Structure and stability of *closo*-hexaboranes and their heteroanalogs*

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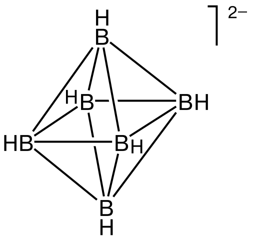
The molecular and electronic structures of *closo*-hexaboranes $B_6H_6^{2-}$, $B_6H_7^-$, and B_6H_8 and *closo*-heterohexaboranes XYB_4H_4 (X = Y = CH, N; X = BH, Y = CH⁻, N⁻, NH, O) were studed by the *ab initio* (MP2(full)/6-311+G**) and density functional (B3LYP/6-311+G**) methods. The bridging H atoms in *closo*-hexaboranes $B_6H_7^-$ and B_6H_8 can undergo facile low-barrier migrations around the boron cage (the barrier heights are about 10—15 kcal mol^{-1}). All heteroboranes having octahedron-like structures with hypercoordinated N and O atoms are rather stable and can be the subject of synthetic research efforts.

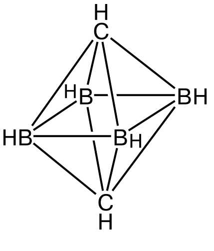
Key words: *closo*-hexaboranes, *closo*-heterohexaboranes, structure, stability, *ab initio* quantum-chemical calculations, density functional calculations.

The amazing stability of the regular octahedral structure of *closo*-hexaborane dianion $B_6H_6^{2-}$ (**1**) results from the closed electron shell of this system and from a rather wide energy gap between the occupied and unoccupied MOs.[1,2]

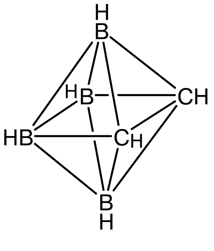


1, O_h

Hypercoordination (pentacoordination) of the boron centers in this species is due to the formation of the multicenter MOs that are responsible for simultaneous bonding of the entire cage, which is exclusively governed by the molecular structure and depends only slightly on the presence of heteroatoms or other substituents (three-dimensional aromaticity).[3] Therefore, high electronic and structural stability of the "octahedral" systems similar to species **1** must also retain upon isoelectronic replacement of one or two B atoms by carbons. Indeed, stable carboranes **2** and **3** containing pentacoordinated B and C atoms were obtained.[1,2,4—6]

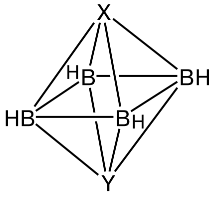


2, D_{4h}



3, C_{2v}

On going from boranes to carboranes and then to heteroboranes **4** and **5** one can expect that two last-mentioned compounds will retain structural and electronic stability upon isoelectronic (relative to the parent hexaborane dianion **1**) replacement of boron centers by other main group element atoms.



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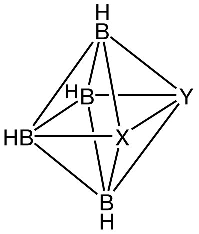

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X = Y = CH, N; X = BH, Y = CH⁻, N⁻, NH, O

In this work we report the results of *ab initio* (MP2(full)/6-311+G**)[7,8] and DFT (B3LYP/6-311+G**)[7,8] studies on the stability of hypothetical *closo*-heteroboranes **4** and **5**. These systems contain hypercoordinated N and O atoms and are isostructural and isoelectronic to *closo*-hexaborane dianion **1**.

Calculation Procedure

All calculations were carried out using the DFT approach with the B3LYP functional and by the restricted Hartree—Fock method with inclusion of electron correlation at the second-order Møller—Plesset level of perturbation theory for all (valence and core) electrons (MP2(full)) in the split-valence 6-311+G** basis set using the GAUSSIAN-94 program.[8] Full optimization of the geometry of the molecular structures corresponding to the energy minima (λ = 0; hereafter λ is the index of a stationary point, which is equal to the number of negative eigenvalues of the Hesse matrix at a given stationary point)[9] and to the saddle points (λ = 1) on the potential energy surfaces

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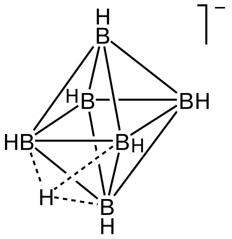
(PES) was carried out using the "tight" optimization criterion (GAUSSIAN-94). The structures corresponding to the energy minima on the PES were found by the steepest descent method (movement along the gradient line) from the saddle point to the neighboring stationary point (a saddle point or a minimum).[9] The initial direction of the gradient line was specified by minor displacement (1/10 of the length of the normalized transition vector) along the transition vector. Molecular structure images (see Figs. 1—3) were obtained using the ORTEP program[10] for which the corresponding Cartesian atomic coordinates taken from the results of calculations served as input parameters.

