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Theoretical Design of New Sandwich Compounds of Boron, Carbon, Nitrogen, and Oxygen

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Abstract—Energetic and structural characteristics of new sandwich compounds of the second row elements X $(Y_3)_2$ and $X(Y_4)_2$ ($X = B^{5-}, C^{4-}, N^{3-}, O^{2-}$, Y = C, Si) stabilized with lithium cations were investigated using the methods of density functional theory B3LYP/6-311+G(d,p) and ab initio MP2(full)/6-311+G(d,p). Carbon sandwich systems were found to be thermodynamically more stable than their silicon analogs. In all systems the formation of hypercoordinated central atom is observed. For the most representative structures the Bader topological analysis of electron density was performed. The key types of distortions in the silicon-containing systems were found.

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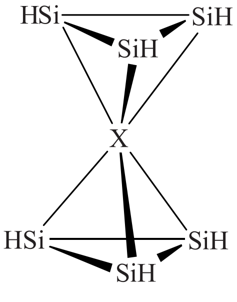
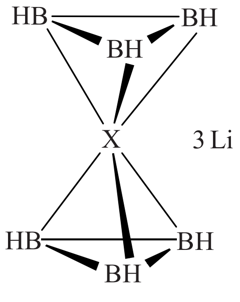
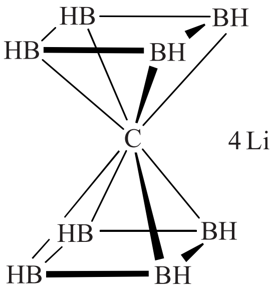
More than half a century passed since ferrocene, the first sandwich compound, was discovered in 1951 [1]. At present, sandwich structures are known which contain not only transition metals, metals of the main groups and actinides, but also non-transition elements [2–6]. Stable systems of this type must obey the octet rule [7, 8] as was demonstrated on the example of molecules and ions **1** $X[(SiH)_3]_2$ ($X = B^-$, C) [9], **2** $X[(BH)_3]_2 \cdot Li_3$ ($X = C^-$, N, O^+), and **3** $C[(BH)_4]_2 \cdot Li_4$ [10–12].



1, D_{3h}, D_{3d}
$X = B^+, C^{2+}$



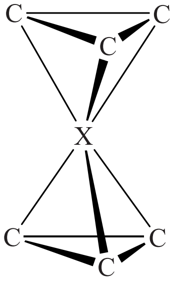
2, D_{3h}
$X = C^-$, N, O^+



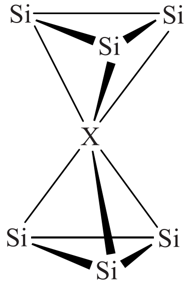
3, D_{4h}

It is noteworthy that compounds **2**, **3** are additionally stabilized by lithium cations, and such an approach allows an expantion of the class of sandwich systems by including sandwich clusters. Apart from the stabilizing electrostatic factor (neutralization of the extra charge of the anion), lithium cations can increase the coordination number of the central atom by forming covalent bonds with it [10–12]. In the present work we have examined new sandwich clusters with three- and four-membered carbon and silicon rings, containing as a central atom the elements of the 2nd row (B, C, N, O) and stabilized with lithium cations.

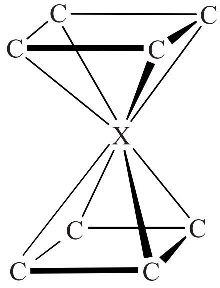
According to the octet rule stating that the sum of all π-electrons of the basal electrons and the valent electrons of the central atom for stable sandwich structures formed by the elements of the main rows cannot be larger than eight [7, 8], the sandwich systems **4** and **5** in a stable state must have large negative charge leading to strong electrostatic repulsions and, finally, to destabilization of the system. According to the performed B3LYP/6-311+G(d,p) calculations, not a single minimum or transition state with sandwich structure were found on the corresponding potential energy surfaces (PES) for systems **4** and **5**.



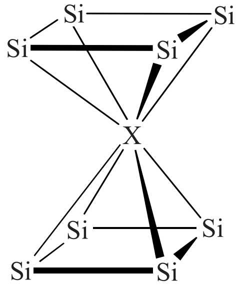
4a, D_{3h}



4b, D_{3h}



5a, D_{4h}

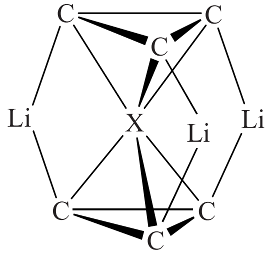


5b, D_{4h}

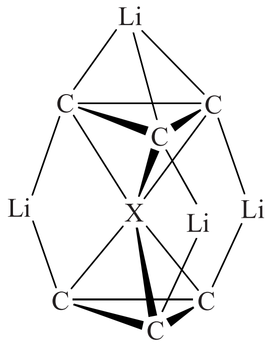
X = B^{5-}, C^{4-}, N^{3-}, O^{2-}

However, compensation of the negative charge by adding lithium cations allowed us to stabilize some of these systems as clusters. With this, two alternatives are possible for coordination of the counterions in the equatorial zone of the original sandwich system: to the edges or faces of the trigonal or tetragonal prisms. While only isomers with coordination of counterions to the faces were described for systems **2** and **3** [10–12], in systems **4** and **5**, in general, both options were realized. In order to clarify in which cases the lithium cations are included in the coordination sphere of the central atom, we performed topological analysis of distribution of the electron density for most representative structures among the systems presented in this paper.

Structure and stability of sandwich molecules and ions 4a. Symmetrical addition of three lithium cations to systems **4a** with retention of the original symmetry D_{3h} stabilizes not all of the starting systems. As follows from our calculations at both levels of the theory, only two structures **4a** (X = C^{4-}, N^{3-}) with coordination of the lithium cations to the edges of the carbon prisms (**6** and **7**, respectively) correspond to energy minima (λ = 0, hereinafter λ denotes the number of negative eigenvalues of the Hessian matrix in this point) on the PES. The corresponding isomeric forms of systems **6** and **7** with coordination of lithium cations to the faces of the carbon prisms are destabilized by 16 and 24 kcal mol^{-1}, respectively, compared to the stable forms and, according to DFT calculations, correspond to stationary points of the second order (λ□2); therefore, they will not be further considered. Geometry characteristics and Mulliken charges on the atoms of systems **6** and **7** are presented in Fig.1, energy characteristics are given in Table 1.

