# Hypercoordinate carbon in polyhedral organic structures

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Carbon holds a unique position among the elements. It forms more than 14 millions of currently known organic compounds, structural organization of which is governed by the beautifully simple principles of tetravalence and tetrahedral stereochemical configuration. In the past decades, the edifice of the classical structural theory of organic compounds has been complemented with new approaches allowing a rational design of polyhedral clusters with hypercoordinate carbon centres.

Why the bonding capacity of transition metal compounds is much richer and their stereochemical types are more diversified as compared with those of main group element compounds, in particular, organic compounds – the compounds of carbon? The answer to this question is that by possessing low-lying *d*-orbitals transition metal atoms may use the expanded set of orbitals to bind surrounding ligands, whereas the set of valence orbitals of carbon and other main group elements is confined by only one *s* and three *p* orbitals. With these four valence orbitals, carbon cannot form more than four covalent, *i.e.* two-centre, two-electron (2c-2e) bonds directed, as van' Hoff and Le Bel ingeniously foresaw, to the corners of a tetrahedron. The tetravalence of carbon and the tetrahedral geometry of its single bonds are the concepts fully sufficient for the qualitative description of the structural organization of virtually all currently known ~14 millions of organic compounds and, in general, of other main group element compounds. Some of the latter present, however, essential exclusions to this elegantly simple bonding scheme. Thus, in many organoboron compounds, even in the hydrocarbon equivalents, boranes, the boron centres are covalently bound to more than four ligands; this is a consequence of their electron deficiency and the formation of multicentre bonds.

In electron-deficient compounds, the number of electrons on the valence orbitals of a central atom is insufficient to form 2c-2e bonds with each of the neighbouring ligating atoms. This necessitates accommodation of the electronic structure of a compound to sharing one or more of electron pairs among three or more atoms, which leads to the formation of structures with hypercoordinated atoms. Carbonium ions are the closest isoelectronic analogues of electron-deficient boranes and it is within this class of organic compounds that the first experimentally and computationally characterised species with hypercoordinate carbon atoms were discovered.[1,2] Methonium cation **1**, which was first detected in a gas phase by mass spectroscopy,[3] is the archetypal compound with a pentacoordinate carbon. Its structure is usually described by three standard 2c-2e bonds and a three-centre, two-electron (3c-2e) bond. As shown by the high level *ab initio* calculations,[4] further replacing 2c-2e C–H bonds in **1** by the 3c-2e HCH bonds results in ions **2** and **3** possessing structures with hexacoordinate and heptacoordinate carbon atoms, respectively.



**1**, $C_s$     **2**, $C_{2v}$     **3**, $C_{3v}$
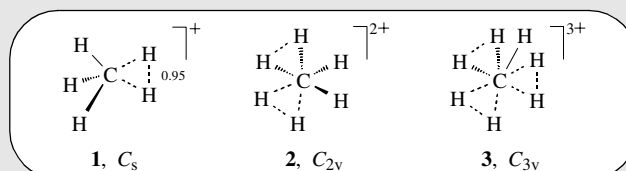
The structures of ions **1**–**3** present no violation of the Lewis octet rule since the bonding in them is maintained by the same four electron pairs as in methane, but in **1**–**3** these are distributed in a way that ensures the binding of carbon to seven hydrogen atoms. This leads to the extreme stereochemical nonrigidity of the protonated methane ions containing a hypercoordinate carbon. In methonium ion **1**, proton exchange processes are almost barrier-free even at 0 K. This highest fluxionality is reflected by the IR spectrum of **1** containing ~900 spectral lines in the range 2770–3150 cm$^{-1}$ alone and not compatible with any definite structure.[5] The retardation of ligand permutations around the hypercoordinate carbon centres and the consolidation of structures containing such centres is attained through replacing hydrogen atoms in **1**, **2** by bulkier groups, as in the aurated carbon cations C(AuPPh$_3$)$_5^+$ and C(AuPPh$_3$)$_6^{2+}$,[6] and the inclusion of ligands surrounding these centres into a rigid network, as in pyramidal cations **4** and **5**.[1,2,7–9]