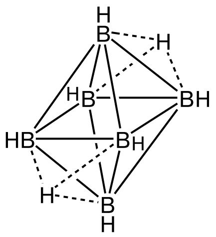
Results and Discussion

***closo*-Hexaboranes $B_6H_6^{2-}$, $B_6H_7^-$, and B_6H_8.** Applicability of the computational methods employed in this work to heteroboranes **4** and **5** was established by calculating the molecular and electronic structure of *closo*-hexaborane dianion **1** and its protonated (**6**) and diprotonated forms (**7** and **8**). Earlier, structures **1** and **6** have been the subject of thorough experimental and theoretical studies.[1,2,11—14]

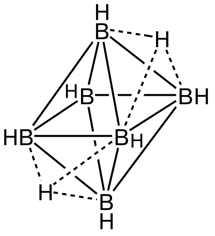
According to our calculations, structures **1** and **6—8** correspond to rather deep minima on their PES. The calculated geometric parameters of these structures and of the transition states (TS) **9** and **10** are shown in Fig. 1 and the corresponding energy characteristics are listed in Table 1. The geometric characteristics of dianion **1** obtained in this work are in good agreement with the results of theoretical studies.[12,13] However, the calculated B—B distances are somewhat shorter than the experimentally determined B—B bond lengths in *closo*-hexaboranes containing various counterions.[11] A possible explanation is provided by the packing effects.



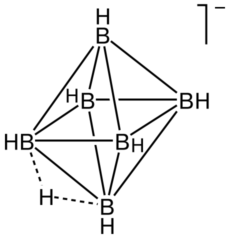
6, C_{3v}



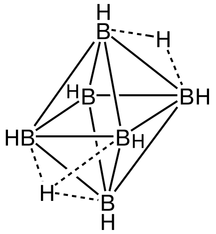
7, D_{3h}



8, C_{2v}



9, C_{2v} (TS)



10, C_s (TS)

In hexaboranes **6—8**, the bridging H atoms are coordinated by three centers, which is responsible for long distances between these atoms and B atoms. In these systems, the bridging H atoms play the role of counterions. They bear a relatively small positive charge (~ 0.1 e), while the remaining H atoms bear a small negative charge

Table 1. Results of DFT (B3LYP/6-311+G**) and MP2 (MP2(full)/6-311+G**) calculations of the structures of *closo*-hexaboranes **1** and **6—10**

Structure	Symmetry	Method	$-E_{total}$/a.u.	λ	ΔE/kcal mol^{-1}	ZPE/a.u.	$\omega_1/i\omega$ (cm^{-1})
$B_6H_6^{2-}$ (**1**)	O_h	DFT	152.724517	0	0	0.074301	441 (T_{2u})
		MP2	152.241740	0	0	0.074613	453 (T_{2u})
$B_6H_7^-$ (**6**)	C_{3v}	DFT	153.424990	0	0	0.086394	368 (E)
		MP2	152.938918	0	0	0.087802	411 (E)
B_6H_8 (**7**)	D_{3d}	DFT	153.929297	0	0	0.097701	319 (E_u)
		MP2	153.438894	0	0	0.099808	367 (E_u)
B_6H_8 (**8**)	C_{2v}	DFT	153.908813	0	12.85	0.096357	377
		MP2	153.418478	0	12.81	0.098171	424
$B_6H_7^-$ (**9**)	C_{2v}	DFT	153.411238	1	8.63	0.085930	*i*562
		MP2	152.920658	1	11.51	0.086528	*i*741
B_6H_8 (**10**)	C_s	DFT	153.906695	1	14.18	0.095528	*i*347
		MP2	153.412664	1	16.46	0.097369	*i*481

Note. E_{total} is the total energy (1 a.u. = 627.5095 kcal mol^{-1}); λ is the number of negative eigenvalues of the Hessian; ΔE is the relative energy of the isomeric structure calculated without inclusion of zero-point vibrational energy correction; ZPE is the zero-point vibrational energy correction; and $\omega_1/i\omega$ is the lowest or imaginary harmonic frequency.

