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Structure and stability of the C-doped boron fullerenes $B_{60}C_{12}$ and $B_{80}C_{12}$ with quasi-planar pentacoordinated cage carbon atoms: a quantum-chemical study

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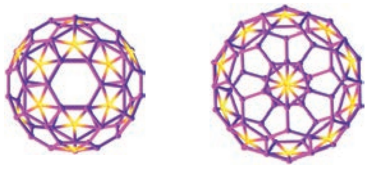
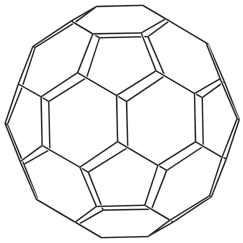
The novel stable C-doped boron fullerenes $B_{60}C_{12}$ and $B_{80}C_{12}$ with quasi-planar pentacoordinated cage carbon atoms have been computationally designed using DFT B3LYP/6-311+G(d,p) and M06/6-311+G(d,p) methods.



$B_{60}C_{12}$ $B_{80}C_{12}$

Due to their unusual aesthetically appealing structure and a wide range of potentially useful properties, fullerenes attract the attention of theoretical chemists and materials science researchers.[1,2] Whereas the synthesis, structure and various applications of carbon fullerenes have been already studied in much detail, investigation into boron fullerenes initiated by the computational prediction of spherical boron forms[3] and photoelectron spectroscopy detection of a cage-like B_{40}-cluster[4] has begun only recently.



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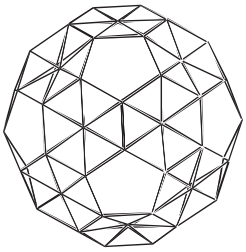

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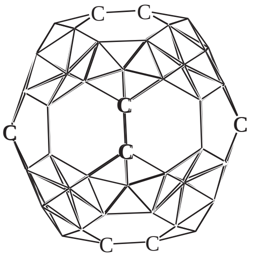

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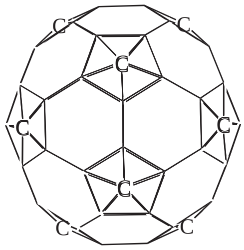
A usual approach to the theoretical design of boron fullerenes isoelectronic to the basic carbon analogs consists in capping the hexagonal and pentagonal faces of a spherical boron frame with additional boron atoms.[3] Thus, based on the carbon fullerene C_{60}, its isoelectronic boron analog B_{80} can be formed, in which icosahedral B_{60} framework **1** is completed by 20 apical boron atoms above the hexagonal faces (structure **2**).

The structural modification of fullerene systems includes endohedral, exohedral or substitutional doping with heteroatoms,[1] which leads to new structural types. Thus, the replacement of 12 borons by carbon atoms in B_{80} **2** gives rise to cluster **3** ($B_{68}C_{12}$) with the three-dimensional arrangement of non-classical quasi-planar tetracoordinate carbon centers.[5] It can be expected that the boron fullerene cage can serve as an appropriate basis for the formation of non-classical molecular systems with hypercoordinated centers and rigid boron frameworks.[6] Here, we report novel C-doped boron fullerenes **4** and **5** designed on the basis of icosahedral B_{60} and B_{80} frameworks, respectively, which contain 12 pentacoordinated carbon apexes with a quasi-planar bond configuration.



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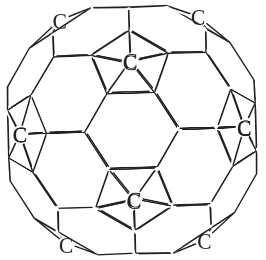