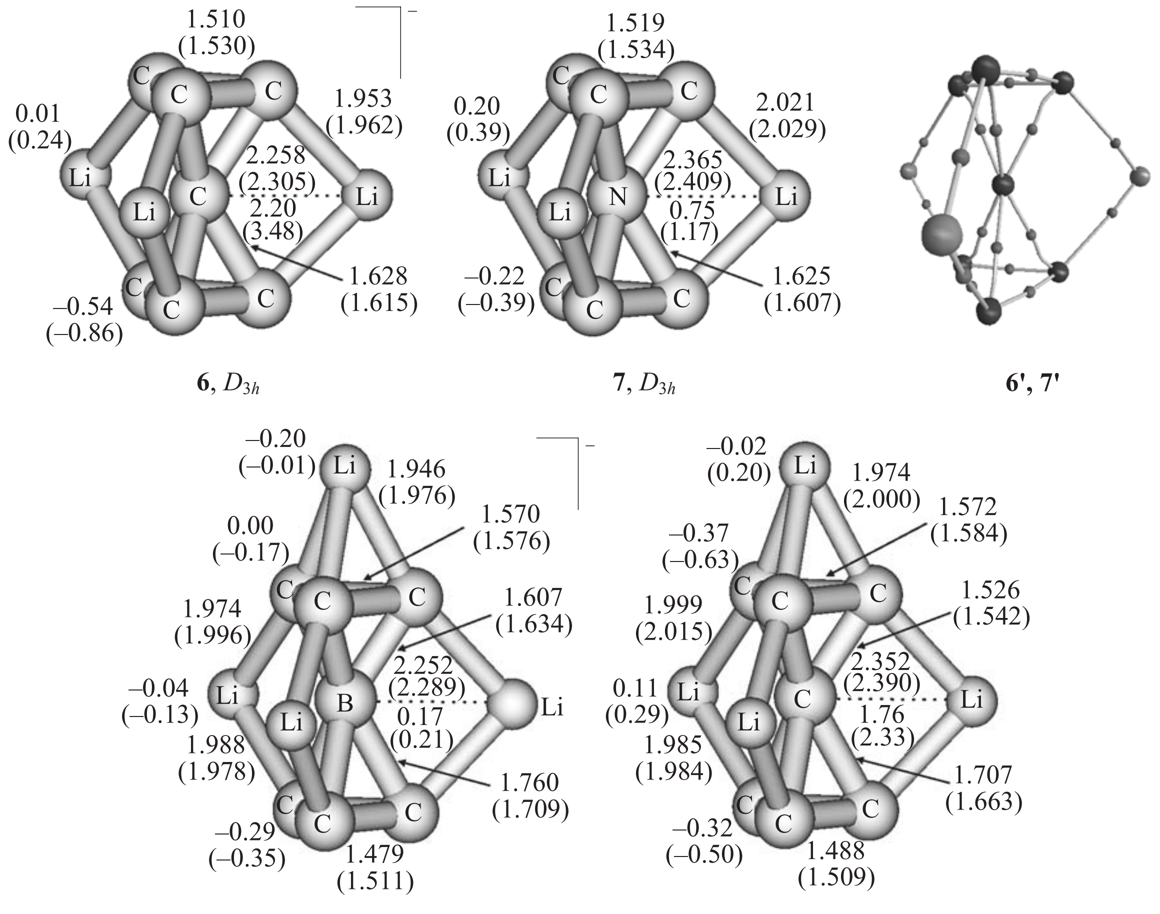


6, D_{3h}, X = C^{-}
7, D_{3h}, X = N



8, C_{3v}, X = B^{-}
9, C_{3v}, X = C

The C–C bond lengths in the rings in structures **6** and **7** lie within the range of ordinary C–C bond lengths and are equal to 1.510 and 1.519 Å from the DFT calculations and 1.530 and 1.534 Å from the MP2 calculations, respectively (see Fig. 1). The C_{center}–C bond lengths in anion **6** (1.628 (DFT) and 1.615 Å (MP2)) also fall in the range of the covalent C–C bond lengths (for ordinary C–C bond this range is 1.48–1.72 Å [20]). The N–C bond lengths in neutral system **7** are 1.625 (DFT) and 1.607 Å (MP2). The performed Bader topological analysis of the electron density has shown the absence of the X–Li interactions in systems **6** and **7**, as could be anticipated from the geometric characteristics: The X···Li distances in clusters **6** and **7** substantially (by 0.2–0.5 Å) exceed the sum of the corresponding covalent radii [21]. Thus, on the molecular graphs (see Fig. 1, graphs **6'** and **7'** quail-



6, D_{3h} **7**, D_{3h} **6', 7'**

8, C_{3v} **9**, C_{3v}

Fig. 1. Geometrical characteristics and Mulliken atomic charges for systems **6**–**9** calculated by B3LYP/6-311+G(d,p) and MP2(full)/6-311+G(d,p) methods (in parentheses). In the right upper corner the molecular graph for structures **6** and **7** is shown. Here and hereinafter the bond distances are in Å; only the bonding pathways and bond critical points (3, –1) are shown.

tatively coincide) of the carbon systems **6** and **7** the central atoms of carbon and nitrogen are connected by bonding pathways only with the ring carbon atoms indicative of their hexacoordination. However, specific features of coordination allow the lithium atoms to approach the ring carbon atoms to a covalent distance (~2 Å, see Fig. 1) and to form the stabilizing skeleton of compounds **6** and **7**, as proved by topological analysis.

As was shown by the natural bond orbital analysis (NBO analysis) [22], in the sandwich skeletons of systems **6** and **7** a donor–acceptor interaction is realized based on the electron density transfer from the filled *p*-orbitals of the central atom to vacant π-orbitals of the rings. This is also confirmed by the Mulliken charge distribution: the central atoms of carbon and nitrogen are charged positively, whereas the ring carbon atoms, negatively (see Fig. 1). Reconstructive molecular orbital analysis of system **6** also corroborates these results (Fig. 2). Participation of the lithium atoms in stabilization of clusters **6** and **7** consists in the donation of the electron density to the sandwich skeleton: the lithium atoms bear positive Mulliken charge which increases with the electronegativity of the central atom on going from X = C to X = N in systems **6** and **7**, respectively.

Addition of four Li cations to systems **4a** results in stabilization of the structures with X = B^{5-}, C^{4-} (systems **8** and **9**, respectively, see Fig. 1 and Table 1). The equatorial lithium atoms in clusters **8** and **9**, as in systems **6** and **7**, are also coordinated to the edges of the original carbon prisms.