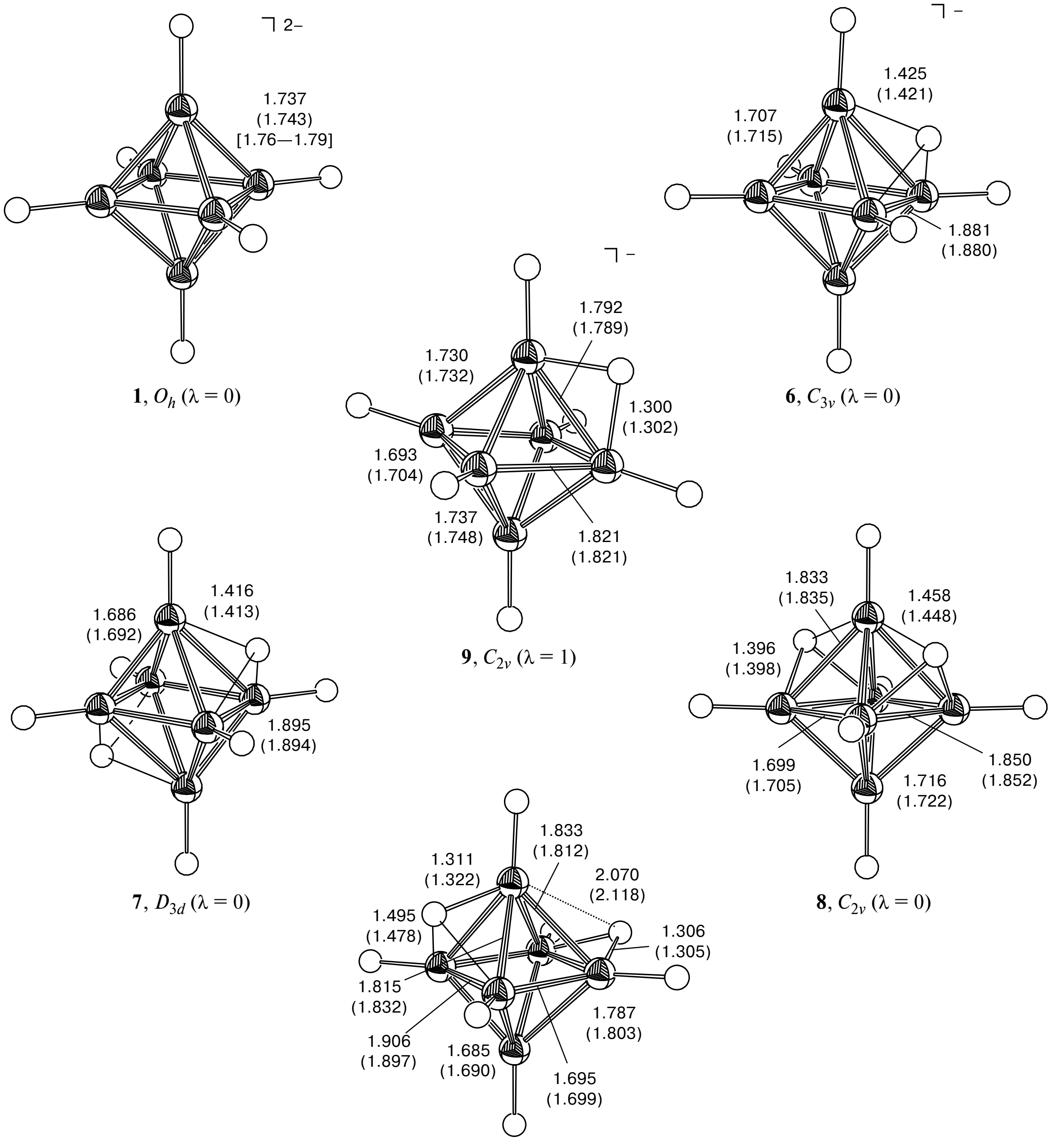
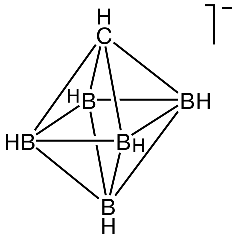


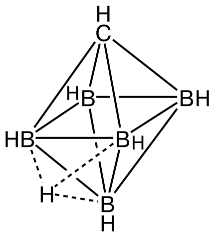
Fig. 1. Geometric parameters of the structures of *closo*-hexaboranes **1** and **6—10** obtained from B3LYP/6-311+G** and MP2(full)/6-311+G** (figures in parentheses) calculations. Experimental data (figures in brackets) for system **1** were taken from the literature.[11] Hereafter the bond lengths are given in Å.

(~ –0.01 e). Because of the weak bonding to B atoms, the bridging H atoms can undergo a facile migration from one face to another face around the "octahedral" boron cage. In anion **6**, such a migration can follow three equivalent routes *via* TS **9** with an energy barrier of 8.6 (DFT) and 11.5 kcal mol^{-1} (MP2). In neutral systems **7** and **8** (the energy of the former is 12.9 (DFT) and 12.8 kcal mol^{-1} (MP2) lower than that of the latter), the migration of counterions occurs *via* TS **10** and involves successive shift of each proton with an energy barrier of 14.2 (DFT) and 16.5 kcal mol^{-1} (MP2). No other TS of migrations of the bridging H atoms were located on the PES of the systems B_6H_8.

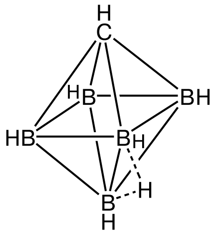
***closo*-Carboranes $CB_5H_6^-$, CB_5H_7, 1,6-$C_2B_4H_6$, and 1,2-$C_2B_4H_6$.** According to our calculations, the *closo*-carborane anion $CB_5H_6^-$ (**11**) and its protonated form CB_5H_7 (**12**), which are isoelectronic to the parent *closo*-hexaborane dianion **1**, correspond to energy minima on the corresponding PES.



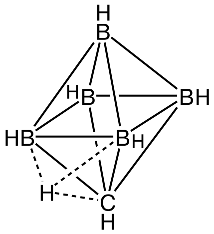
11, C_{4v}



12, C_s



13, C_s (TS)

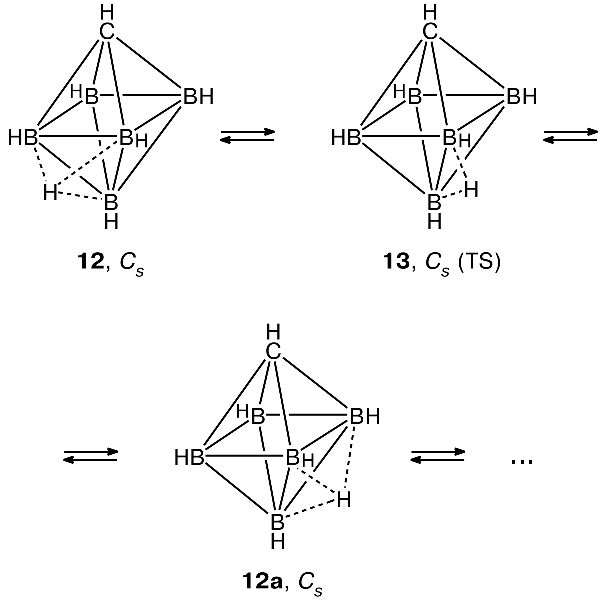


13´, C_s

The calculated geometric parameters of structures **11**, **12**, and TS **13** are shown in Fig. 2. The corresponding energy characteristics are listed in Table 2.