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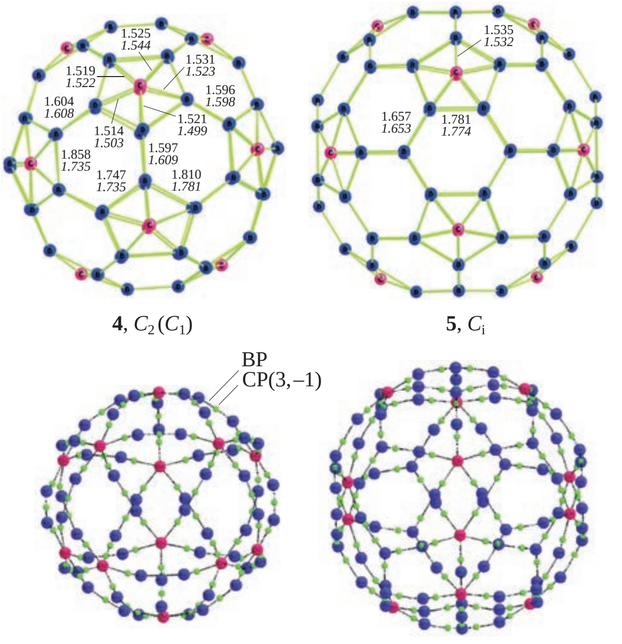
The density functional theory (DFT) calculations were performed with the B3LYP[7] and M06[8] functionals and 6-311+G(d,p)[9] valence-split basis set using the Gaussian-09 program package.[10] The stationary points on the potential energy surfaces (PESs) were located with full geometry optimizations, identified by calculating the matrices of second derivatives (force constants) and checked for the stability of Hartree-Fock solutions. Natural bond orbital (NBO) analysis[11] was performed using the NBO 6.0 program.[12] The AIM (Atoms in Molecules) analysis[13] was carried out using the AIMAll Professional program.[14] The drawings were made using the ChemCraft[15] program suite with calculated atomic coordinates as input parameters.

According to the calculations at both levels of approximation, the fullerene structure $B_{60}C_{12}$ formed on the basis of the icosahedral framework B_{60} is stable in low-symmetry form **4** (C_2 symmetry at the B3LYP level and C_1 symmetry at the M06 level) and corresponds to the energy minimum ($\lambda = 0$; hereafter, λ denotes the number of negative eigenvalues of the matrix of second derivatives) on the PES. The high-symmetry I_h structure does not correspond to a stable form (number of imaginary frequencies

Table 1 Energy parameters[a] of systems **4** and **5** calculated using the B3LYP and M06 (italicized) methods with the 6-311+G(d,p) basis set.

Structure	E_{tot}	λ	ω_1
4, C_2	–1947.234957	0	39.3
C_1	*–1946.133585*	*0*	*92.7*
5, C_i	–2444.138831	0	79.9
	–2442.696687	*0*	*99.4*

[a] E_{tot} (a.u.) is the total energy; λ is the number of negative hessian eigenvalues; ω_1 (cm^{-1}) is the lowest harmonic vibration frequency.



4, $C_2\,(C_1)$ **5**, C_i

4a **5a**

Figure 1 Geometric characteristics (bond lengths, Å) of systems **4** and **5** calculated using the B3LYP and M06 (italicized values) methods with 6-311+G(d,p) basis set. The Bader molecular graphs **4a** and **5a** of structures **4** and **5**, respectively, are given at the bottom, BP designates the Bader bond path, CP (3,–1) – the bond path critical point.

$\lambda \geqslant 2$). Figure 1 and Table 1 show the structural and energetic parameters of **4**.

The structure of $B_{60}C_{12}$ **4** contains 12 five-membered and 20 six-membered faces and 12 additional carbon atoms in the apical positions above the five-membered rings. According to the calculations, the spherical structural form of a B_{60} cage (I_h) does not correspond to the stationary point on the PES and relaxes into closed-cluster form **6** with three-, tetra-, penta- and hexagonal faces. Therefore, the introduction of additional carbon atoms in apical positions stabilizes the spherical fullerene structure.

