



Structure and bonding of new boron and carbon superpolyhedra

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Abstract

Using the DFT methods, we computationally predict the stability of cage compounds $E_{4n}R_n$ ($E = B, C$; $R = H, F$; $n = 4, 8, 12, 24$) based on Platonic bodies and Archimedean polyhedrons in which all vertices are replaced by tetrahedral E_4R fragments. Cage compounds $B_{60}R_{12}$ and C_{60} with pyramidal units B_5R or C_5 are also examined and it is shown that only boron compounds are stable. The nature of chemical bonding in the discussed compounds is analyzed using the AdNDP and NBO methods. The hydrocarbons have classical 2c-2e C-C σ -bonds, while the boron compounds are formed by the polyhedral units with the delocalized multicenter bonds which connected three and more boron atoms. The new example of spherical aromaticity according to the $2(N+1)^2$ rule in the case of $B_{16}F_4$ with multicenter 16c-2e bonds are revealed. Stable compound $B_{60}H_{12}$ contains 12 5c-2e B-B bonds.

Keywords Cage clusters · Chemical bonding · 3c-2e bond · Spherical aromaticity · AdNDP · NBO

Construction of novel allotropic forms of carbon based on the tetrahedrane- and cubane-like building blocks was proposed by Burdett and Lee [1] and by Johnston and Hoffmann [2] in the 1980's. One should, however, bear in mind that superpolyhedral hydrocarbons consisting of the sterically strained and thermodynamically unstable tetrahedrane blocks also have highly strained and metastable structures. Tetrahedrane C_4H_4 itself is a hypothetical compound (for some recent studies, see ref. [3–5]) but its substituted derivatives such as $C_4^tBu_4$ and $C_4(SiMe_3)_4$ are experimentally realized [6, 7] and are stable due to the bulky groups. The carbon skeleton of tetrahedrane C_4H_4

was proposed [1] as the system with the same symmetry as sp^3 -carbon to replace the carbon atoms in the diamond lattice. In such a model, neighboring tetrahedral units can be regarded as bulky substituents providing safety for other tetrahedral units. Following this idea, new polyhedrons such as supertetrahedral prismanes and dodecahedrane, as well as some solid-state structures, were successfully designed [8–11]. Moreover, recently Ortiz et al. suggested adamantane as a building unit [12].

On the other hand, electron-deficient boron and aluminum tetrahedral structures with delocalized 3c-2e bonds are not only kinetically but also thermodynamically stable [5] which provides stability of their supertetrahedral compositions. Such types of boron and aluminum structures derived on the basis of Platonic bodies were recently described [8, 10, 11]. Considering boron building units for supertetrahedral modeling, it should be noted that boron tetrahedral structure B_4H_4 is also still hypothetical [5, 13]. However, peralkylated tetraboratetrahedrane $B_4^tBu_4$ [14, 15] and boron halides B_4Cl_4 and B_4Br_4 [16] are known for many years and exhibit tetrahedral structures. Moreover, the B_4R_4 ($R \neq H$) derivatives are predicted to have T_d -symmetry ground state [17]. Overall, boron tetrahedral skeleton B_4 is also a good candidate for modeling supertetrahedral structures, as is the carbon C_4 unit.

Furthermore, pyramidal blocks could also be considered for super structure modeling if the parent structure has atom

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centers with appropriate configuration of five bonds. Then, the pyramidal unit could replace such an atom center. In this case, the building blocks are based on the pyramidane C_5H_4 [18–21] and pyramidal boron hydride B_5H_5 [22, 23] structures. Further supporting probability of the hypothetical pyramidal structures, we can notice that hybrid carbon-based pyramidanes $E[C_4(SiMe_3)_4]$ ($E = Ge, Sn, Pb$) were recently isolated [24, 25], and the boron atom can also manifest pentacoordinated square-pyramidal bond configuration, as was demonstrated in the recently reported $CIB[C_4(SiMe_3)_4]$ [26].

Following our previous calculations [8, 10, 11] of supertetrahedral cubane, dodecahedrane, and [n]-prismane systems, we extend now the number of structures with tetrahedral units and report on the computational design of a series of the supertetrahedral cage structures based on Platonic bodies (tetrahedron **a** and cube **b**, Fig. 1) and Archimedean solids (truncated tetrahedron **c**, truncated hexahedron **d**, truncated octahedron **e**), as well as superpyramidal molecules based on the cuboctahedron **f**. The building principle of such structures is the replacement of all vertices by the tetrahedral E_4R or pyramidal E_5R fragments ($E = C, B; R = H, F$) in solids **a**–**f** (Fig. 1). To simplify the calculations, we used the smallest substituent R.

Computational details

Geometry optimization, frequency analysis, wave function stability, and all related calculations were performed using the Gaussian 09 program [27] based on the B3LYP/6-

311G(d,p) (DFT1) and M06/6-311G(d,p) (DFT2) levels of theory. All discussed structures are local minima (there are no negative harmonic vibrations) on the potential energy surfaces in the gas phase. The NBO 6.0 program was used to carry out the NBO analysis [28]. The analyses of chemical bonding were performed within the Adaptive Natural Density Partitioning (AdNDP) method [29] at the B3LYP/6-311G(d,p) level of theory. The pictures of the optimized geometries and the AdNDP results were generated using the Chemcraft 1.8 program [30].

Results and discussions

Tetrahedron The smallest possible supertetrahedral hydrocarbon **1-ch** based on tetrahedron **a** is presented in Fig. 2. The calculated apex-to-base C-C bond lengths of the tetrahedrane fragments are equal to 1.480 (1.465) Å at DFT1 (DFT2 here and thereafter) levels; lengths of the basal C-C bonds of the tetrahedrane fragments are equal to 1.546 (1.530) Å. The C-C bonds between tetrahedrane fragments (hereafter referred to as intertetrahedrane bonds) have lengths 1.402 (1.394) Å. We have performed NBO and AdNDP analyses of chemical bonding providing for the stability of the compounds. In the case of $C_{16}H_4$ **1-ch**, both approaches (DFT1) lead to the same (up to 0.01 |e|) result and predict realization of the classical structure with 2c-2e σ -bonds [for the details of NBO and AdNDP results see the Supporting Information (SI)].