The calculated geometric parameters of structure **12** (see Fig. 2) are in good agreement with the data of experimental microwave spectroscopy and gas-phase electron diffraction studies[15,16] and with the results of earlier calculations.[17] No experimental data for the anion structure **11** are available as yet. Earlier,[15] CNDO calculations predicted the existence of an isomer **13´** containing a bridging H atom centered at the CBB face. However, the results of our calculations are inconsistent with this conclusion. Namely, geometry optimization of the structure **13´** with the starting orientation of the H atom toward the center of the CBB face revealed a barrierless structure relaxation into **12**. The dipole moment of system **12** equals 1.364 (DFT) and 1.401 D (MP2), being in good agreement with the experimental value (1.43±0.04 D) obtained using the Stark effect.[15]

The bridging H atom playing the role of counterion is bound to the boron cage much weaker than other hydrogen atoms. It can undergo a facile low-barrier migration between the equivalent PES minima **12** $\rightleftharpoons$ **13** $\rightleftharpoons$ **12a** $\rightleftharpoons$... . The top of the barrier corresponds to TS **13** and the energy characteristics of such migration are as follows: $\Delta E^{\ddagger}$ = 14.7 (DFT) and 16.4 kcal mol^{-1} (MP2) and $\Delta G^{\ddagger}$ = 14.2 (DFT) and 15.4 kcal mol^{-1} (MP2). Note that fast tautomeric rearrangement of monocarbon carborane ($\Delta G^{\ddagger}$ = 14.0±0.5 kcal mol^{-1}) interpreted as a low-barrier migration **12** $\rightleftharpoons$ **13** $\rightleftharpoons$ **12a** $\rightleftharpoons$... of the bridging proton was detected by dynamic ^{11}B NMR spectroscopy.[18]



12, C_s

13, C_s (TS)

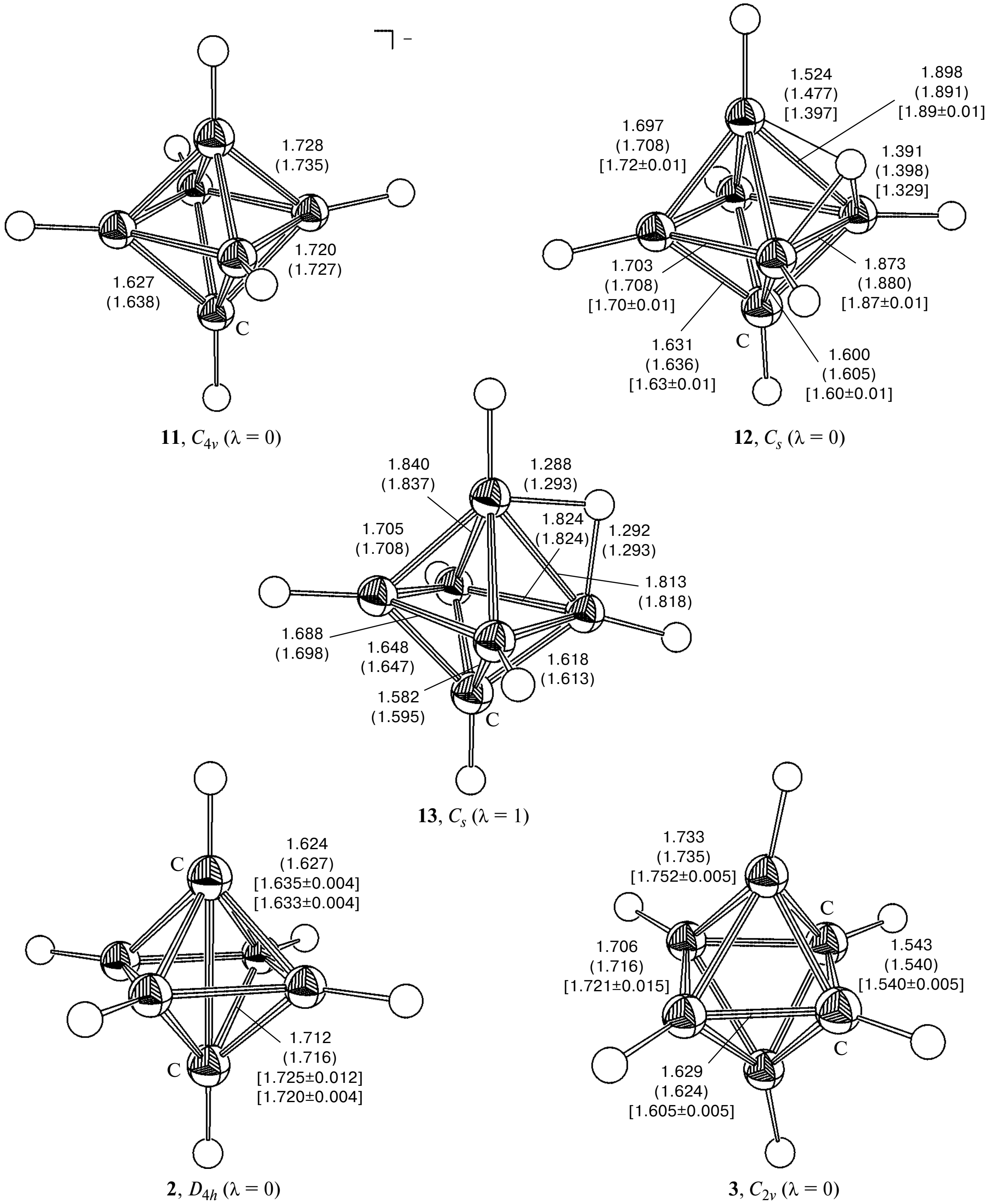
12a, C_s

According to calculations, *closo*-dicarboranes **2** and **3** are rather stable systems. The calculated geometric pa-

