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Low-energy barrier B_4 ring puckering rearrangement of 1,6-diaza-*closo*-hexaborane: an *ab initio* study

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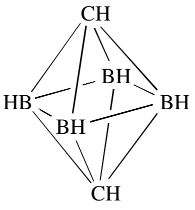
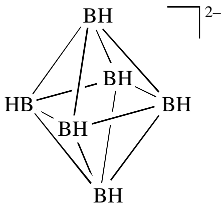
The *ab initio* [MP2(fu)/6-311+G] and DFT (B3LYP/6-311+G**) calculations predict stable structures of *closo*-diazaboranes 1,6-$N_2B_4H_4$ and 1,2-$N_2B_4H_4$, with the low-energy barrier B_4 ring puckering rearrangement occurring in the 1,6-$N_2B_4H_4$ stable structure.**

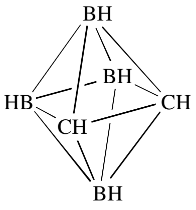
According to both experimental[1–3] and computational data,[4,5] *closo*-dicarborane 1,6-$C_2B_4H_6$ **1**, which is isoelectronic to *closo*-borane $B_6H_6^{2-}$ **2**, has a stable D_{4h}-symmetry structure and is energetically preferable than its 1,2-isomer **3**.



1, D_{4h}

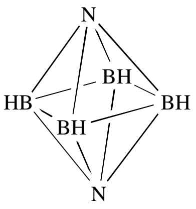


2, O_h

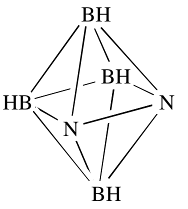


3, C_{2v}

It may be expected that similar stable structures are also characteristic of diaza-*closo*-boranes 1,6-$N_2B_4H_4$ **4** and 1,2-$N_2B_4H_4$ **5** isoelectronic to **1** and **3**, respectively, and that **4** is more stable than its isomer **5**. Indeed, early preliminary PRDDO calculations[6] on $N_2B_4H_4$ showed structure **4** to be more stable than **5**, although the distorted trigonal prism to be predicted the most stable structure.



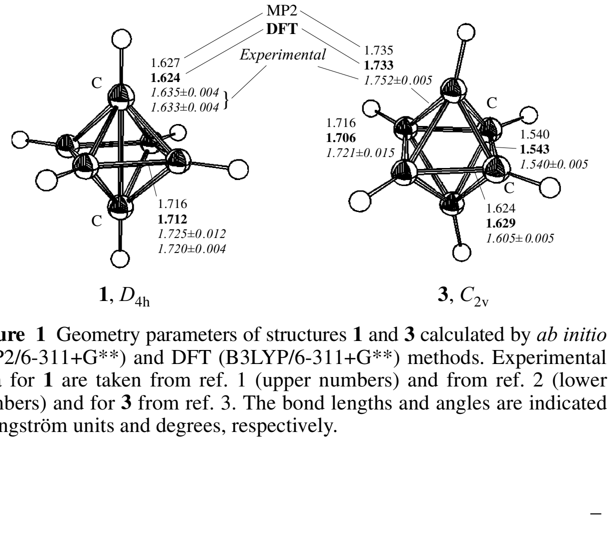
4, D_{4h}



5, C_{2v}

More recent *ab initio* calculations[7,8] also showed that 1,6-isomer **4** is more stable than 1,2-**5**. However, in both cases it was found that structure **4** does not correspond to a minimum on the $N_2B_4H_4$ potential-energy surface (PES) and it was not studied the distortion directions from the D_{4h} structure of **4**.

In this work, we performed *ab initio* [MP2(fu)/6-311+G**] and density functional theory (B3LYP/6-311+G**) calculations[9,10] on compounds **4** and **5**. For comparison, we also calculated the structures of *closo*-dicarboranes **1** and **3** at the same level of approximation.



1, D_{4h} **3**, C_{2v}

Figure 1 Geometry parameters of structures **1** and **3** calculated by *ab initio* (MP2/6-311+G**) and DFT (B3LYP/6-311+G**) methods. Experimental data for **1** are taken from ref. 1 (upper numbers) and from ref. 2 (lower numbers) and for **3** from ref. 3. The bond lengths and angles are indicated in angström units and degrees, respectively.