The polyhedral structures **4**, **5** with penta- and hexacoordinated apical carbons, respectively, can be viewed as π-complexes, the stability of which is ensured by orbital interactions between their fragments, the basal ring and the apical bond.
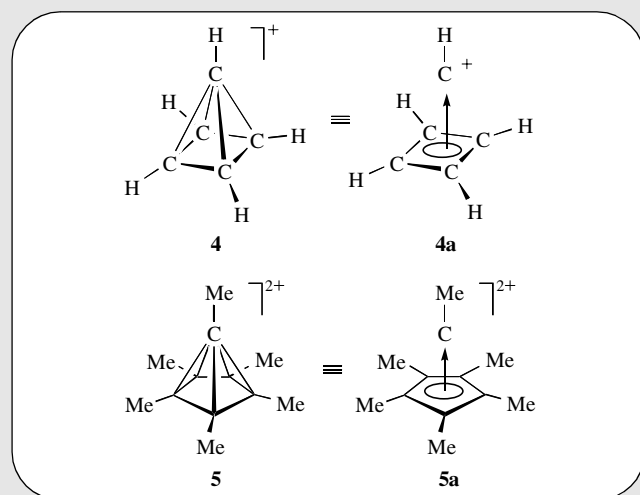
**4**   **4a**

**5**   **5a**

**6** 8e rule   **7** 14e rule   **8** 10e rule   **9** 8e rule

[ref. 10]

[ref. 12]

[ref. 11]

[ref. 13]   [ref. 14]

Using σ- and π-bonds, annulene rings and naked atoms as building blocks, one can construct various molecular polyhedra, *e.g.*, **8–12**, with the multiply edge-shared vertexes and by substituting these with carbon atoms design non-classical organic structures with hypercoordinate carbons.[1,9] The orbitals of the fragments involved into the multicentre bonding in such compounds are frontier π and π* MO of π-bonds and rings and *p*-AOs of σ-bonds and apical atoms. For each particular polyhedron, symmetry conditions dictate the number of bonding MOs, which may be formed as a result of coupling the orbitals of the fragments and, thus, the critical number of electrons which populate these MOs in a stable structure. The electron counting rules[1] for these so-called interstitial electrons (*i.e.*, π-electrons of the rings and valence electrons of the centres **X** and **Y** representing an atom or a σ-bond) are given below along with the samples of main group element non-classic molecules and ions, the structures of which adhere to the requirement of a corresponding rule. As a version of more general 'framework' electron count rules,[15] these rules may be conveniently used as a simple and unambiguous criterion in a search for stable polyhedral structures with hypercoordinate carbons.

The combinations of molecular fragments **6–9** do not exhaust all possible topologies of molecular polyhedra. Suppose, we are seeking for a way of stabilising the $D_{3h}$ configuration of a six-coordinate carbon atom appeared in the fluxional $CH_6^{2+}$ ion **2**. Let us surround a carbon atom with three CC bonds arranged
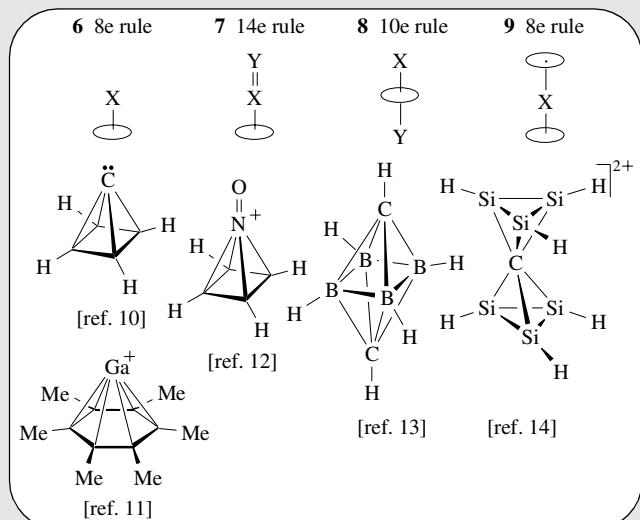
according to this symmetry and consider an orbital interaction diagram leaving aside that a set of π- and σ-orbitals of these bonds, which do not contribute to the multicentre bonding. As can be seen in the orbital interaction diagram (Figure 1), the hypothetical $D_{3h}$ complex $C(HC≡CH)_3$ possesses only three bonding MOs supporting a carbon atom at the centre of the prism. These MOs can be populated by no more than six electrons. This fact requires stripping two electrons from a neutral carbon and stabilization of the structure as a dication. To impart the complex with an appreciable degree of structural rigidity, its peripheral bonds may be integrated into a framework preserving the $D_{3h}$ symmetry of π-bonds providing for the multicentre bonding. As stems from the *ab initio* MP2(fu)/6-311G** calculations,[16] dication $C[C_6(CH_2)_6]^{2+}$ **10** is strongly stabilised relative to its fragments. In contrast with diprotonated methane **2**, all six bonds formed in **10** by the central carbon atom are fully equivalent and their lengths (1.530 Å) are typical of a standard ordinary CC bond.