Table 2. Results of DFT (B3LYP/6-311+G**) and MP2 (MP2(full)/6-311+G**)* calculations of the structures of *closo*-carboranes **2**, **3**, and **11—13**

Structure	Symmetry	Method	$-E_{\text{total}}$/a.u.	λ	ΔE/kcal mol^{-1}	ZPE/a.u.	$\omega_1/i\omega$ (cm^{-1})
1,6-$C_2B_4H_6$ (**2**)	D_{4h}	DFT	179.284851	0	0	0.086128	380
		MP2	178.784605	0	0	0.086648	421
1,2-$C_2B_4H_6$ (**3**)	C_{2v}	DFT	179.270983	0	8.70	0.086115	395
		MP2	178.769941	0	9.20	0.086734	433
$CB_5H_6^-$ (**11**)	C_{4v}	DFT	166.101098	0	0	0.081228	425
		MP2	165.603042	0	0	0.081686	447
CB_5H_7 (**12**)	C_s	DFT	166.607438	0	0	0.091742	318
		MP2	166.105954	0	0	0.093138	387
CB_5H_7 (**13**)	C_s	DFT	166.583977	1	14.72	0.090940	*i*711
		MP2	166.079797	1	16.41	0.091632	*i*788

* See note to Table 1.



11, C_{4v} ($\lambda = 0$)

12, C_s ($\lambda = 0$)

13, C_s ($\lambda = 1$)

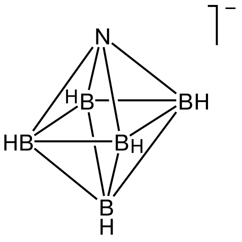
2, D_{4h} ($\lambda = 0$)

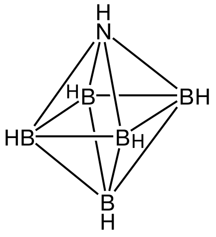
3, C_{2v} ($\lambda = 0$)

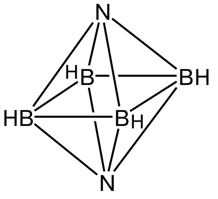
Fig. 2. Geometric parameters of the structures of *closo*-dicarbahexaboranes (**2**, **3**) and *closo*-monocarbahexaboranes (**11—13**) obtained from B3LYP/6-311+G** and MP2(full)/6-311+G** (figures in parentheses) calculations. Experimental data (figures in brackets) for structures **2**, **3**,[4—6] and **12** [15,16] were taken from the literature.

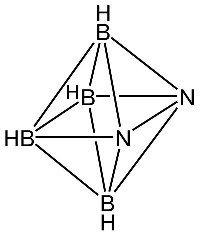
rameters of these species (see Fig. 2 and Table 2) are in good agreement with the gas-phase experimental data[1,2,4—6] and with the results of theoretical studies.[17,19—23] We found that *closo*-1,6-dicarbahexaborane **2**, 1,6-$C_2B_4H_6$, is 8.7 (DFT) and 9.2 kcal mol^{-1} (MP2) more stable than the 1,2-isomer **3**. This is also consistent with the results of MP2/6-31G** calculations[19] (9.5 kcal mol^{-1}) and experimental data.[4—6] No experimental data on the heats of formation of compounds **2** and **3** are available as yet.

***closo*-Azaboranes $NB_5H_5^-$, NB_5H_6, 1,6-$N_2B_4H_4$, and 1,2-$N_2B_4H_4$.** Based on the assumption mentioned above, one can expect that *closo*-azahexaboranes **14—17**, which are isoelectronic and isostructural to the *closo*-hexaborane dianion **1**, will also have stable structures.

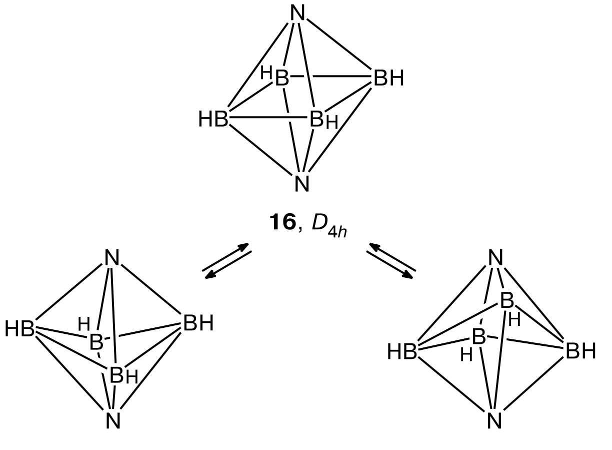

14, C_{4v}


15, C_{4v}


16, D_{4h}


17, C_{2v}

Indeed, our calculations of octahedron-like systems **14**, **15**, and **17** revealed their correspondence to rather deep PES minima. At the same time, contrary to the expectations and to the results of the earlier PRDDO [24] and MP2/6-31G* [19] studies, our MP2(full)/6-311+G** and B3LYP/6-311+G** calculations[25] showed that structure **16** with D_{4h} symmetry corresponds to a saddle point on the PES of the $N_2B_4H_4$ system, being the TS of low-barrier flip-flop isomerization **18a** $\rightleftharpoons$ **16** $\rightleftharpoons$ **18b**. This was also established in RHF/6-31G* calculations;[21] however, no structure corresponding to the energy minimum was located.