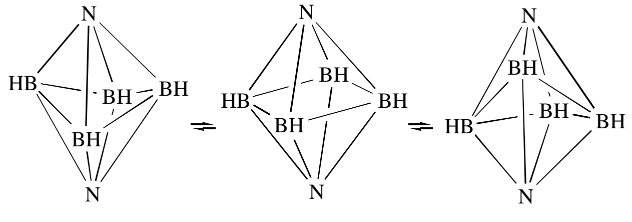
Table 1 Results of *ab initio* [MP2(fu)/6-311+G**] and DFT (B3LYP/6-311+G**) calculations for the structures of **1**, **3**–**7**.[a]

Structure	Method	E_{tot}	λ	ΔE	ZPE	ΔE_{ZPE}	ω_1
1, D_{4h}	MP2	–178.784605	0	0	0.086648	0	421
	DFT	–179.284851	0	0	0.086128	0	380
3, C_{2v}	MP2	–178.769941	0	9.2	0.086734	9.2	433
	DFT	–179.270983	0	8.7	0.086115	8.7	395
4, D_{4h}	MP2	–210.822065	1	1.0	0.060956	1.3	*i*184
	DFT	–211.348393	1	4.2	0.060449	4.6	*i*268
5, C_{2v}	MP2	–210.804263	0	12.2	0.061988	13.1	314
	DFT	–211.333654	0	13.5	0.061182	14.3	253
6, D_{2d}	MP2	–210.823731	0	0	0.060607	0	231
	DFT	–211.355047	0	0	0.059728	0	300
7, C_s	MP2	–210.757200	0	41.7	0.056079	38.9	17
	DFT[b]	–211.294522	slope	37.9	—	—	—
B_4H_4, T_d	MP2	–101.584553	0	—	0.050657	—	617
	DFT	–101.409193	0	—	0.049508	—	609
N_2, $D_{\infty h}$	MP2	–109.346230	0	—	0.005570	—	2445
	DFT	–109.559694	0	—	0.004906	—	2151

[a] E_{tot} (in a.u.) and ΔE are the total and relative energies (1 a.u. = 627.5095 kcal mol^{-1}); λ is the number of the negative hessian eigenvalues; ZPE (in a.u.) is the harmonic zero-point correction; ΔE_{ZPE} (in kcal mol^{-1}) is the relative energy including harmonic zero-point correction; ω_1 (in cm^{-1}) is the smallest or imaginary harmonic vibration frequency. [b] Results correspond to a slope point with 5 Å distance from N_2 to the BB bond.

In agreement with published data,[7,8] our *ab initio* calculations revealed that the structure of **4** of D_{4h} symmetry corresponds to a saddle point rather than a minimum on the PES $N_2B_4H_4$ and is the transition state for the low-energy barrier of the B_4 ring puckering rearrangement **6a** $\rightleftharpoons$ **4** $\rightleftharpoons$ **6b**. At the same time, 1,2-isomer **5**, much like as its isoelectronic analogue **3**, has a stable structure of C_{2v} symmetry and is energetically less favourable than 1,6-isomer **6**.

According to the calculations, the structures of **1**, **3** and **5**, **6** correspond to minima ($\lambda = 0$; hereafter, λ designates the number of negative hessian eigenvalues) on the PESs of $C_2B_4H_6$ and $N_2B_4H_4$, respectively. The calculated geometric and energy parameters of these structures and the saddle point for the structure of **4** are depicted in Figures 1 and 2 and listed in Table 1. As can be seen in Table 1 and Figure 1, the calculated geometric characteristics of *closo*-dicarboranes **1** and **3** are in good agreement with the gas-phase experimental data[1–3] and those obtained in previous theoretical studies.[4,5] All calculated bond lengths are in



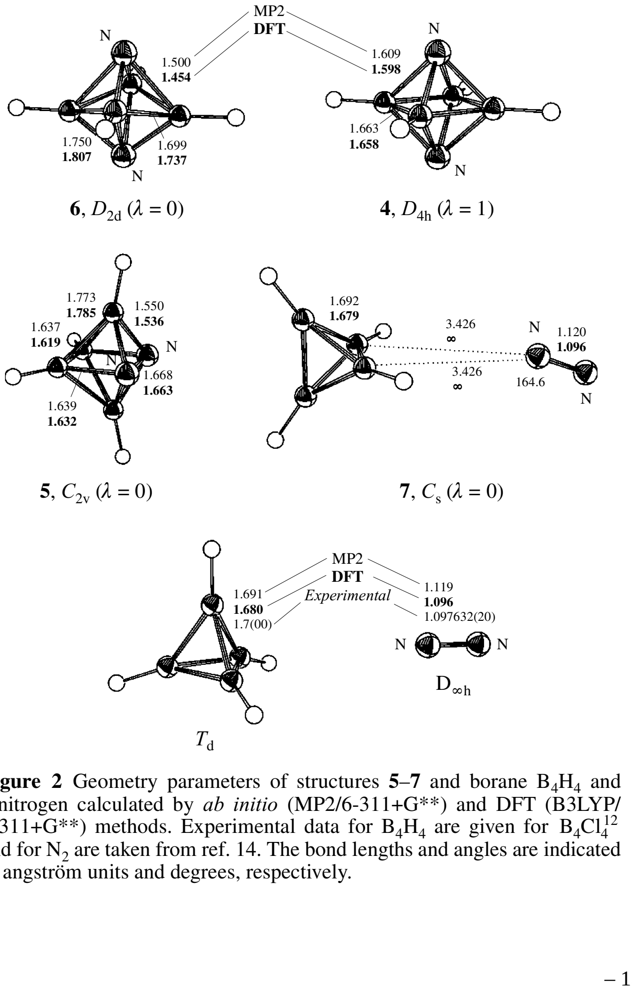
6a, D_{2d} **4**, D_{4h} **6b**, D_{2d}

the range of the experimental values accounted for experimental errors. 1,6-Dicarbo-*closo*-hexaborane **1**, 1,6-$C_2B_4H_6$ was found to be more stable than 1,2-isomer **3** by 9.2 kcal mol^{-1} at the MP2 level and by 8.7 kcal mol^{-1} at the DFT level. These values are consistent with the previous estimation (9.5 kcal mol^{-1}) obtained at the MP2/6-31G** level.[4] No experimental data on the heats of formation of **1** and **3** are currently available.