**10**
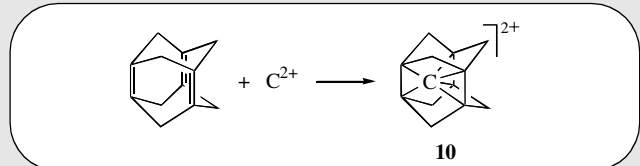
An approach[17] to the stabilization of organic structures in which hypercoordination at a carbon centre is progressed to its highest point is illustrated by the design of organolithium compounds **11** and **12** shown in Figure 2. One starts from the carbon sandwiches of type **9** with $(BH)_n$ rings. Since the π-orbitals of these rings are empty, all bonding MOs of the sandwiches will be filled with the interstitial electrons provided that the structures acquire a total charge equal to –4. Even though the $C[(BH)_3]_n^{4-}$ ($n = 3–5$) ions have closed-shell electronic configurations corresponding to the 8e rule, they are strongly destabilised due to electrostatic reasons. Can the repulsion of the negatively charged atoms in the anions be neutralised by surrounding these with proper counter-ions, *e.g.*, Li+? Not only it has been found to be the case, but because of the proneness of



**Figure 1** Orbital interaction diagram for the dication $C[(HC≡CH)]^{2+}$, the precursor of **10**.[16]
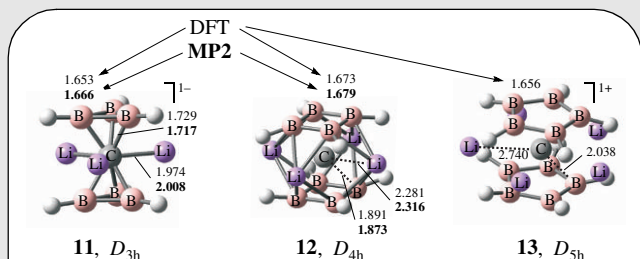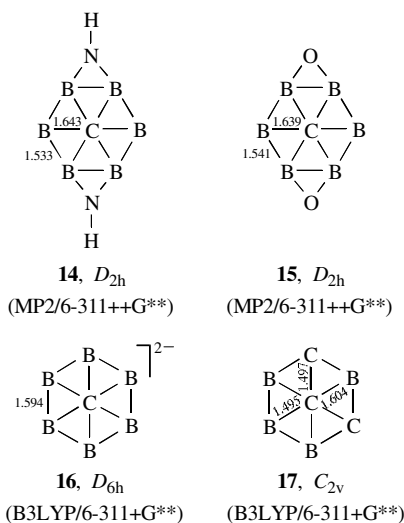


**Figure 2** Calculated structures of carbon sandwiches **11–13**.[17] The geometries of **11** and **12** are optimised at MP2/6-311+G** (MP2) and B3LYP/6-311+G** (DFT) and that of **13** is optimised at B3LYP/6-311+G**.