The calculated electron distribution of the fluorine-substituted compound $C_{16}F_4$ **1-cf** varies depending on the DFT potentials: at DFT2, the predicted structure is analogous

Fig. 1 Polyhedrons used for the supermolecule construction. In brackets are the numbers of vertices

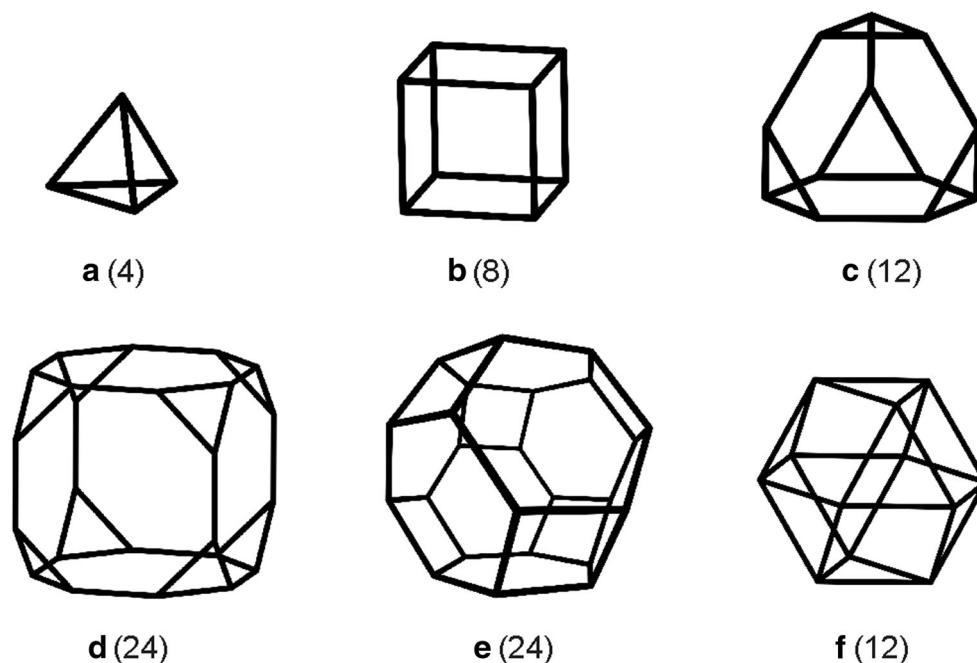
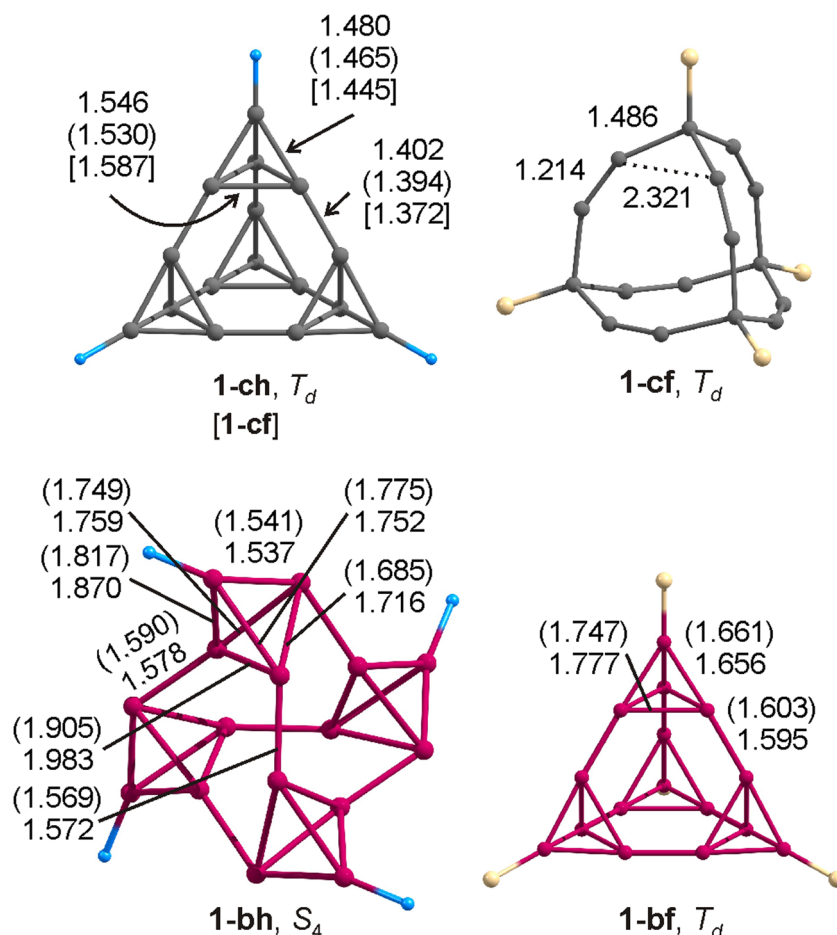


Fig. 2 Optimized geometries of **1-ch**, **1-cf**, **1-bh**, **1-bf** at DFT1 (DFT2) levels. In square brackets are the bond lengths for **1-cf** at DFT2. Here and hereinafter, bond lengths are given in Å



to that of $C_{16}H_4$ **1-ch**; at the DFT1 level of approximation, no tetrahedral fragments can be localized at all because of elongation of the C-C basal distances (up to 2.321 Å) which leads to the formation of double “intertetrahedrane” bonds (1.241 Å). Both NBO and AdNDP analyses of chemical bonding show classical structure with 2c-2e σ -bonds for **1-cf** and confirm supertetrahedral framework.

Calculated NICS(0) [31] of structure faces indicate to electron delocalization: -30.4 (-32.4) for C_6 -rings of **1-ch** at DFT1 (DFT2), -38.2 for C_6 -rings of **1-cf** at DFT2.

Boron structure $B_{16}H_4$ of T_d -symmetry represents a third-order saddle point destabilized by 32 (63) kcal/mol relative to the minimum **1-bh** with deformed S_4 -geometry (Fig. 2). Replacement of hydrogen atoms by fluorine atoms stabilizes tetrahedral geometry of boron skeleton. The apical B-B bond lengths in $B_{16}F_4$ **1-bf** are 1.656 (1.661) Å; B-B bonds between tetrahedrane fragments have the lengths of 1.595 (1.603) Å. B-B distances between basal atoms are longer (1.777 (1.747) Å) than the sum of covalent radii of boron atoms (1.70 Å [32]).