The presence of an unsymmetrical apical lithium atom distorts the sandwich structure of compounds **8** and **9**: the difference in the distances of the two types of the B–C bonds in $B(C_3)_2Li_4^-$ amounts to 0.15 (DFT)

Table 1. DFT (RB3LYP/6-311+G**) and MP2 (RMP2(full)/6-311+G**) data for sandwich structures **6–17**[a]

Structure	Formula	Method	E_{tot}	$E_{tot} + ZPE$	ΔE	λ	ω_1
6, D_{3h}	$C(C_3)_2Li_3^-$	DFT	–289.003745	–288.972062	–	0	159
		MP2	–288.242538	–288.210611	–	0	144
7, D_{3h}	$N(C_3)_2Li_3$	DFT	–305.565707	–305.535951	–	0	155
		MP2	–304.765983	–304.735716	–	0	147
8, C_{3v}	$B(C_3)_2Li_4^-$	DFT	–283.380890	–283.346969	–	0	152
		MP2	–282.602094	–282.568321	–	0	146
9, C_{3v}	$C(C_3)_2Li_4$	DFT	–296.536677	–296.502908	–	0	120
		MP2	–295.736113	–295.702348	–	0	136
10, D_{3h}	$B(Si_3)_2Li_3^{2-}$	DFT	–1784.558961	–1784.541784	–	0	70
		MP2[b]	–1782.153263	–1782.135296	–	0	32
11a, D_{3h}	$C(Si_3)_2Li_3^-$	DFT	–1797.838486	–1797.821298	–	0	62
11b, C_{2v}	$C(Si_3)_2Li_3^-$	MP2	–1795.419828	–1795.402226	–	0	38
12a, D_{3h}	$N(Si_3)_2Li_3$	DFT	–1814.409838	–1814.393790	16.6	0	76
		MP2	–1811.925466	–1811.909034	45.7	0	60
12b, C_{2v}	$N(Si_3)_2Li_3$	DFT	–1814.435723	–1814.420207	0	0	85
		MP2	–1811.974654	–1811.958337	0	0	104
13, D_{3h}	$O(Si_3)_2Li_3^+$	DFT	–1834.676058	–1834.661793	–	0	28
		MP2	–1832.140635	–1832.125505	–	0	68
14a, C_{3v}	$B(Si_3)_2Li_4^-$	DFT	–1792.175061	–1792.156297	–	0	35
14b, C_s	$B(Si_3)_2Li_4^-$	MP2[b]	–1789.741782	–1789.721934	–	0	34
15, C_{3v}	$C(Si_3)_2Li_4$	DFT	–1805.289329	–1805.271017	–	0	24
16a, C_{2v}	$B(Si_3)_2Li_5$	DFT	–1799.639141	–1799.618704	23.0	0	59
16b, C_{2v}	$B(Si_3)_2Li_5$	DFT	–1799.675451	–1799.655371	0	0	40
17, D_{3h}	$C(Si_3)_2Li_5^+$	DFT	–1812.679951	–1812.660375	–	0	62
		MP2	–1810.167690	–1810.148135	–	0	6

[a] E_{tot} (a.e.) is the total energy (1a.e. = 627.5095 kcal mol^{-1}); *ZPE* (a.e.) is the energy of zero harmonic vibrations; ΔE (kcal mol^{-1}) is the relative energy of the isomers with *ZPE*; λ is the number of negative eigenvalues of the Hessian matrix; ω_1 (cm^{-1}) is the lowest harmonic vibrational frequency. [b] RMP2(full)/6-311G**.

and 0.07 Å (MP2), whereas in the system $C(C_3)_2Li_4$ the lengths of the two types of the C_{center}–C bonds differ by 0.18 (DFT) and 0.12 Å (MP2). As in the structurally related systems **6** and **7**, the B···Li and C_{center}···Li distances in clusters **8** and **9** are too large for the interaction between these atoms to be realized; however, the lengths of the $C_{carcass}$–Li bonds also fall in the range of the covalent values. According to the performed NBO analysis, the character of the stabilizing bonding in systems **8** and **9** qualitatively coincides with that in systems **6** and **7**. In spite of distortions of the sandwich skeleton in clusters **8** and **9** due to the presence of one apical lithium atom, systems **6**–**9** can be considered as new examples of the structures containing hexacoordinate atoms of boron, carbon, and nitrogen.

As was shown by the DFT calculations, the neutral isomeric systems $B(C_3)_2Li_5$ of C_{3v}-symmetry with two apical lithium atoms do not correspond to any stationary point on PES.

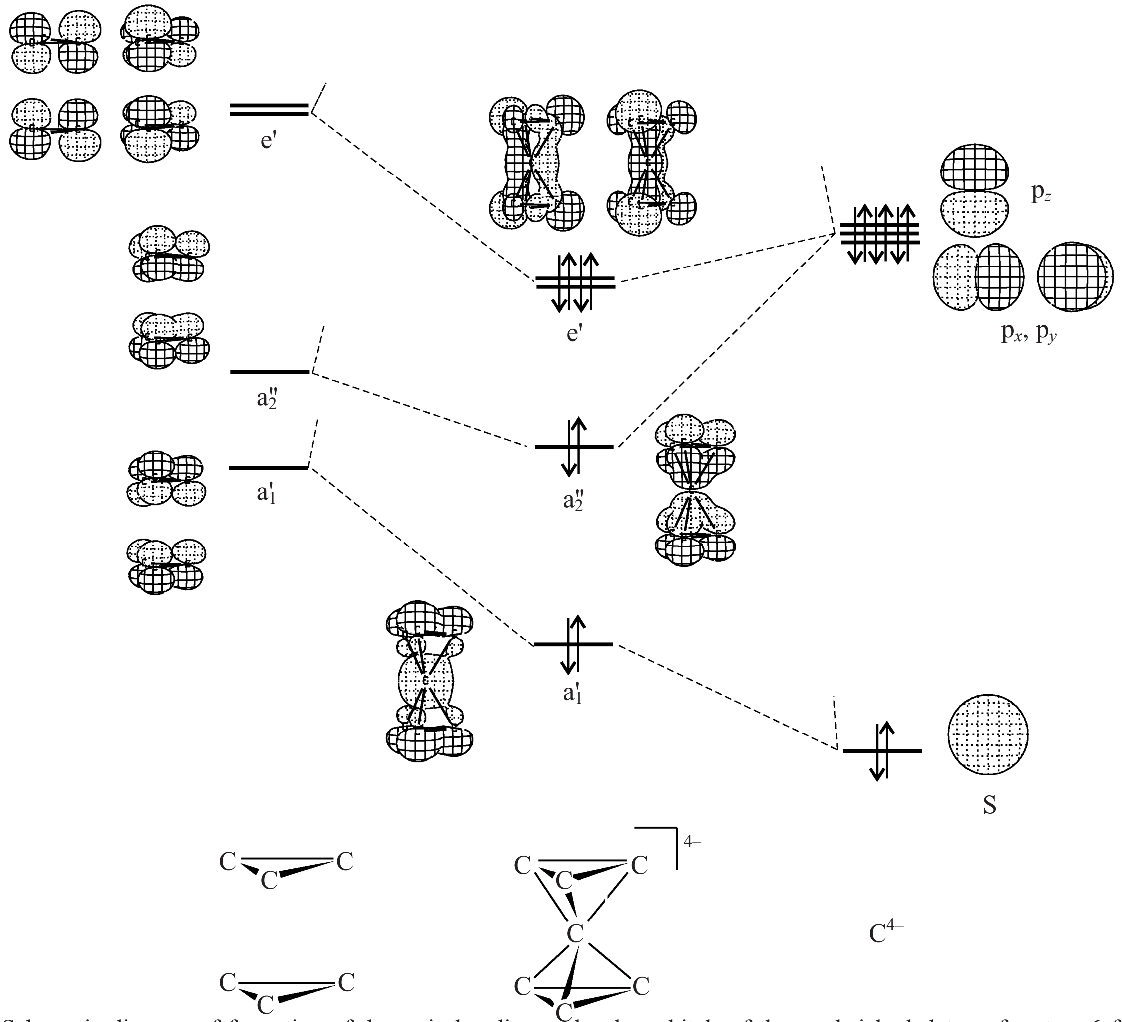
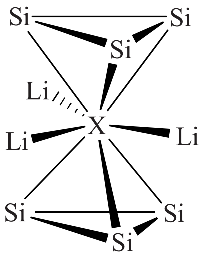