16, D_{4h}

18a, D_{2h}

18b, D_{2h}

The calculated geometric parameters of structures **14—18** are shown in Fig. 3 while their energy characteristics are listed in Table 3.

The *closo*-monoazahexaborane anion is stabilized in the form **14** with C_{4v} symmetry. Its geometric characteristics are very close to those of *closo*-monocarbahexaborane **11**. Similarly to this carborane, protonation of system **14** leads to a stable structure **19** with the bridging H atom located above the BBB face.

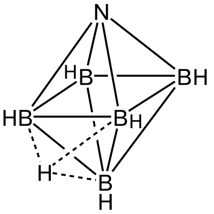
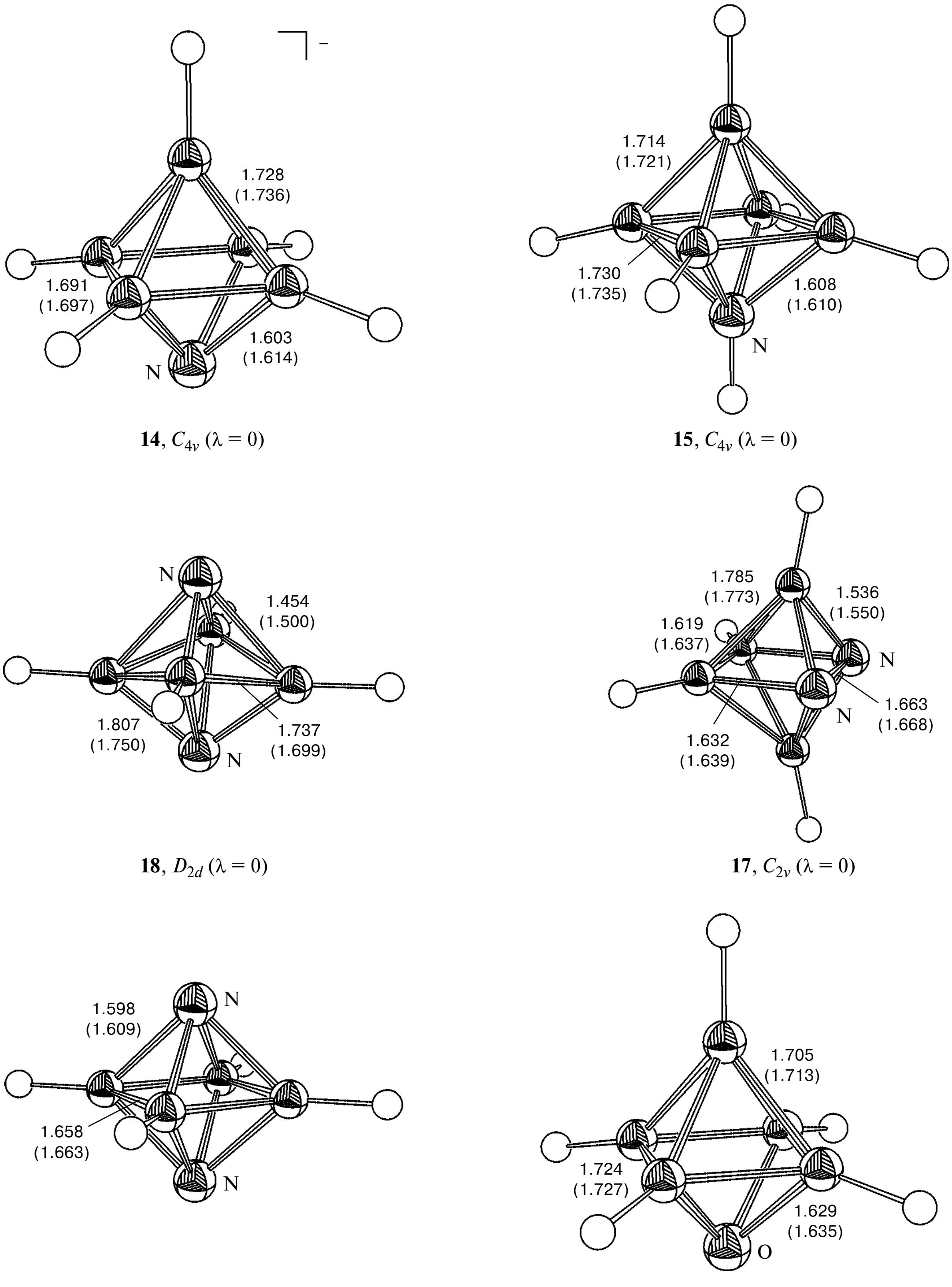

19, C_s

Table 3. Results of DFT (B3LYP/6-311+G**) and MP2 (MP2(full)/6-311+G**)* calculations of the structures of *closo*-azahexaboranes **14—19** and *closo*-oxahexaborane **21** and its isomer **22**