**11**, $D_{3h}$   **12**, $D_{4h}$   **13**, $D_{5h}$

lithium to render its low-lying empty AOs to electrons from the neighbouring donor centres, in $Li_3C[(BH)_3]^{2-}$ and $Li_4C[(BH)_4]_2$ carbon atoms have been found to complement their coordination sites with additional three and four partially covalent C–Li bonds, respectively. In **12**, the formal coordination number of carbon is 12. To obey the 8e rule,[1,18] the next member of this $D_{nh}$ sandwich family **13** (Figure 2) must be positively charged, which, indeed, has been found to be the case. Due to a larger size of the boron rings in **13**, the lithium ions cannot approach the carbon so closely as in **11** and **12**, and its structure may be regarded as an ionic cluster.

A new challenging direction in the study of non-classical organic compounds with hypercoordinate carbon atoms is the quest for structures in which these atoms occur in a planar arrangement of adjacent ligating centres. Such an arrangement has long been thought as inconceivable even for tetracoordinate carbon (ptC), but now computational and experimental evidence for a solution to the problem of stabilization of ptC centres, first posed by Hoffmann,[19] are plentiful.[9,20] In 2000, two independent research groups reported on the computational findings of stable structures containing planar hexacoordinate carbon atoms placed into the centre of a rigid cage composed of boron atoms. These are exemplified here by compounds **14**, **15**,[21] **16** and **17**.[22] Analysis of the electronic structure of compounds **14–17** shows that they have closed-shell aromatic 6π-electron systems. The electron-donor hexacoordinate carbon atoms bear substantial positive charges (0.8–0.9), which decrease the effective radius of carbon and reduce the steric strain in the planar system. The aromatic nature of **14–17** and their derivatives is in accordance with both structural and magnetic criteria of aromaticity: the shortened peripheral BB bonds,[21,22] which are 0.06–0.08 Å shorter than a standard double BB bond, and a typical dia-magnetic π-ring current.[23]



**Figure 3** Shapes and energy levels of the π-orbitals of anion **18** calculated by the B3LYP/6-311G** method.[24]

conceived as the next member of the family of planar organo-boron clusters with hypercoordinate carbon atoms, but in this symmetry, the distances between the central carbon and peripheral boron atoms exceed the limit of the longest single bonds of carbon, already met in **19**. The $D_{8h}$ structure of **20** corresponds to a hill-top on the $CB_8$ PES rather than a minimum.

To match the geometry demands dictated by the conditions for the sufficient overlap between AOs of the central and peripheral atoms, one can place a bulkier atom with an appropriate electronic configuration in the centre of the eight-membered boron wheel. The structures of **21–23** designed in this way have been proven to conform to sufficiently deep local minima on the respective PESs, and for **23**, experimental evidence for its formation under laser vaporization of a target boron cluster has been presented. All the octagonal clusters of **21–23** have π-aromatic electron shells, and **23** exhibits σ-aromaticity.