According to the NBO analysis (DFT1), **1-bf** has six 2c-2e intertetrahedrane B-B σ -bonds with occupation number (ON) = 1.98 |e|, 12 2c-2e B-F σ -bonds with ON = 2.00 |e| for four σ -bonds and 1.99 |e| for eight π bonds. Four LPs at fluorine atoms with ON = 1.98 |e|, 16 LPs at boron atoms with

small ON = 0.80 |e| at 12 edge borons and with ON = 0.70 |e| at four apical borons were also located. Thus, the NBO scheme discovers no B-B tetrahedral bonding in the structure. On the other hand, the AdNDP analysis of chemical bonding (DFT1) shows that 76 valence electrons of **1-bf** form the structure with complete boron cage containing 12 lone pairs (LP) on fluorine atoms, six 2c-2e intertetrahedrane B-B bonds, four 2c-2e B-F bonds, 12 3c-2e apical B-B bonds, and four 16c-2e B-B bonds (Fig. 3). The last 16c-2e bonds filled by eight electrons ensure spherical aromaticity according to the $2(N+1)^2$ rule [33]. Such a result was unexpected because of the previous AdNDP calculations of boranes B_4H_4 and $B_{80}H_{20}$ [10, 13] which showed that each of the tetrahedral units had four 3c-2e B-B bonds as in Fig. 4. Nevertheless, **1-bf** prefers global delocalization involving all cage boron atoms.

Calculated NICS(0) of structure faces of **1-bf** is -17.3 (-14.7) for B_6 -rings at DFT1 (DFT2) which is appreciably lower than for **1-ch** and **1-cf** but they still have negative values indicating the electron delocalization.

Cube The calculated structures of supertetrahedral cube systems **2-ch** and **2-bh** (Fig. 5, Table 1) are in good agreement with our previous study [8]. In the present paper, we would

Fig. 3 The AdNDP calculated distribution of electron density for **1-bf**

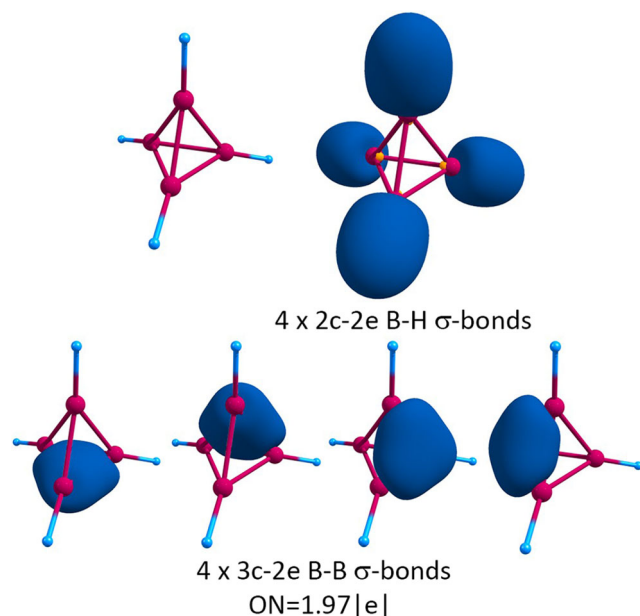
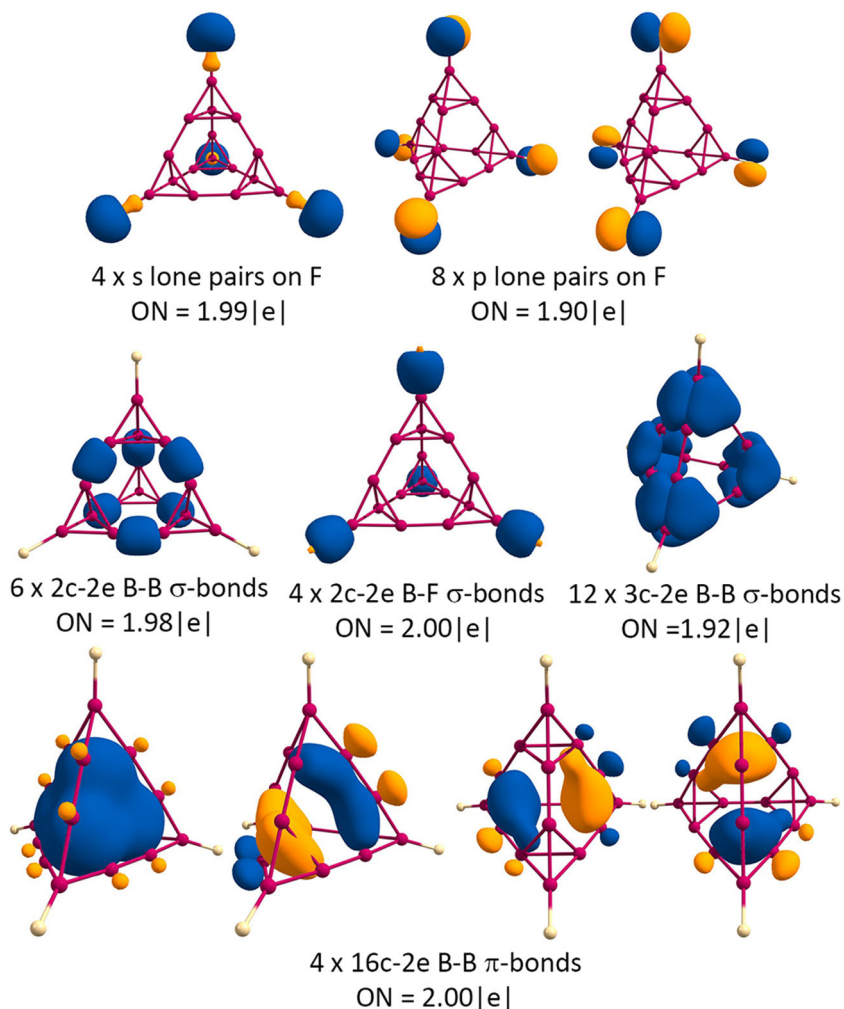