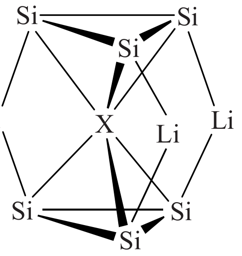
Fig. 2. Schematic diagram of formation of the main bonding molecular orbitals of the sandwich skeleton of system **6** from the orbitals of the fragments.

Structure and stability of sandwich molecules and ions 4b. Unlike carbon systems **4a**, the analogous silicon-containing systems **4b** are stabilized by three lithium cations for the whole series of the central atoms X = B, C, N, O. Clusters **10–13** correspond to energy minima on PES ($\lambda = 0$) as judged from the data of both methods. The exception was the system $C(Si_3)_2Li_3^-$ **11a** with parallel rings, which according to the MP2 calculations turned out to be the point of the second order ($\lambda = 2$) leading to minimum **11b** with deviation of the rings from being parallel by 6.9°. Geometry characteristics of systems **10–13** are given in Fig. 3, energy characteristics are listed in Table 1.

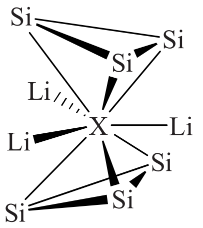
The first harmonic vibrational frequencies for the silicon clusters **10–13** ($\omega_1 = 28–104$, see Table 1) are significantly lower than those calculated for the carbon systems **6–7** ($\omega_1 \sim 150$), which shows their lower thermodynamic stability. As distinct from the carbon systems **6–7**, in the series of silicon structures **10–13** two alternatives for coordination of the lithium atoms exist (see Fig. 3). Thus, in clusters **10**, **11a**, **11b,** and **12b** ($X = B^{2-}$, C^-, N) the lithium atoms coordinate to the faces, while in clusters **12a** and **13** ($X = N$, O^+) they coordinate to the edges of the silicon prisms. In the case of the system $N(Si_3)_2Li_3$ both alternatives of lithium coordination are realized although the isomer with the lithium atoms coordinated to the faces is unstable in the D_{3h} symmetry ($\lambda = 2$ according to calculations by both methods) and has a distorted C_{2v}-structure **12b** with non-parallel rings [deviation from being parallel is 9.7° (DFT) and 11.5° (MP2)]. Isomer **12b** turned out to be 16.6 (DFT) and 45.7 (MP2) kcal mol^{-1} (with *ZPE* taken into account) energetically more stable than the isomer with parallel rings **12a**.