**14**, $D_{2h}$
(MP2/6-311++G**)

**15**, $D_{2h}$
(MP2/6-311++G**)

**16**, $D_{6h}$
(B3LYP/6-311+G**)

**17**, $C_{2v}$
(B3LYP/6-311+G**)

The unique capacity of boron to afford its empty p-AOs for the formation of multicentre π-bonding MOs with suit-able π-electron donating centres can be exploited for further expanding the six-membered boron wheel of **16**. The DFT (B3LYP/6-311+G**) calculations[24] showed that the nearest homologue of $CB_6^{2-}$, anion **18** with a planar heptacoordinate carbon atom immersed into the centre of the seven-membered ring of boron atoms, has a stable structure with the aromatic closed 6π-electron shell (Figure 3). By replacing boron in the ring by a carbon atom, a stable electrically neutral structure of **19** can be designed. The $D_{8h}$ structure of $CB_8$ **20** might be
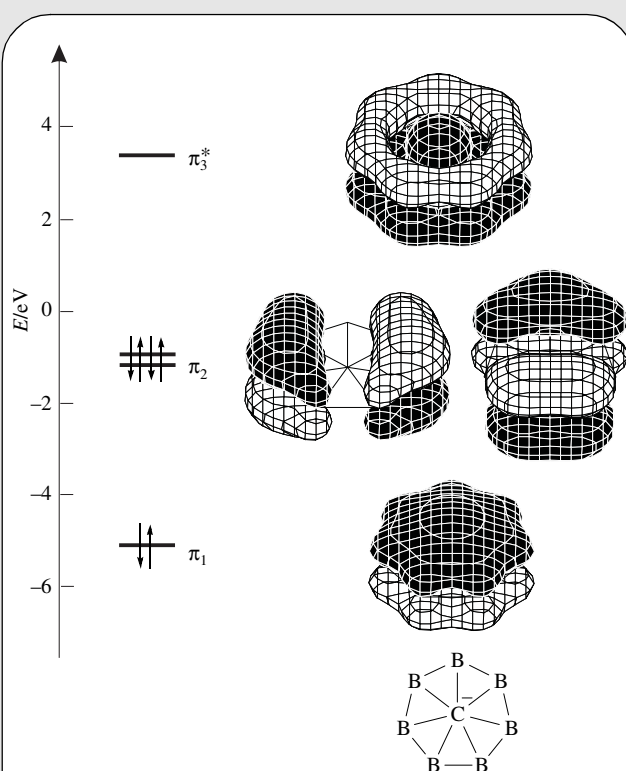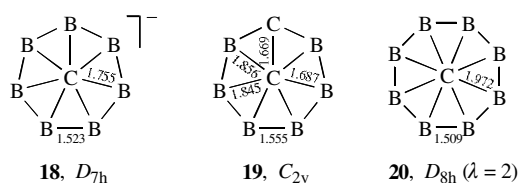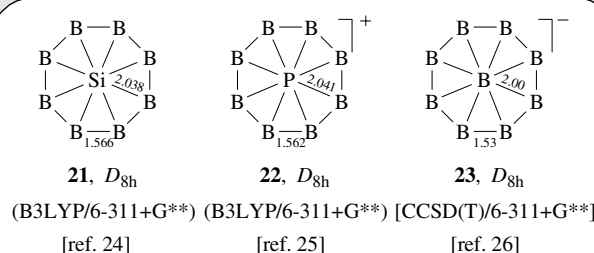


**21**, $D_{8h}$
(B3LYP/6-311+G**)
[ref. 24]

**22**, $D_{8h}$
(B3LYP/6-311+G**)
[ref. 25]

**23**, $D_{8h}$
[CCSD(T)/6-311+G**]
[ref. 26]

The closeness of the electron shells and the wide energy gaps between the electron populated and vacant orbitals are the primary features to be sought in the design of polyhedral non-classical structures with hypercoordinate carbon and other main group element centres. When the basic structural units matching these requirements, *e.g.*, **16**, **19**, are revealed, one can manipu-late with them in the same manner as with the fragments of structures **6–9** collecting the units edge-to-edge, edge-to-face, face-to-face and not forgetting to follow the above principles of three-dimensional aromaticity. In this way, in which Wang and Schleyer have recently constructed hyparene structures with planar pentacoordinate carbons[27] and wheel-shaped molecules with C–C 'axles',[28] the molecular architecture of non-classical



**18**, $D_{7h}$

**19**, $C_{2v}$

**20**, $D_{8h}$ (λ = 2)

organic molecules and ions can be significantly diversified. 'Poor carbon to be tortured – or seduced – in so many ways!' exclaimed the authors of a recent paper[29] devoted to compounds with tetracoordinated carbon centres having a bisphenoidal (half-planar) configuration.

Is an investigation into non-classical organic structures with carbon atoms coordinating 5–8 or more ligands or acquiring non-standard stereochemical configurations when tetracoordinated, just a fascinating computational game for adult researchers? We may confess that it is partially true. However, the main goal and the main consequence of this 'game' is gaining a deeper insight into the principles of structural organization of the compounds of carbon, which is a central element in modern material science: fullerenes and multi- and single-wall nanotubes being in the foreground. It is believed that now, when nanotechnological devices approach the atomic and molecular scales, the results of the study of non-classical organic compounds, briefly reviewed herein, will be increasingly helpful for the discovery of novel useful structural motifs.

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