Fig. 4 The AdNDP calculated distribution of electron density in B_4H_4

like to comment on the bonding nature and the influence of fluorine atoms to these structures. As it could be expected, hydrocarbon system $C_{32}H_8$ **2-ch** has a classical structure with 2c-2e bonds as was found in both NBO and AdNDP results (with ON up to 0.02 |e|). The same classical bonding framework was found for the fluorinated $C_{32}F_8$ **2-cf**, and no great difference in the ON of C-C bonds for **2-cf** and **2-ch** is observed. However, the structural influence of the fluorine atoms is indeed significant. Thus, apical C-C bonds in **2-cf** are shorter [1.476 (1.460) Å] than those in **2-ch** [1.494 (1.476) Å], intertetrahedrane C-C bonds in **2-cf** are shorter as well [1.442 (1.431) Å] than in **2-ch** [1.437 (1.435) Å], but basal C-C bond in **2-cf** are longer [1.516 (1.501) Å] than in **2-ch** [1.488 (1.474) Å] at the DFT1 (DFT2) levels.

NBO analysis (DFT1) of boron structure $B_{32}H_8$ **2-bh** does not reveal the complete bonding framework: 104 valence electrons form only 44 bonds [for these and other NBO results see the SI]. The AdNDP analysis recovers all 52 bonds as it is shown in Fig. 6: twelve 2c-2e B-B intertetrahedrane σ -bonds with ON = 1.99 |e|, eight 2c-2e B-H bonds with ON = 1.99 |e|, 24 3c-2e B-B apical bonds with ON = 1.93 |e|, and eight 3c-2e

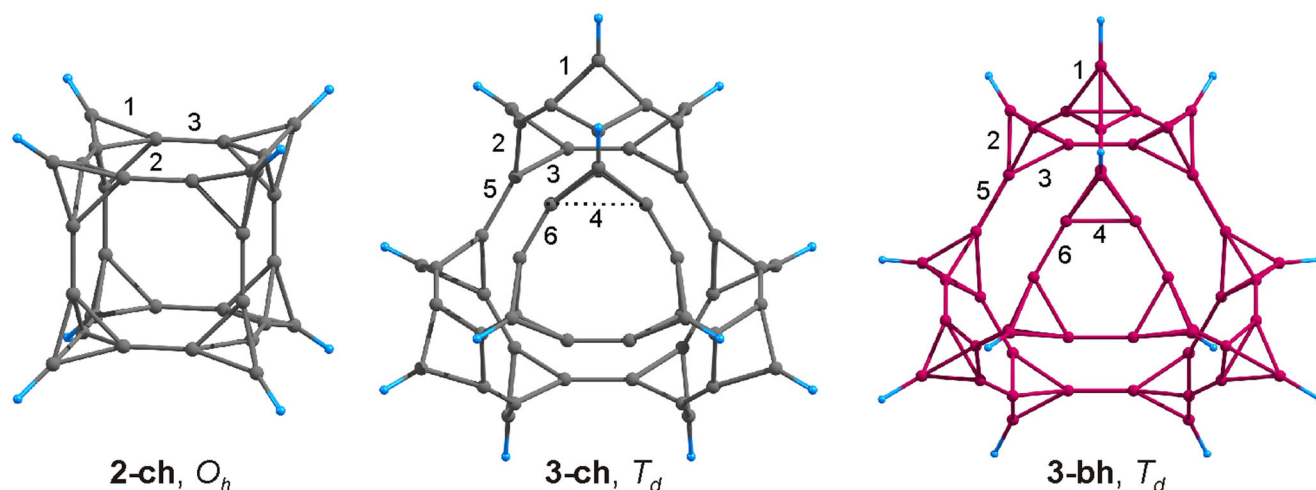


Fig. 5 Optimized geometries of **2-ch**, **3-ch**, **3-bh**. Boron structure **2-bh** has the same bond framework as the **2-ch**. Fluorinated systems **2-cf**, **2-bf**, **3-cf** and **3-bf** have the same bond frameworks as their H-substituted analogues in this figure. Bond lengths are listed in Table 1

B-B basal bonds with $ON = 1.86$ |e|. Fluorinated $B_{32}F_8$ **2-bf** has the same supertetrahedral structure with eight 3c-2e B-B basal bonds, according to the AdNDP analysis (see the SI). Thus, **2-bh** and **2-bf** have the bonding structure strictly determined by the B_4H_4 building blocks.

Structural alterations of boron structures caused by fluorination are not as significant as those which occurred in the carbon systems. For instance, apical B-B distances in **2-bf** are shorter [1.673 (1.671) Å] than those in **2-bh** [1.680 (1.677) Å], basal B-B distances in **2-bf** are slightly longer [1.711 (1.704) Å] than in **2-bh** [1.708 (1.703) Å], and in contrast to carbon structures, the intertetrahedrane B-B bonds in **2-bf** are somewhat longer [1.651 (1.645) Å] than in **2-bh** [1.649 (1.643) Å] at the DFT1 (DFT2) levels.

Calculated NICS(0) of structure faces are equal to the following: -4.1 (-4.6) for C_8 -rings of **2-ch**, -6.2 (-6.9) for C_8 -rings of **2-cf**, -4.0 (-4.0) for B_8 -rings of **2-bh**, -3.8 (-4.1) for B_8 -rings of **2-bf** at DFT1 (DFT2).

Truncated tetrahedron Hydrocarbon structure $C_{48}H_{12}$ **3-ch** does not contain tetrahedral fragments because of small

triangle planes in the parent truncated tetrahedron **c** (Fig. 1). Thus, distances number four (R4) is elongated up to 2.029 (2.012) Å (Fig. 4, Table 1). The fluorinated **3-cf** has the same structure with distances R4 increasing up to 2.051 (2.036) Å at the DFT1 (DFT2) levels.