10, D_{3h}, X = C^{2-}
11a, D_{3h}, X = C^{-}

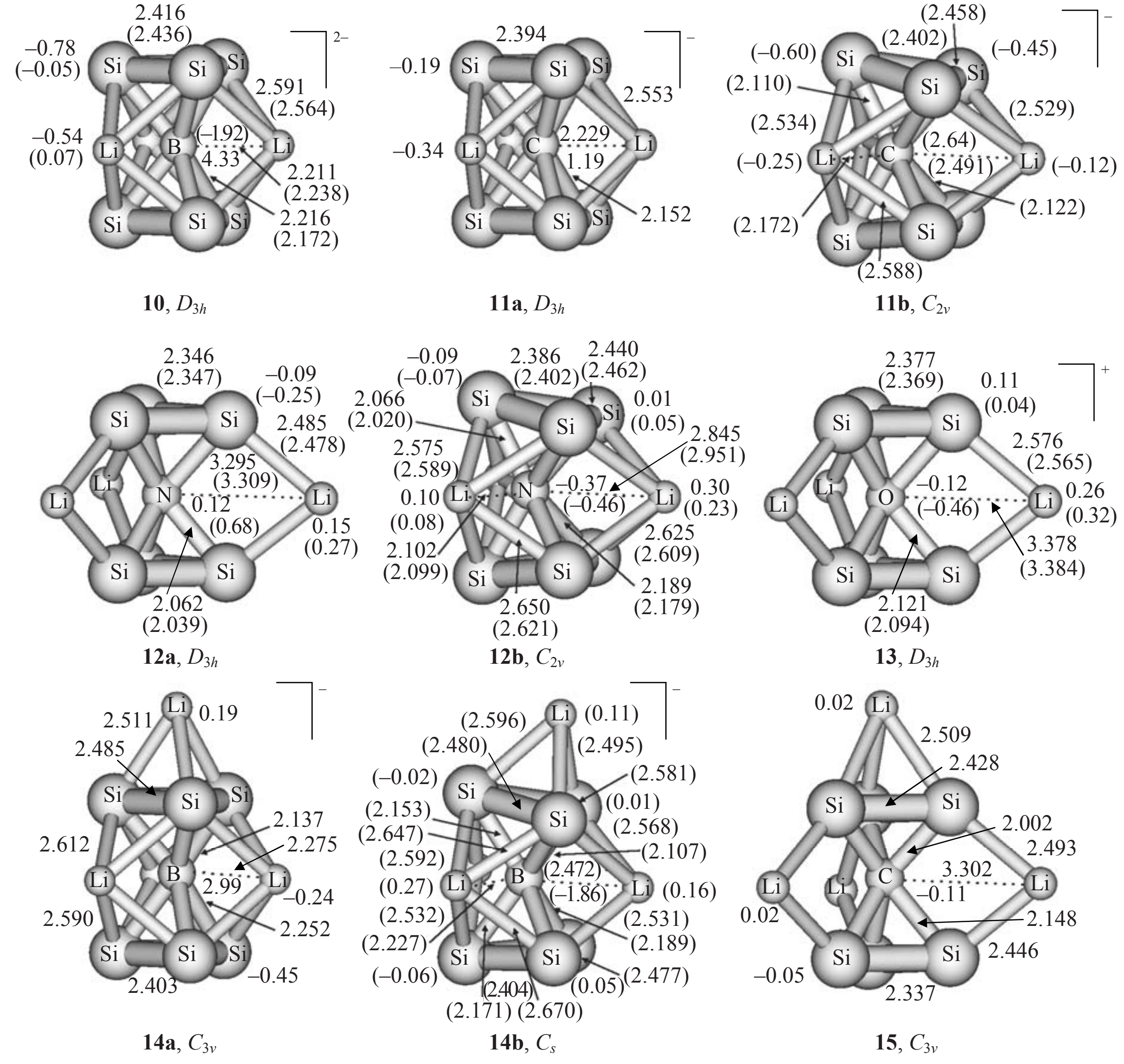


12a, D_{3h}, X = N
13, D_{3h}, X = O^{+}



11b, C_{2v}, X = C^{-}
12b, C_{2v}, X = N

The Si–Si bond distances in systems **10–13** fall in the range from 2.346 (**12a**, DFT) to 2.462 Å (**12b**, MP2), close to the lengths of ordinary Si–Si bonds (~2.34 Å [21]). The X–Si distances (X = B, C, N, O) in silicon clusters **10–13** exceed the corresponding typical covalent distances by ~0.1 (**10**)–0.3 Å (**12b**, **13**). And,

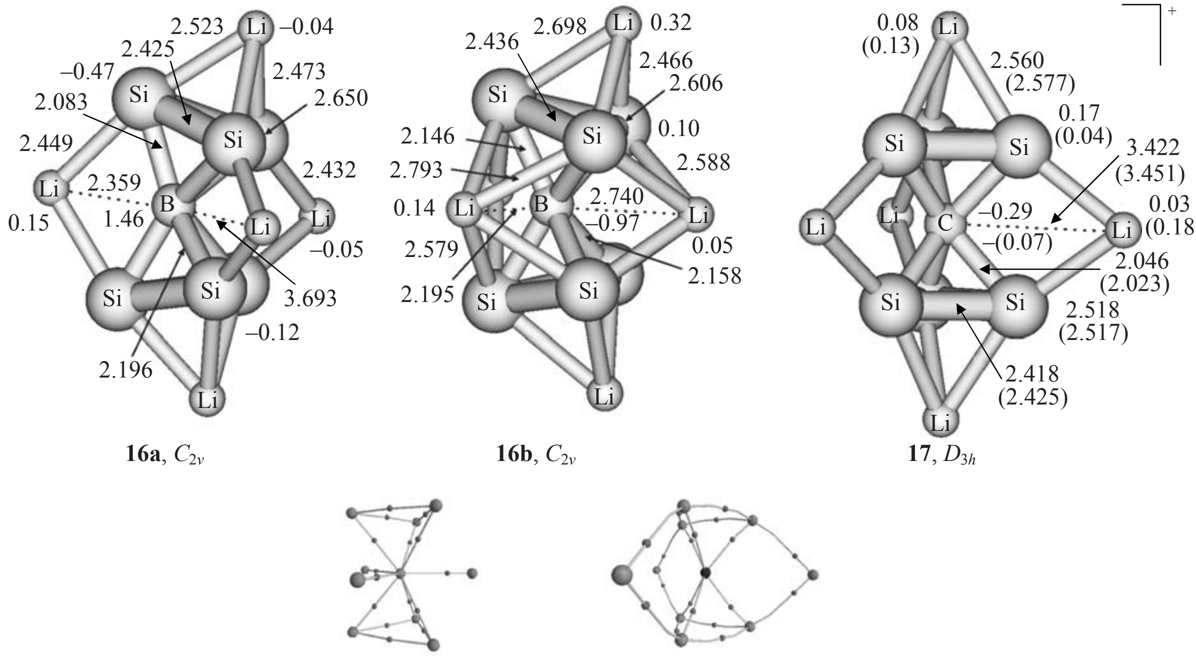


10, D_{3h} **11a**, D_{3h} **11b**, C_{2v}

12a, D_{3h} **12b**, C_{2v} **13**, D_{3h}

14a, C_{3v} **14b**, C_s **15**, C_{3v}

Fig. 3. Geometrical characteristics and Mulliken atomic charges for systems **10–17** calculated by B3LYP/6-311+G(d,p) and MP2(full)/6-311+G(d,p) methods (in parentheses). Below the molecular graphs for structures **10**, **11a**, **12a**, and **13** are shown.



16a, C_{2v} **16b**, C_{2v} **17**, D_{3h}

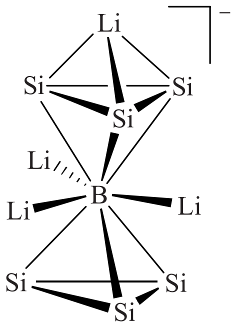
10', 11a' **12a', 13'**

Fig. 3. (Contd.)

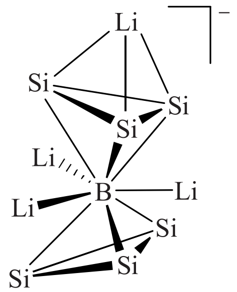
although the bond distances B–Li in **10** and C–Li in **11a** are somewhat larger than the average covalent values, the Bader topological analysis has shown the presence of bonding pathways between these atoms along with the B–Si and C–Si interactions (see Fig. 3, graphs **10'** and **11a'** qualitatively coincide). The presence of nine bonding pathways connecting the central atoms X with the atoms of the skeleton and the lithium atoms can be interpreted as nonacoordination of the B and C atoms in systems **10** and **11a**, respectively. It should be mentioned, that such a high coordination number of X atoms in clusters **10** and **11a** is realized due to the location of the lithium atoms on the faces of the trigonal silicon prisms, that makes possible the X–Li interactions to occur, as in the earlier studied hydroboron clusters **2** [10–12]. The importance of the manner of the lithium atoms coordination is corroborated by the example of systems **12a** and **13**: when lithium atoms are coordinated to the edges of the trigonal silicon prisms, the X···Li distances are too large for the interaction between these atoms to occur and, according to the topological analysis, clusters **12a** and **13** contain only hexacoordinate N and O atoms (see Fig. 3), as do the related systems **6** and **7**. Geometrical distortion of structures **11b** and **12b** does not allow at this stage of investigation to unambiguously conclude on the type of coordination of the central atom.