Structure	Symmetry	Method	$-E_{\text{total}}$/a.u.	λ	ΔE/kcal mol^{-1}	ZPE/a.u.	$\omega_1/i\omega$ (cm^{-1})
$NB_5H_5^-$ (**14**)	C_{4v}	DFT	182.152573	0	0	0.069479	288
		MP2	181.638929	0	0	0.069889	312
NB_5H_6 (**15**)	C_{4v}	DFT	182.693603	0	0	0.083198	369
		MP2	182.171740	0	0	0.083828	388
1,6-$N_2B_4H_4$ (**16**)	D_{4h}	DFT	211.348393	1	4.17	0.060449	*i*228
		MP2	210.822065	1	1.04	0.060956	*i*184
1,2-$N_2B_4H_4$ (**17**)	C_{2v}	DFT	211.333654	0	13.40	0.061182	253
		MP2	210.804263	0	12.21	0.061988	314
1,6-$N_2B_4H_4$ (**18**)	D_{2d}	DFT	211.355047	0	0	0.059728	299
		MP2	210.823730	0	0	0.060607	231
NB_5H_6 (**19**)	C_s	DFT	182.646565	0	29.52	0.079221	134
		MP2	182.129029	0	26.80	0.08	188
OB_5H_5 (**21**)	D_{4h}	DFT	202.542320	0	0	0.069413	263
		MP2	201.996932	0	0	0.070201	279
OB_5H_5 (**22**)	C_s	DFT	202.534166	0	5.10	0.067684	277
		MP2	201.974802	0	13.88	0.068605	286

* See note to Table 1.



14, C_{4v} ($\lambda = 0$) **15**, C_{4v} ($\lambda = 0$)

18, D_{2d} ($\lambda = 0$) **17**, C_{2v} ($\lambda = 0$)

16, D_{4h} ($\lambda = 1$) **21**, C_{4v} ($\lambda = 0$)

Fig. 3. Geometric parameters of the structures of *closo*-heterohexaboranes **14—18** and **21** obtained from B3LYP/6-311+G** and MP2(full)/6-311+G** (figures in parentheses) calculations.

However, system **19** is much more destabilized relative to isomer **15** containing a protonated N atom with unusual valence pentacoordination. Because of the large energy difference between structures **15** and **19** (over 25 kcal mol^{-1}, see Table 3) the activation barrier to rearrangement **19** → **15** is rather low and seems to be at most 2—3 kcal mol^{-1} (all our attempts to locate the true TS of this rearrangement led to a two-dimensional hill with $\lambda = 2$ and a top being only 4 kcal mol^{-1} higher than the energy minimum **19**).

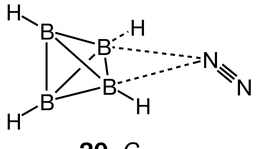
closo-1,6-Diazahexaborane **18** has a stable structure with D_{2d} symmetry. This system is characterized by two short and two long B—N bonds. The former are 1.500 (MP2) and 1.454 Å (DFT) while the latter are 1.750 (MP2) and 1.807 Å (DFT). The basal ring, B_4, has a boat conformation characterized by the B—B bond lengths of 1.699 (MP2) and 1.454 Å (DFT). These value are very close to the characteristics of the basal boron—boron bonds in molecules **2** and **3**. Flattening of the basal ring B_4 (passage to structure **16**) is accompanied by equalization of the B—N bond lengths and shortening of the B—B bonds. Structure **16** is the TS of a flip-flop isomerization **18a** $\rightleftharpoons$ **16** $\rightleftharpoons$ **18b** proceeding with an energy barrier of 1.0 (MP2) and 4.2 kcal mol^{-1} (DFT). The inclusion of zero-point vibrational energy (ZPE) correction has almost no effect on the barrier height.

A trend toward $D_{4h} \rightarrow D_{2d}$ distortion of the structure of *closo*-1,6-diazahexaborane **16** can be explained using the orbital interaction diagram (Fig. 4). Indeed, structural distortion causes a slight shift of the energy level of the bonding 1e-orbitals of the D_{2d} cluster toward lower energies.

Structure **16** with D_{4h} symmetry fulfils the electron count rules which govern the stability of bipyramidal structures of main group element compounds.[26] In spite of this fact in structure **16** the orbital interactions responsible for stabilization of such structures (namely, the interaction between the antibonding combination of p-orbitals of the apical center and the e_g-orbitals of the basal plane) are much weaker than in the carbon-containing analog **2**. This is due to an increase in the energy gap between these orbitals resulting from greater electronegativity of the N atom in the nitrogen-containing derivative **16** and also leads to lower diffusivity of p-orbitals and to weak overlap of these orbitals with the e_g-orbitals of the basal ring atoms.