Interatomic CB distances in system **4** are nonequivalent and laying in a range of 1.514–1.531 Å (B3LYP) or 1.510–1.522 Å (M06) corresponding to the parameters of covalent carbon–boron bonds (1.56 Å[16]). The calculated Wiberg bond index (WBI) of CB bonds (0.9) witnesses the significantly covalent nature of these bonds. According to AIM analysis data (molecular graph **4a** is shown in Figure 1), each carbon atom linked by five bond paths to the neighboring boron atoms can be characterized as a pentacoordinated center. Table 2 presents the calculated AIM parameters for the bond critical point (BCP) corresponding to the CB interactions in **4**. The BCPs are characterized by the positive Laplacian $\nabla^2\rho(r)$, characteristic of closed-shell type interactions.[14] However, the values of the electron density $\rho(r)$ at the BCPs are large (0.16) and close to those of covalent single bonds (~0.25–0.30). Simultaneously, the negative sign of the total electron energy density, $H_\text{b}(r)$, indicates the covalent character of the bonds. The above characteristics of electron density distribution [large $\rho(r)$ and positive $\nabla^2\rho(r)$] are indicative of so-called ‘charge-shift’ type bonds,[17,18] which are assigned to interactions intermediate between closed-shell and covalent in terms of the AIM theory. The ‘charge-shift’ bond character is known to be inherent in a number of hypercoordinated molecules and systems with non-standard bond configurations (for instance, the central inverted bond in [1.1.1]propellane).[17–19]

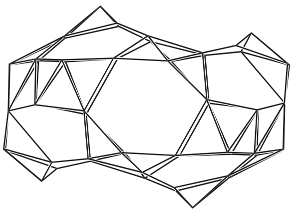


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Table 2 AIM parameters[a] (a.u.) for the bond critical point (BCP) corresponding to the C–B bonding in systems **4** and **5** calculated using the B3LYP and M06 (italicized) methods with the 6-311+G(d,p) basis set.

Structure	$\rho(r)$	$\nabla^2\rho(r)$	$H_\text{b}(r)$
4	0.158	0.175	–0.143
	0.159	*0.174*	*–0.143*
5	0.157	0.182	–0.140
	0.158	*0.153*	*–0.143*

[a] $\rho(r)$ is the electron density; $\nabla^2\rho(r)$ is the electron density Laplacian; $H_\text{b}(r)$ is the total electron energy density.

In **4**, the apical hypercoordinated quasi-flat (pyramidalization of bonds does not exceed 10°) carbon atoms are significantly positively charged (the Mulliken charge is +1.6*e*). The calculated BB distances connecting the neighboring CB_5 fragments (1.59–1.60 Å) are considerably shortened compared with the lengths of single covalent BB bonds (1.75 Å[16]). The BB distances along the perimeter of CB_5 fragments are slightly lengthened in comparison with the interfragment BB bonds (1.68–1.83 Å). According to the AIM and NBO analyses, all boron atoms are dicoordinated (Figure 1, molecular graph **4a**) and *sp*-hybridized, and they form bond paths only with carbon and boron atoms of the adjacent CB_5 fragment. The absence of BB bonding along the perimeter of CB_5 fragments facilitates the planarization of carbon centers. The stabilization of non-classical hypercoordinated carbon centers in **4** is sterically enforced by the rigid spherical closed cage, and it is also sustained by the π-acceptor properties of boron atoms providing for drawing off electron density from carbons. Molecular orbital analysis indicates that the principal component contributing to the stabilization of **4** is electron density donation from the filled p_z orbitals of hypercoordinated carbons to the vacant p_z orbitals of the adjacent boron atoms, which leads to the formation of the delocalized multicenter π orbitals of CB_5 fragments [Figure 2(*a*)]. Therefore, the stability of a composite fullerene structure with hypercoordinated carbon atoms is determined by the stabilization of its constituent structural fragments.

The stability of a spherical fullerene form with hypercoordinated carbon atoms is retained upon increasing the cage structure size. Calculations at both levels of approximation show that the fullerene structure of **5** ($B_{80}C_{12}$) corresponds to the energy minimum ($\lambda = 0$) on the PES. The structural and energy characteristics of **5** are shown in Figure 1 and Table 1.