Boron system $B_{48}H_{12}$ **3-bh** preserves the intact supertetrahedral fragments (Fig. 4). It has elongated B-B apical bonds R1 (Fig. 4, Table 1) and shortened apical bonds R2 in comparison with the pyramidal bonds R1 of the $B_{32}H_8$ **2-bh** structure. The basal tetrahedral bonds (R3 and R4) of **3-bh** are longer than same bonds R2 of **2-bh**. At the boron structure, **3-bh** bonds R5 and R6 between tetrahedral fragments are shortened (especially R6) compared with bonds of **2-bh**. Fluorination causes an elongation of the intertetrahedrane B-B bonds (up to 0.01 Å) and small changes in both directions (up to ± 0.007 Å) of apical and basal bonds at tetrahedral fragments of system **3-bf**.

The AdNDP analysis of **3-bh** shows complete bonding framework including all apical and basal B-B bonds: 12 B-H 2c-2e bonds with $ON = 1.99$ |e|, 18 2c-2e B-B intertetrahedrane bonds with $ON = 1.99$ |e| for bonds R6 and $ON = 1.98$ |e| for

Table 1 Optimized bond lengths (in Å) of structures **2** and **3** at the DFT1/DFT2 levels. Bond numbering can be seen in Fig. 5

Structure	C-C or B-B bond and distances					
	1	2	3	4	5	6
2-ch	1.494/1.476	1.488/1.474	1.442/1.435	–	–	–
2-cf	1.476/1.460	1.516/1.501	1.437/1.431	–	–	–
2-bh	1.680/1.677	1.708/1.703	1.649/1.643	–	–	–
2-bf	1.673/1.671	1.711/1.704	1.651/1.645	–	–	–
3-ch	1.483/1.473	1.553/1.528	1.479/1.468	2.029/2.012	1.454/1.448	1.329/1.324
3-cf	1.468/1.458	1.531/1.518	1.500/1.485	2.051/2.036	1.450/1.443	1.329/1.325
3-bh	1.687/1.684	1.666/1.663	1.714/1.707	1.727/1.716	1.644/1.640	1.622/1.621
3-bf	1.680/1.679	1.665/1.662	1.716/1.708	1.722/1.711	1.651/1.645	1.632/1.629

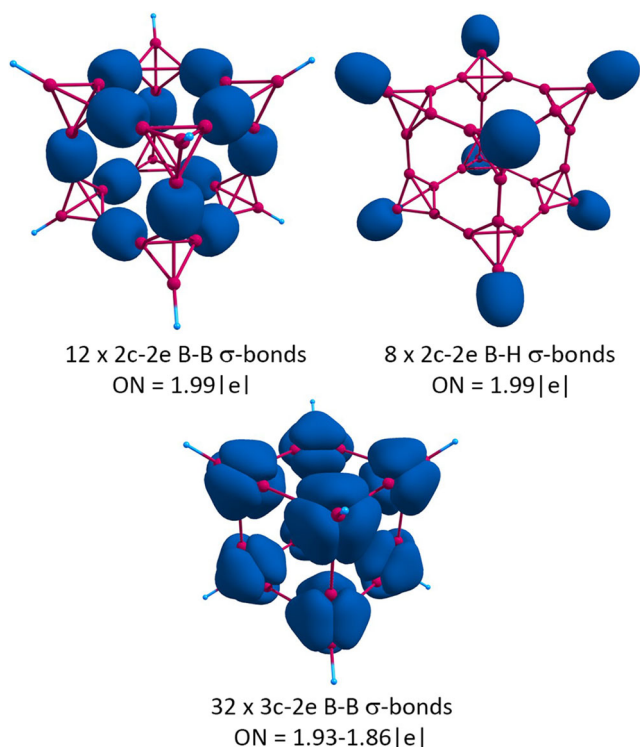


Fig. 6 Results of the AdNDP localization for **2-bh**

bonds R5, 48 B-B 3c-2e apical and basal bonds with ON = 1.92, 1.85 and 1.82 |e|. The AdNDP analysis of **3-bf** is similar (see the SI). Therefore, **3-bh** and **3-bf** have 2c-2e and 3c-2e B-B bonds like **B₄H₄** and **2-bh**, **2-bf** structures.

Calculated NICS(0) of structure faces are equal to -9.7 (-9.8) for B_8 -rings and $+3.2$ ($+2.7$) for B_{12} -rings of **3-bh**, -7.1 (-6.9) for B_8 -rings and $+1.3$ ($+1.5$) for B_{12} -rings of **3-bf** at DFT1 (DFT2).

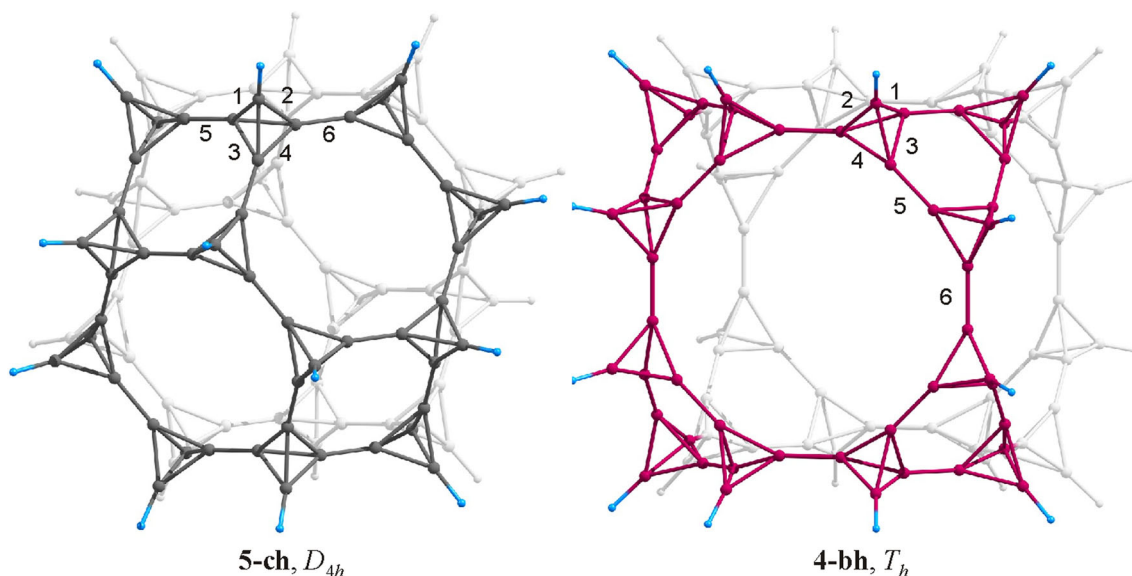


Fig. 7 Optimized geometries of **5-ch**, **4-bh**. Structures **5-bh** and **5-bf** have the same bond framework as that of **5-ch**. Fluorinated system **4-bf** has the same bond framework as **4-bh**. Bond lengths are given in Table 2