Similarly to *closo*-1,2-dicarbahexaborane **3**, *closo*-1,2-diazahexaborane **17** has a stable structure with C_{2v} symmetry and a planar basal ring characterized by two types of B—N bond. Short B—N bonds are 1.550 (MP2) and 1.536 Å (DFT) while long B—N bonds are 1.639 (MP2) and 1.632 Å (DFT). Isomer **17** is 12.2 (MP2) and 13.5 kcal mol^{-1} (DFT) energetically less stable than the 1,6-isomer **18**. Here, it should be noted that in contrast to similar results of MP2 and DFT calculations of dicarboranes **2** and **3** and *closo*-1,2-diazahexaborane **17** both computational methods give significantly different (by about 0.05 Å) bond lengths in the molecule of *closo*-1,6-diazahexaborane **18**. System **17** can be treated as a result of the reaction between N_2 molecule and B_4H_4. In this connection it was of interest to establish whether N_2 can form a stable pre-reaction complex with B_4H_4. According to DFT calculations, this is impossible because the N_2 and B_4H_4 molecules are in the action range of repulsive potential at any distance between them up to the van der Waals contact. This is in agreement with the well-known fact that the density functional theory incorrectly describes long-range interactions.[27] On the contrary, MP2 calculations predict the existence of a pre-reaction complex **20** stabilized by dipole-dipole interactions between B_4H_4 and N_2.[25]

The stabilization energy of complex **20** calculated relative to the sum of the energies of isolated components is 1.1 kcal mol^{-1} without inclusion of the basis set superpo-



20, C_s

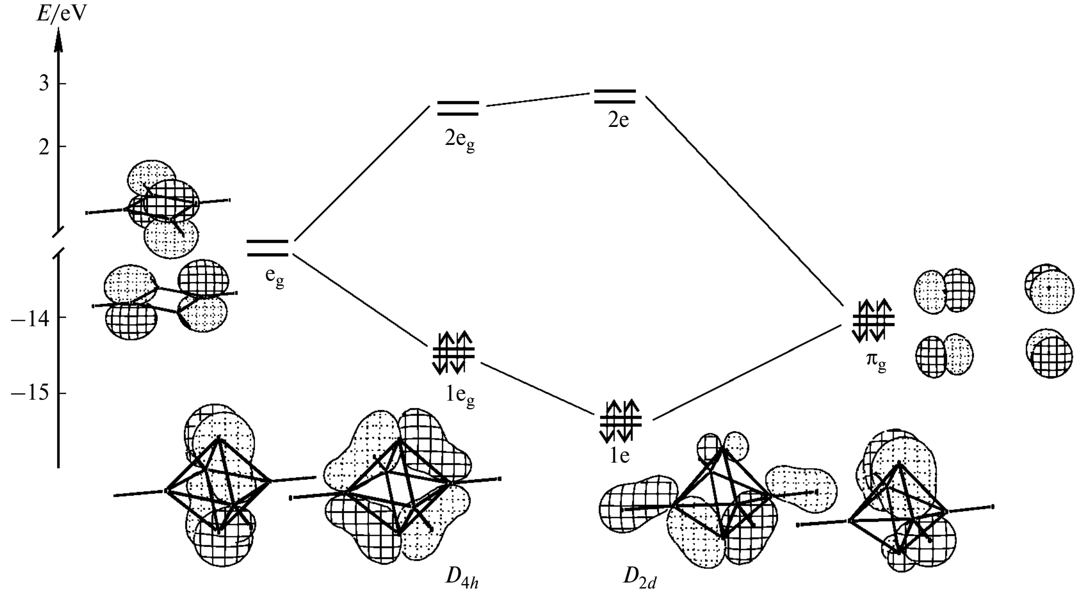
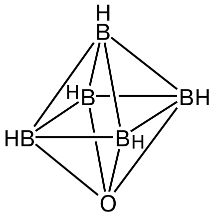


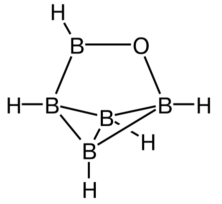
Fig. 4. Correlation diagram of π-MO energy levels for *closo*-1,6-diazahexaborane in structures **18** (D_{2d} symmetry) and **16** (D_{4h} symmetry).

sition error. Such a weak interaction causes no significant changes in the geometric parameters of the N_2 and B_4H_4 constituents of the complex compared to those of the corresponding isolated molecules. Complex **20** is 41.7 (MP2) and 37.9 kcal mol^{-1} (DFT) less energetically stable than 1,2-isomer **17**.

***closo*-Oxahexaborane OB_5H_5 (21)** has a stable octahedron-like structure. This is similar to monocarbon carborane **11** and monoazahexaborane **15**. The calculated geometric parameters of structure **21** are shown in Fig. 3 and the energy characteristics are listed in Table 3. The B—B bonds in species **21** are somewhat shorter than in system **15** while the B—O bonds are longer than the B—N bonds in **15**. This indicates that the orbital interaction between the apical O atom and the boron hydride fragment in system **21** is weaker than in other octahedron-like systems (**11** and **15**) due to an increase in the energy gap between the orbitals of the apical and basal fragments and to a decrease in the diffusivity of the orbitals of the apical center resulting from an increase in the electronegativity of the heteroatom.



21, C_{4v}



22, C_s

At the same time, in spite of weakening of the bonding between the oxygen center in *closo*-oxahexaborane **21**, the nearest-neighboring classical isomer **22** is 5.1 (DFT) and 13.9 kcal mol^{-1} (MP2) less energetically stable.

Thus, polyhedral borane molecules can serve as a structural cage for stabilization of non-classical compounds with pyramidal hypercoordinated centers. This type of anions can be stabilized in neutral form by introducing bridging hydrogens that play the role of counterions and enhance the stability of the electron shell of the polyhedral system. Weak bonding between the bridging H atoms and borons allows low-barrier proton migrations around the "octahedral" boron cage to occur in these systems.

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