According to the performed NBO analysis, stabilization of the sandwich skeleton of clusters **10–13** is based on the electron density donation from the occupied p_z-orbital of the central atom X to free π-orbitals of the rings; that is in line with the character of bonding in the carbon systems **6**–**7**. The distribution of the Mulliken charges in the series of the systems **10–13** is affected by the increase of electronegativity of the central atom X in this series and the total charge of each system. Thus, according to DFT calculations, in cluster **10** the lithium atoms have maximum negative charge (–0.54 *e*), its value being decreased along the series, so that in systems **12**, **13** the lithium atoms are charged already positively (up to 0.30 *e* in nonsymmetrical cluster **12b**).

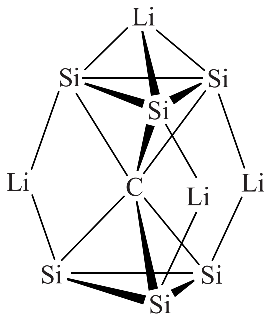
In the case of systems **10** and **11** further neutralization of the negative charge is possible. Thus, addition of one apical lithium cation to system **10** gives rise to formation of anion **14** $B(Si_3)_2Li_4^-$ with retention of coordination of equatorial lithium cations on the faces of the silicon prism, while system **11** in the same manner affords a neutral cluster **15** $C(Si_3)_2Li_4$, in which the coordination of the equatorial Li atoms changes as compared to that in **11** (see Fig. 3 and Table 1). From the MP2 calculations, system **14a** is a point of the second order (λ = 2) on the way to the minimum **14b** with the distorted structure of C_s symmetry.



14a, C_{3v}

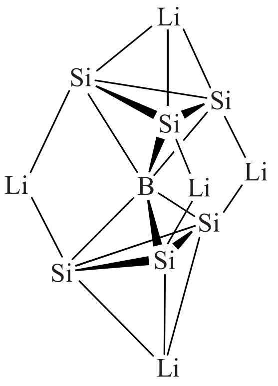


14b, C_s

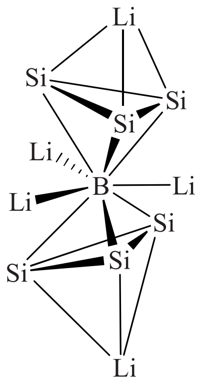


15, C_{3v}

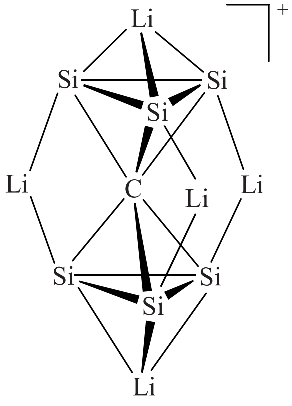
Addition of the second apical lithium cation to systems **14** and **15** allows results in neutral isomeric systems **16a, 16b** $B(Si_3)_2Li_5$, as well as a cationic cluster **17** $C(Si_3)_2Li_5^+$ (see Fig. 3 and Table 1). In systems **16a, 16b** the same type of distortion occurs as in systems **11b**, **12b** and **14b**; they have C_{2v} symmetry, and the corresponding to them compounds $B(Si_3)_2Li_5$ of D_{3h} symmetry are the points of the second order (λ = 2) according to DFT calculations (MP2 method failed to localize stationary points for systems **16a, 16b**, either of C_{2v} or of D_{3h} symmetry). According to DFT calculations, deviation of the ring from parallel arrangement in systems **16a, 16b** is 14.5° and 14.0°, respectively. Isomer **16b** is 23 kcal mol^{-1} (with ZPE taken into account) energetically more favorable than **16a**.



16a, C_{2v}

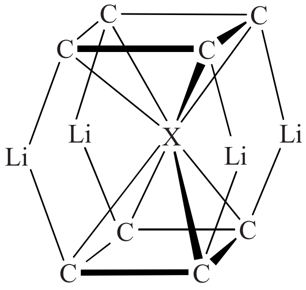


16b, C_{2v}

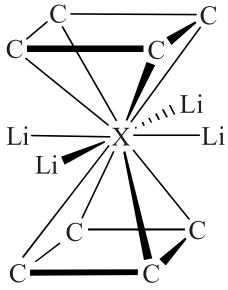


17, D_{3h}

Structure and stability of sandwich molecules and ions 5a. As follows from the calculations performed, the symmetrical addition of the four lithium cations along the equator of systems **5a** stabilizes only the clusters with B and C as the central atoms. With this, in each case both alternatives of coordination of the lithium cations existed: both to the edges and the faces of the tetragonal carbon prisms. From the data of calculations using both methods, systems **18a, 18b** and **19a, 19b** correspond to energy minima on PES (λ = 0). The characteristics of systems **18** and **19** are given in Table 2 and Fig. 4.



18a, D_{4h}, X = B^-
19a, D_{4h}, X = C



18b, D_{4h}, X = B^-
19b, D_{4h}, X = C

In the case of systems **18a, 18b** $B(C_4)_2Li_4^-$, structure **18b** with the lithium atoms coordinated to the faces was found to be energetically more favorable than **18a** in which the lithium atoms are coordinated to the edges

Table 2. DFT (RB3LYP/6-311+G**) and MP2 (RMP2(full)/6-311+G**) data for structures **18–22**[a]

Structure	Formula	Method	E_{tot}	E_{tot} + *ZPE*	Δ*E*	λ	ω_1
18a, D_{4h}	$B(C_4)_2Li_4^-$	DFT	–359.465950	–359.423455	1.0	0	142
		MP2	–358.525516	–358.482525	9.9	0	101
18b, D_{4h}	$B(C_4)_2Li_4^-$	DFT	–359.465511	–359.425107	0	0	85
		MP2	–358.540313	–358.498387	0	0	169
19a, D_{4h}	$C(C_4)_2Li_4$	DFT	–372.565388	–372.523425	0	0	123
		MP2	–371.594790	–371.552794	0	0	102
19b, D_{4h}	$C(C_4)_2Li_4$	DFT	–372.531679	–372.494316	18.3	0	110
		MP2	–371.571919	–371.532554	12.7	0	109
20a, C_{4v}	$B(C_4)_2Li_5$	DFT	–366.989428	–366.944949	0	0	125
C_1		MP2	–366.011053	–365.966596	1.2	0	63
20b, C_{4v}	$B(C_4)_2Li_5$	DFT	–366.974152	–366.933464	7.2	0	79
C_1		MP2	–366.010776	–365.968454	0	0	98
21a, D_4	$B(Si_4)_2Li_4^-$	DFT	–2371.145532	–2371.123939	0	0	26
21b, D_{4h}	$B(Si_4)_2Li_4^-$	DFT	–2371.145481	–2371.123915	0.01	1	*i*37
22, D_4	$C(Si_4)_2Li_4$	DFT	–2384.282156	–2384.261334	–	0	41