Truncated octahedron and truncated hexahedron

Hydrocarbon structure $C_{96}H_{24}$ **4-ch** based on **d** has no supertetrahedral moieties because of the triangle planes in **d** causing steric hindrances for the carbon tetrahedral fragments like in the structure **3-ch**. Pseudo-basal C-C distances are equal to 2.038 (2.023) Å. The fluorinated system **4-cf** has the structure similar to **4-ch** with the C-C distances of 1.999–2.077 (1.965–2.127) Å (see structures in the SI, Fig. S1). According to the NBO and AdNDP analysis (DFT1), the isomeric hydrocarbon $C_{96}H_{24}$ **5-ch** based on truncated hexahedron **e** acquires the supertetrahedral framework of bonds (Fig. 7, Table 2) and has the classical structure formed by 2c-2e bonds. The calculated NICS(0) of structure faces are equal to -5.0 (-5.2) for C_8 -rings and $+0.3$ ($+0.4$) for C_{12} -rings of **5-ch** at DFT1 (DFT2).

The fluorinated system **5-cf** has a structure without C_4 -tetrahedrons (see Fig. S1 in the SI). As was shown by the example of **2-ch** and **2-cf**, fluorination causes the elongation of basal C-C bonds; thus, in the case of **5-cf**, it was determinant and led to a non-tetrahedral structure.

Both isomeric boron systems $B_{96}H_{24}$ **4-bh** and **5-bh** have supertetrahedral structures as stems from their geometry characteristics (Fig. 7, Table 2). **4-bh** is destabilized by 105 (94) kcal/mol at the DFT1 (DFT2) levels with zero-point correction (ZPC) with respect to **5-bh** because of steric factors (small triangle planes in the parent polyhedron **d**). Fluorinated **4-bf** is destabilized by 128 (117) kcal/mol at the DFT1 (DFT2) levels with ZPC towards **5-bf**. The AdNDP analysis of **4-bh**, **5-bh** and fluorinated **4-bf**, **5-bf** shows complete bonding framework with 2c-2e and 3c-2e B-B bonds (see the SI).

Calculated NICS(0) values of structure faces are -9.7 (-9.7) for B_6 -rings and $+1.2$ ($+1.0$) for B_{16} -rings of **4-bh**, -6.5 (-6.2) for B_6 -rings and $+0.1$ ($+0.3$) for B_{16} -rings of **4-bf**,

Table 2 Optimized bond lengths (in Å) of supertetrahedral structures **4**, **5**, and **6** calculated at the DFT1/DFT2 levels of approximation. Bond numbering can be seen in Figs. 7 and 8

Structure	C-C or B-B bonds and distances					
	1	2	3	4	5	6
4-bh	1.691/1.689	1.670/1.667	1.727/1.715	1.711/1.704	1.620/1.620	1.640/1.637
4-bf	1.683/1.682	1.668/1.666	1.725/1.714	1.713/1.706	1.630/1.628	1.650/1.646
5-ch	1.475/1.460	1.509/1.495	1.513/1.499	1.484/1.467	1.437/1.431	1.434/1.429
5-bh	1.681/1.679	1.681/1.677	1.705/1.699	1.707/1.701	1.645/1.640	1.644/1.641
5-bf	1.674/1.674	1.676/1.673	1.708/1.701	1.710/1.703	1.651/1.645	1.651/1.647
6-bh	1.717/1.714	1.680/1.692	1.758/1.729	1.666/1.661	1.760/1.722	1.629/1.634
6-bf	1.687/1.694	1.687/1.694	1.754/1.730	1.715/1.697	1.715/1.697	1.643/1.644

−1.5 (−1.8) for B₈-rings and +0.3 (+0.7) for B₁₂-rings of **5-bh**, and −1.6 (−2.2) for B₈-rings and +0.0 (+0.6) for B₁₂-rings of **5-bf** at DFT1 (DFT2).

Cuboctahedron The same construction principle was used for the superpyramidal systems based on the cuboctahedron **f** in which all 12 vertices were replaced by pyramidal fragments C₅ or B₅H. It would be interesting to obtain such unusual superpyramidal structures with 12 5c-2e C-C or B-B bonds which were founded in pyramidane C₅H₄ and borane B₅H₅ (Fig. 8).

Unfortunately, the superpyramidal carbon structure C₆₀ is unstable and under geometry optimization converts to superhousene **6-c** (Fig. 9). It could be expected since the pyramidal building block, pyramidane C₅H₄, has strong deviation

of C-H bonds from the basal ring plane towards the apical atom [20,2 1], while the superpyramidal structure provides the opposite direction for the C-C interpyramidane (C-H for C₅H₄) bonds. This inconsistency leads to the formation of superhousene **6-c** which building blocks are formed by the distorted pyramidane units corresponding to its nearest isomer [20]. Structure **6-c** is destabilized by 1664 (1576) kcal/mol towards fullerene C₆₀.