The structure of **5** is derived based on the icosahedral framework of B_{80} **7** consisting of 12 pentagonal and 30 hexagonal faces *via* capping the five-membered faces with twelve additional

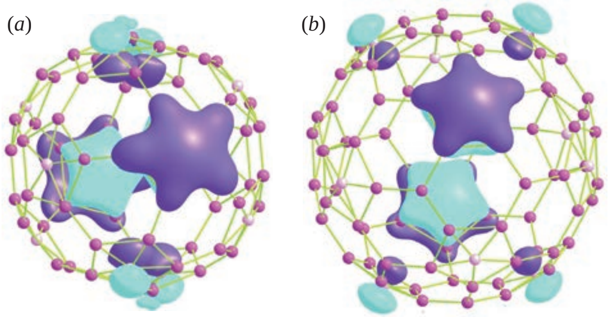
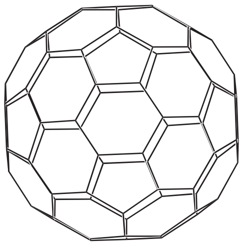


Figure 2 Shapes of multicenter bonding π-molecular orbitals of hypercoordinated fragments in systems (*a*) **4** and (*b*) **5**.

carbon atoms. Similar to B_{60}, the spherical form **7** of B_{80} does not correspond to a stationary point on the PES and relaxes into closed-cluster species **8** with three-, penta-, hexa- and heptagonal faces.



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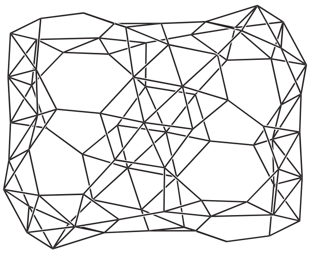

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In contrast with **4**, all interatomic CB distances in **5** are equivalent and equal to 1.535 (B3LYP)–1.532 Å (M06), which corresponds to the parameters of single covalent bonds. The calculated high WBI index (0.7) indicates a significantly covalent character of these bonds. The AIM analysis (molecular graph **5a** is presented in Figure 1) shows that each carbon atom in **5** forms five bond paths with the adjacent boron centers; thus, it is pentacoordinated. As in the case of **4**, the parameters of bond paths (high electron density values and positive values of the Laplacian, see Table 2) correspond to the charge-shift bond type of CB bonds. The hypercoordinated apical carbon atoms in **5** bear a considerable Mulliken positive charge of 1.2*e*. The slight pyramidalization of CB bonds, which does not exceed 10°, allows us to consider the stereochemical configuration of carbons as quasi-flat. According to the AIM and NBO analyses, cluster **5** contains two types of boron atoms differing in their hybridization states. The boron atoms surrounding carbon atoms are dicoordinated and, as in the case of **4**, they do not form bonds along the perimeter of CB_5 fragments. Their state can be defined as *sp*-hybridized. The interfragment boron atoms form three bond paths with boron atoms of the adjacent CB_5 fragments, and they are characterized as sp^2-hybridized centers. The calculated distances between *sp*- and sp^2-hybridized boron atoms are 1.658 (B3LYP) or 1.653 Å (M06). These are considerably shortened compared to the intrafragment perimetral BB distances [1.782 (B3LYP) or 1.775 Å (M06)]. The presence of interfragment sp^2-hybridized boron atoms in system **5** increases π-electron delocalization that leads to a small elongation of CB bonds compared to system **4**. As in **4**, the major factor of stability of fullerene **5** with quasi-flat hypercoordinated carbon centers is the donation of electron density from the carbon p_z orbitals to the vacant p_z orbitals of the surrounding boron atoms resulting in the formation of delocalized π orbitals of CB_5 fragments [Figure 2(*b*)].

In summary, the calculations revealed a new structural type of fullerene boron systems with a three-dimensional arrangement of non-classical pentacoordinated quasi-flat carbon centers. The doping with carbon atoms in apical positions above the five-membered rings stabilizes the spherical boron fullerene forms due to the multicenter interactions of carbon p_z orbitals and adjacent boron atoms.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.11.008.

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