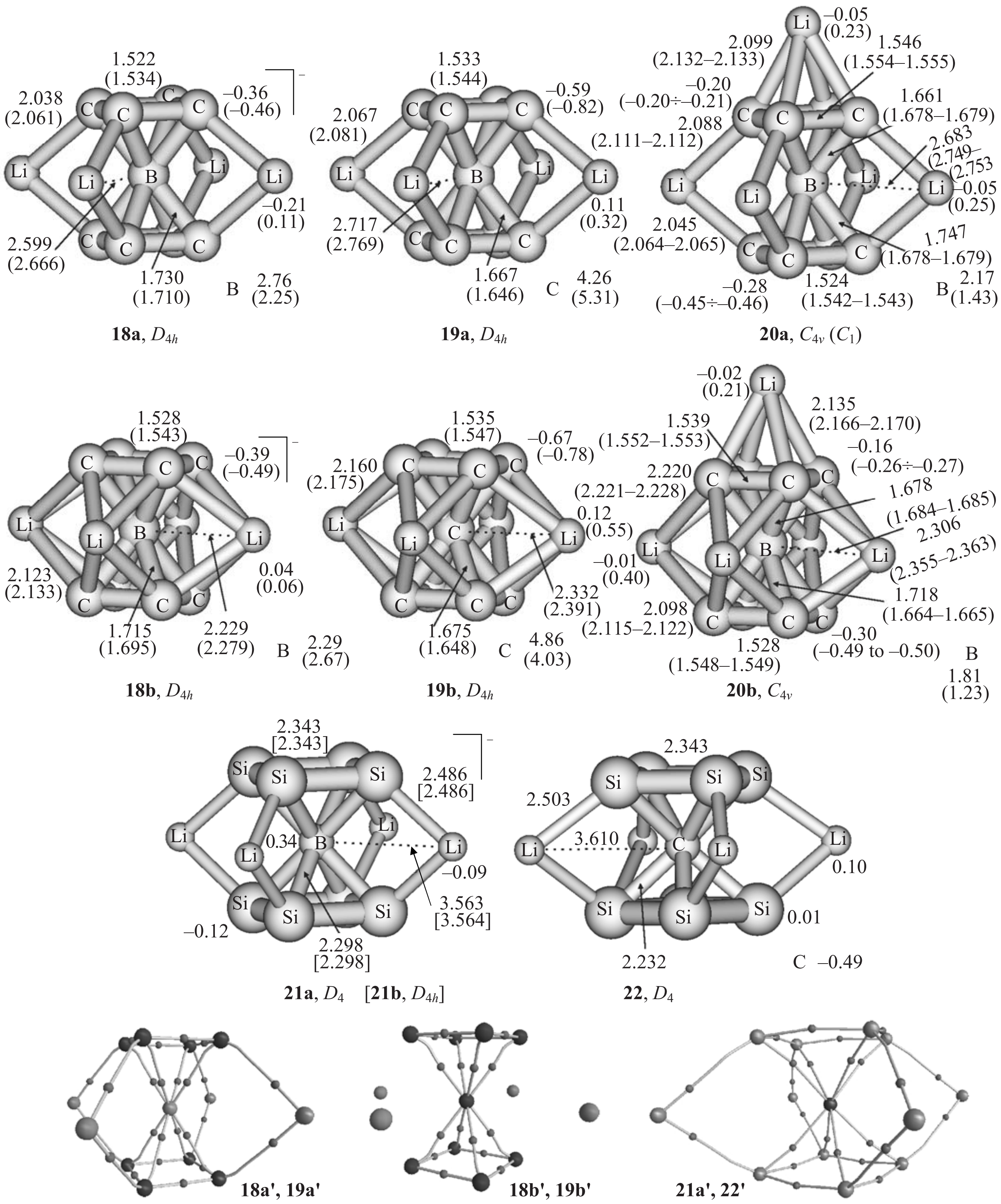
[a] See Table 1.

of the carbon prism by 1.0 (DFT) and 9.9 kcal mol^{-1} (MP2) with ZPE taken into account. Among the isomers $C(C_4)_2Li_4$ **19a, 19b**, on the contrary, structure **19a** with the lithium atoms coordinated to the edges of the carbon prism is preferable by 18.3 (DFT) and 12.7 kcal mol^{-1} (MP2) with *ZPE* taken into account.

The C–C bond lengths in the rings in systems **18** and **19** correspond to standard values for ordinary C–C bonds and lie within 1.522–1.547 Å. The lengths of the B–C and C_{center}–C bonds in **18**, **19** also fall within the range of covalent values [20]. These geometrical characteristics are proved by the Bader topological analysis: graphs for clusters **18** and **19** contain eight bonding pathways each, connecting the central atom with the carbon atoms of the rings (see Fig. 4). As in previous similar cases, the X–Li (X = B, C) interaction is lacking in systems **18a** and **19a** with coordination of lithium atoms to the edges of the silicon prisms, therefore these compounds can be considered as new examples with octacoordinate atoms of B and C. For the isomers with coordination of lithium atoms to the faces of the silicon prisms (**18b** and **19b**) the topological analysis of the electron density showed neither B–Li nor C_{center}–Li interactions in spite of close values of the X–Li (X = B, C) bond lengths (from DFT, 2.23 and 2.33 Å, respectively) with those in **10** and **11a** (from DFT, 2.21 and 2.23 Å, respectively). The absence of any bonding interaction on the lithium atoms on graphs **18b'** and **19b'** may result from nonclassical electronic structure of systems **18b** and **19b**, which, perhaps, is to some extent ignored by the program [19]. Therefore, it is possible to talk definitely only about octacoordination of the B and C atoms in clusters **18b** and **19b**, respectively, although formally the coordination number of the central atoms X in these systems might be increased to twelve.