In contrast to the hydrocarbon, boron system B₆₀H₁₂ **6-bh** has the superpyramidal structure (Fig. 9), which stabilization is favored by the B-H bond deviation opposite to the apex of the building B₅H₅ blocks [22, 23]. The lengths of the pyramidal B-B bonds in **6-bh** are 1.717 (1.714) and 1.680 (1.692) Å, while in B₅H₅ lengths of these bonds [1.711 (1.711) Å] are close to the sum of

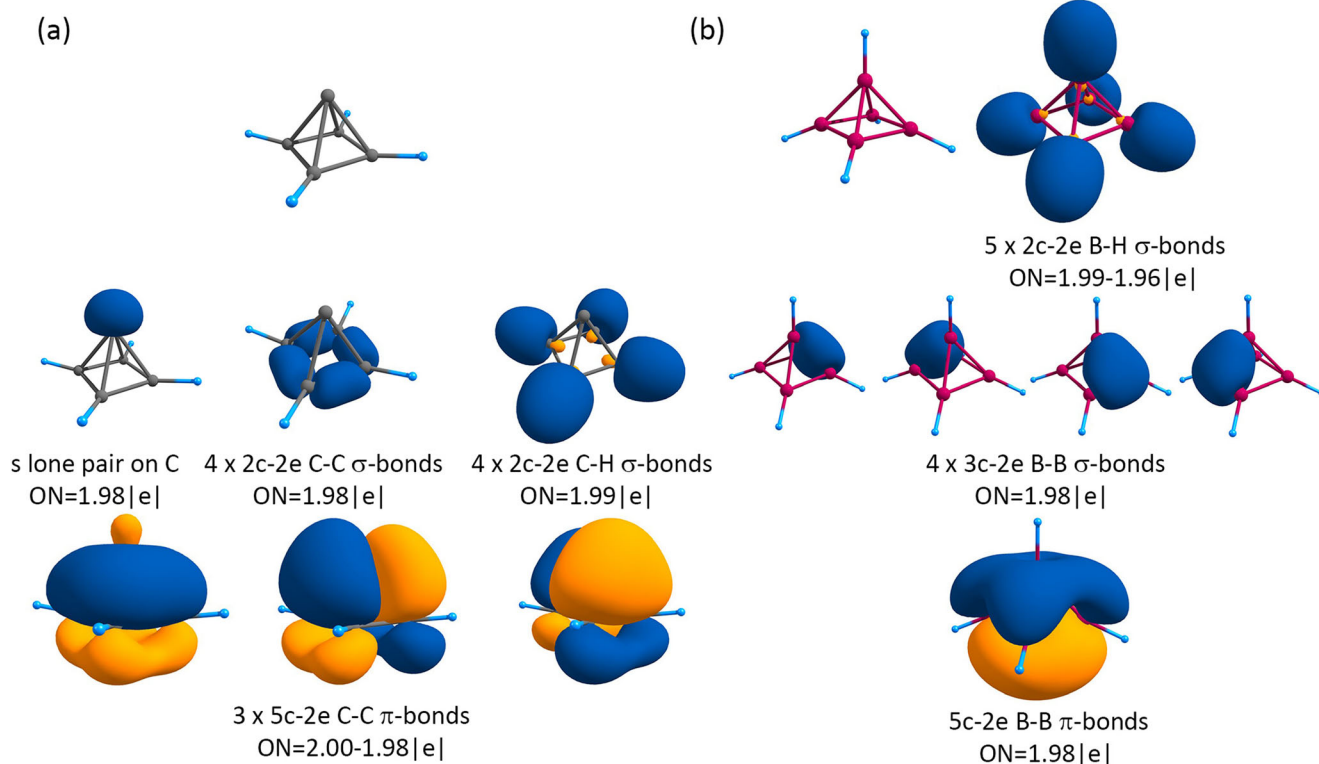


Fig. 8 The AdNDP localization: (a) C₅H₄; (b) B₅H₅

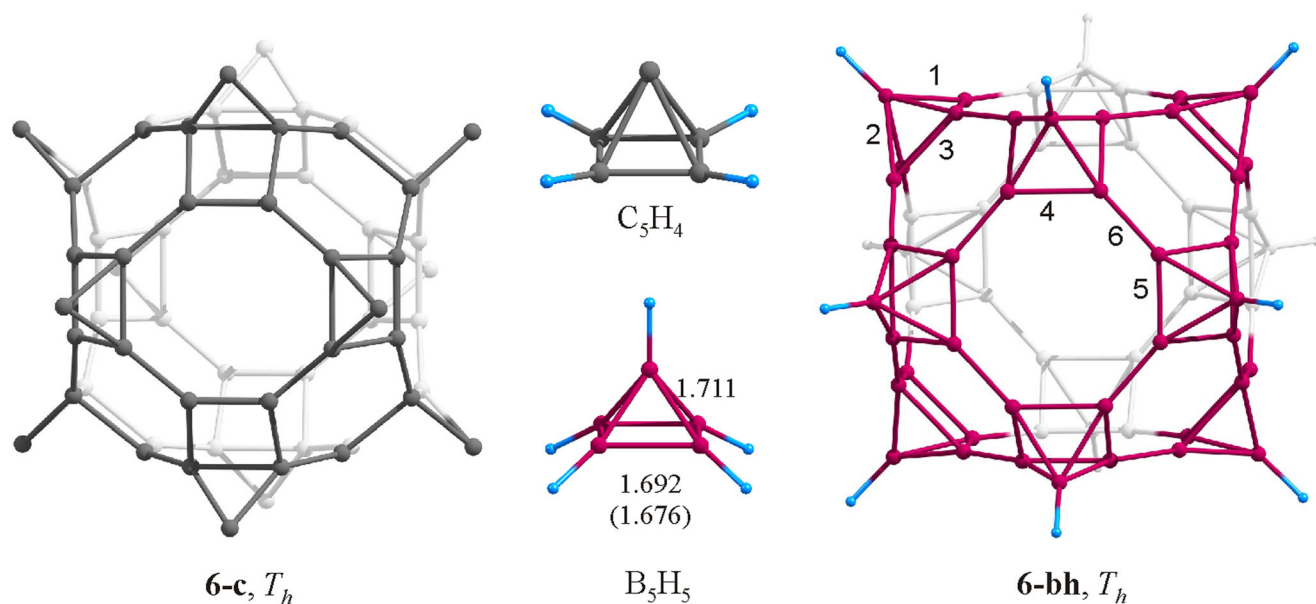
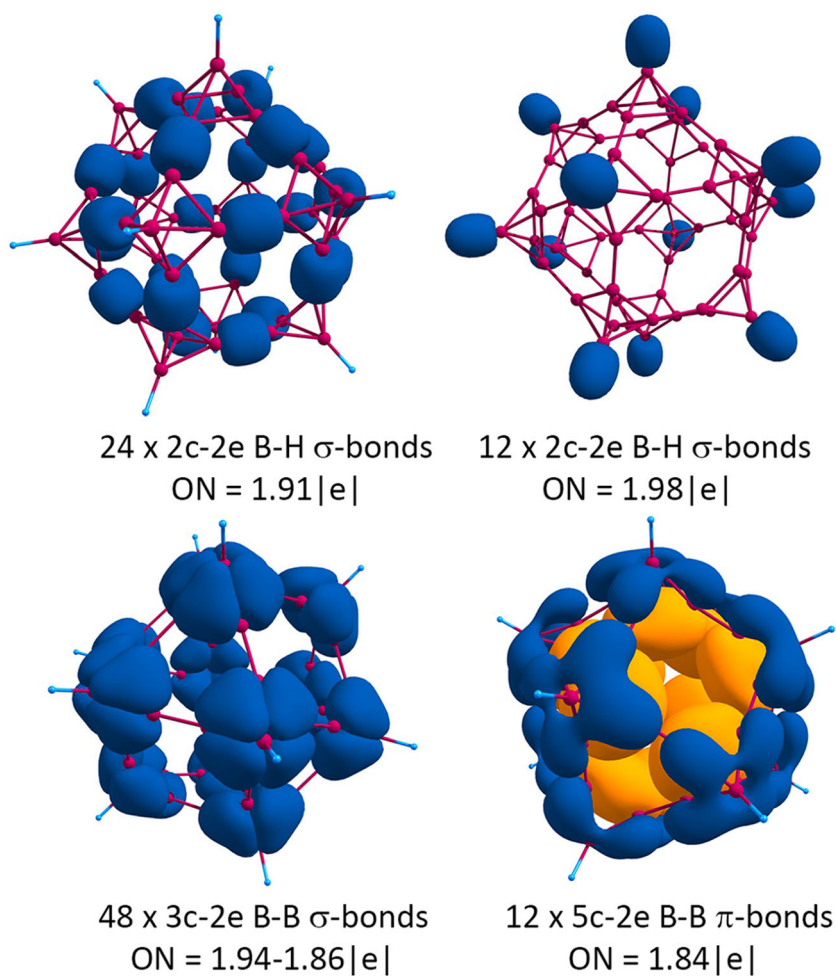


