 12 Schematic diagram, showing the construction of wheel structure from flat discs.

be attempted from through-bond interaction as in p-benzyne. Through bond interaction makes the bonding combination (σ_{C1-C4}) of sp-hybrid orbitals on the carbon atoms at para position (C1 and C4) higher in energy than the antibonding combination (σ^*_{C1-C4}). When 1,4-carbon atoms of p-benzyne are brought closer, the bonding σ_{C1-C4} orbital energy becomes lower than the antibonding combination σ^*_{C1-C4} . Occupation of this orbital generates a single bond between C1 and C4 leading to butadiene. A similar structure, *para*-carboryne with a C–C bond, is found to be minima and is an interesting molecular drum with an axis (**23**, Fig. 12). Thus, the *para*-carboryne exhibits bond-stretch isomerism. This type of wheel structure is also calculated for $C_2B_{12}H_{10}$, the carboryne analog of fourteen-vertex polyhedral borane (**22**, Fig. 12).²¹

7. Prospects

The initial examples of hypercoordinate carbon centred around structures where only one carbon is hypercoordinate while the rest of the atoms had normal coordination. The electron deficient three dimensional carbocations and polyhedral boranes changed this view totally. All the atoms of the skeleton in polyhedral boranes and related molecules are hypercoordinated. Condensed polyhedral carboranes have only just began appear in the chemical literature. Now that the rules for condensation are known, there could be greater interest in this area. The condensation modes represented in Fig. 1 could be expanded to all polyhedral structures and their

derivatives such as *nido*- and *arachno*- structures. Thus further examples of hypercarbons in the polyhedral carborane chemistry are anticipated. A better understanding of the structures would help to bridge the gap between carboranes and boron-rich boroncarbides, even though one does not view them currently as structures with hypercoordinate carbons.

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