According to the performed NBO analysis, the binding inside the sandwich skeleton in systems **18a, 18b** has predominantly ionic character: stabilization occurs due to the electron density transfer from the bonding orbitals of the rings to free orbitals of the boron atom. On the contrary, in clusters **19a, 19b** the covalent interaction predominates inside the sandwich skeleton, whose character is similar to the interaction in systems **6**–**7**.

Introduction of an additional apical lithium cation into systems **18** leads to neutral systems **20** (see Fig. 4 and Table 2). Among the isomers $B(C_4)_2Li_5$, cluster **20a** with coordination of the lithium atoms to edges is 9.6 (7.2 with ZPE) kcal mol^{-1} lower in energy than



18a, D_{4h} **19a**, D_{4h} **20a**, C_{4v} (C_1)

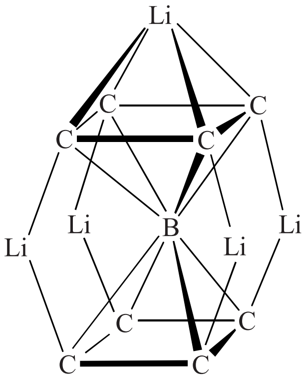
18b, D_{4h} **19b**, D_{4h} **20b**, C_{4v}

21a, D_4 [**21b**, D_{4h}] **22**, D_4

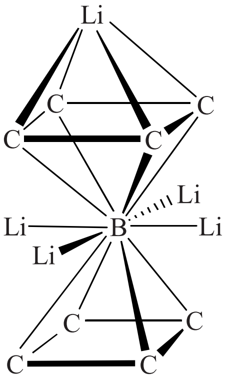
18a', 19a' **18b', 19b'** **21a', 22'**

Fig. 4. Geometrical characteristics and Mulliken atomic charges for systems **18**–**22** calculated by B3LYP/6-311+G(d,p) and MP2(full)/6-311+G(d,p) methods (in parentheses). The charges on central atoms are given to the right from the structures. Below the molecular graphs for structures **18a, 18b**, **19a**, **19b**, **21a,** and **22** are shown.

isomer **20b** (from DFT calculations). According to MP2 calculations, system **20** of C_{4v} symmetry correspond to the points of the second order ($\lambda = 2$) on the way to the respective minima of C_1 symmetry. With this, from MP2 calculations, isomer **20a** with coordination of lithium atoms to the edges is 0.2 kcal mol^{-1} lower in energy (without *ZPE*), whereas with *ZPE* isomer **20b** becomes 1.2 kcal mol^{-1} more favorable.



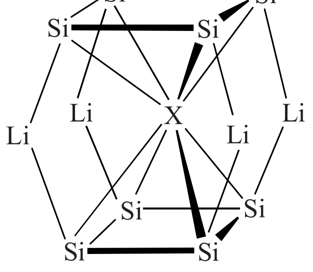
20a, C_{4v}



20b, C_{4v}

According to the NBO analysis, the binding inside the sandwich skeleton in systems **20**, as inside their precursors **18a, 18b** has predominantly ionic character: the stabilization occurs due to electron density transfer from carbon to boron atoms.

Structure and stability of sandwich molecules and ions 5b. As in the case of sandwich molecules of the type **5a**, only two systems of the type **5b** containing B and C as central atoms could be stabilized by lithium cations. The corresponding clusters **21a** and **22** have stable structure of D_4 symmetry (from DFT, they are energy minima with $\lambda = 0$), in which the parallel silicon rings are turned with respect to each other by 4.8° (X = B) or 28.3° (X = C), and the lithium atoms are coordinated to the edges of the twisted silicon prisms.



21a, D_4, X = B$^-$
22, D_4, X = C

The similar system **21b** of D_{4h} symmetry in the case of $B(Si_4)_2Li_4^-$ is a transition state ($\lambda = 1$) and lies only 0.03 (0.01 with *ZPE*) kcal mol^{-1} higher in the energy according to DFT data. In the case of $C(Si_4)_2Li_4$ the system of D_{4h} symmetry does not correspond to any stationary point on PES from DFT calculations. MP2 method failed to localize stationary points for systems **21** and **22** of D_4 or D_{4h} symmetry. Characteristics of the systems **21** and **22** see in Table 2 and Fig. 4.

The Si–Si bond lengths in clusters **21a** and **22** correspond to ordinary Si–Si bonds, the X–Si distances in **21a** by ~0.3 and in **22** by ~0.4 Å exceed the average covalent values. Structural differences of the systems **21a** and **21b** do not exceed 0.001 Å. In spite of geometry distortions, clusters **21a** and **22** retain the topological structure of the class they belong to (as far as the manner of coordination of lithium atoms is concerned), as demonstrated by graphs **21a'** and **22'** in Fig. 4. Therefore, compounds **21a** and **22** can be considered as new examples of the structures with octacoordinate B and C atoms.

According to the NBO analysis, covalent interaction predominates inside the sandwich skeleton in systems **21a** and **22** based, as in most cases above, on the electron density transfer from the central atom to the ring atoms.

Therefore, two types of structural distortions are characteristic of the suggested silicon sandwich cluster systems: a small (by several degrees) rotation of the rings with respect to each other with retention of their parallel arrangement (structures **21a**, **22**) and violation of the parallel arrangement of the rings with retention of the sandwich structure (systems **11b**, **12b**, **14b**, **16a, 16b**).

Since the most part of clusters was obtained for boron and carbon as central atoms, it was interesting to follow the preferences in coordination of the lithium atoms in these compounds. Thus, in the systems with central carbon atom the lithium atoms are predominantly coordinated to the edges of the carbon and silicon prisms (systems **6**, **9**, **15**, **17**, **19a**, **22**), and only in **11** and **19b** their coordination occurs to the faces of the corresponding prisms. In the systems with the central boron atom, among the considered structures both types of the isomers are present in equal amounts. However, among the three pairs of the isomeric systems (**16a, 16b**, **18a, 18b** and **20a, 20b**) energetically preferable was the coordination of lithium atoms to the faces of the corresponding silicon prisms (systems **16b** and **18b**).

Therefore, we have suggested new sandwich cluster systems with B, C, N and O as central atoms, the coordination number of the central atoms varied from 6 to 9.

Quantum-chemical calculations were performed by the restricted Hartree-Fock method (RHF) taking into account electron correlations for all electrons (valent and core) using the second order Møller-Plesset perturbation theory [MP2(full)] [13] and the density functional theory method (DFT) [13] with three-parameter potential B3LYP and the valence-split basis set 6-311+G**, by the use of the Gaussian-03 program package [14]. Identification of all stationary points was performed by calculation of the Hessian matrices. The Bader topological analysis of distribution of full electron density [15–18] was performed by the use of the original set of programs AIMPAC [19].

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