Fig. 9 Optimized geometries of **6-c**, **6-bh**, pyramidane C_5H_4 and borane B_3H_5 . Fluorinated system **6-bf** has the same bond framework as **6-bh**. Bond lengths are given in Table 2

covalent radii of boron atoms (1.70 Å [32]). In **6-bh** the shortest B-B bonds of 1.629 (1.634) Å are those linking

pyramidane units (bonds 6 at the Fig. 9 and Table 2). The fluorinated system **6-bf** also has the superpyramidal

Fig. 10 The AdNDP localization for **6-bh**



structure with shortened pyramidal and basal and elongated interpyramidane B-B bonds of 1.643 (1.644) Å in comparison with the same bonds of **6-bh**. Calculated NICS(0) of structure faces are of -6.3 (-6.4) for B_6 -rings and $+5.3$ ($+2.2$) for B_8 -rings of **6-bh**, -6.3 (-6.0) for B_6 -rings, and $+4.0$ ($+2.8$) for B_8 -rings of **6-bf** at DFT1 (DFT2).

According to the AdNDP analysis, 192 valence electrons of **6-bh** are distributed over 24 B-B interpyramidane bonds with $ON = 1.91$ |e|, 12 B-H bonds with $ON = 1.98$ |e|, 48 3c-2e B-B pyramidal bonds with $ON = 1.94$ – 1.86 |e| and finally 12 5c-2e B-B bonds with $ON = 1.84$ |e| (Fig. 10). A specific feature of **6-bh** and **6-bf** systems is the presence of 12 pentacoordinated boron centers with pyramidal configuration within the one structure.

A common characteristic of the considered polyhedral structures is a large HOMO-LUMO gap manifesting kinetic stability of the systems. Its value varies in relatively narrow energy range and is somewhat larger when it is calculated at the DFT2 approximation. For fluorinated boron hydrides, the HOMO-LUMO gaps are larger than those of the parent compounds: $\Delta E_{\text{HOMO-LUMO}} = 3.29$ (3.52) eV for **1-bf**; 1.60 (1.86) for **2-bh**; 2.28 (2.58) for **2-bf**; 1.53 (1.87) for **3-bh**; 1.71 (2.00) for **3-bf**; 1.29 (1.62) for **4-bh**; 1.51 (1.79) for **4-bf**; 1.59 (1.87) for **5-bh**; 1.84 (2.11) for **5-bf**; 1.50 (2.00) for **6-bh**; 1.73 (2.15) for **6-bf** at the DFT (DFT2) levels. For hydrocarbon supertetrahedrals: $\Delta E_{\text{HOMO-LUMO}} = 6.82$ (7.06) eV for **1-ch**; (7.29) for **1-cf**; 5.01 (5.37) for **2-ch**; 4.32 (4.71) for **2-cf**; 4.32 (4.75) for **5-ch** at the DFT (DFT2) levels.

In summary, the series of DFT computationally simulated new compounds that have been built on the basis of Platonic bodies and Archimedean solids by replacing some elements on the tetrahedral or pyramidal fragments are investigated. It is found that the cage compounds $E_{4n}R_n$ ($E = B, C$; $R = H, F$; $n = 4, 8, 12, 24$) based on polyhedrons in which all vertices are replaced by tetrahedral E_4R fragment are stable. Also, it is shown that cage compounds $B_{60}R_{12}$ with pyramidal units B_5R ($R = H, F$) has the superpyramidal structure and they are stable also. The new polyhedral hydrocarbon and boron hydride structures with tetrahedral E_4H and pyramidal E_5H vertices have shown that carbon superpolyhedrals $C_{16}R_4$, $C_{32}R_8$ ($R = H, F$), and $C_{96}H_{24}$ have classical 2c-2e C-C bonds. Electron-deficient boron systems contain localized 2c-2e and delocalized 3c-2e, 5c-2e, and 16c-2e bonds between boron atoms, which leads to the extensive number of structures based on polyhedra: $B_{16}F_4$, $B_{32}R_8$, $B_{48}R_{12}$, $B_{60}R_{12}$, $B_{96}R_{24}$ ($R = H, F$).

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