The stable structure of 1,6-diaza-*closo*-hexaborane **6** has D_{2d} symmetry with two short (MP2, 1.500 and DFT, 1.454 Å) and two long (MP2, 1.750 and DFT, 1.807 Å) BN bonds. The basal B_4 ring has a boat conformation; the B–B bond lengths are equal to 1.699 (MP2) and 1.454 (DFT) Å. This value is very close to those of the basal B–B bonds in **1** and **3**. Planarization of the B_4 basal cycle, **6** → **4**, results in equalization of all the BN bonds and shortening of the B–B bonds. The structure of **4** is the true transition state structure ($\lambda = 1$, this identification of stationary point agrees with the result of Jemmis and Subramanian[8] but disagrees with McKee's[7] results $\lambda = 3$) for the puckering rearrangement **6a** $\rightleftarrows$ **4** $\rightleftarrows$ **6b** with the energy barrier as low as 1.0 (MP2) or 4.2 (DFT) kcal mol^{-1}. Accounting for zero-point energy (ZPE) does almost not change the energy barrier.

The tendency of the D_{4h} structure of 1,6-diaza-*closo*-hexaborane **4** to the $D_{4h} \rightarrow D_{2d}$ distortion is explained by the orbital interaction diagram (Figure 3), which shows that this distortion leads to slightly lowering the energy level of the bonding 1*e* orbitals of the D_{2d} cluster. Although the D_{4h} structure **4** satisfies to the 10*e* electrons rule formulated for the stable bipyramidal structures of main-group element clusters,[11] the orbital interaction providing for the stabilization of structures of this type, namely, mixing in the antibonding combination of *p*-orbitals of apical centers and e_g orbitals of the basal cycle, is weakened in **4**, as compared to that in its carbon analogue **1**. This is due to a widened energy gap between these orbitals in **4** caused by a greater electronegativity of nitrogen, which also results in less diffuse *p*-orbitals and their smaller overlap with e_g orbitals of the basal cycle.

As congeneric 1,2-dicarbo-*closo*-hexaborane **3**, 1,2-diaza-*closo*-hexaborane **5** has a stable C_{2v} structure with a planar basal boron ring. It contains BN bonds of two types: short [1.550 (MP2), 1.536 (DFT) Å] and long [1.639 (MP2), 1.632 (DFT) Å]. This diazaborane is by 12.2 (MP2) and 13.5 kcal mol^{-1} (DFT) energy disfavoured as compared to 1,6-isomer **6**. Note that whereas for dicarboranes **1** and **3** and 1,2-diaza-*closo*-hexaborane **5** the results of MP2 calculations are consistent with those of the DFT method, for 1,6-diaza-*closo*-hexaborane **6** the bond lengths predicted by MP2 and DFT methods notably differ (~0.05 Å). The system **5** can be considered as a tight complex resulted from the interaction of dinitrogen with borane B_4H_4. In this context, a question arises whether N_2 and B_4H_4 can form a stable pre-reaction complex subsequently convertible to **5**. No such a complex has been found by DFT calculations: the interaction between N_2 and B_4H_4 was repulsive at any distances. This finding is consistent with the conclusion that DFT methods do not correctly describe long-range interactions.[13] At the same time, MP2 calculations predict the appearance of stable complex **7** stabilised by induced dipole–dipole interactions between its components. The complex is 1.1 kcal mol^{-1} stabilised relative to separated components (no account is done for the superposition error). Such a weak interaction does not affect the geometric parameters of N_2 and B_4H_4 moieties in complex **7** as compared to separated molecules. Complex **7** is 41.7 (at MP2 level) or 37.9 kcal mol^{-1} (at DFT level) less stable than 1,2-isomer **5**.



6, D_{2d} ($\lambda = 0$)

4, D_{4h} ($\lambda = 1$)

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

7, C_s ($\lambda = 0$)

T_d

$D_{\infty h}$

Figure 2 Geometry parameters of structures **5**–**7** and borane B_4H_4 and dinitrogen calculated by *ab initio* (MP2/6-311+G**) and DFT (B3LYP/6-311+G**) methods. Experimental data for B_4H_4 are given for B_4Cl_4[12] and for N_2 are taken from ref. 14. The bond lengths and angles are indicated in angström units and degrees, respectively.

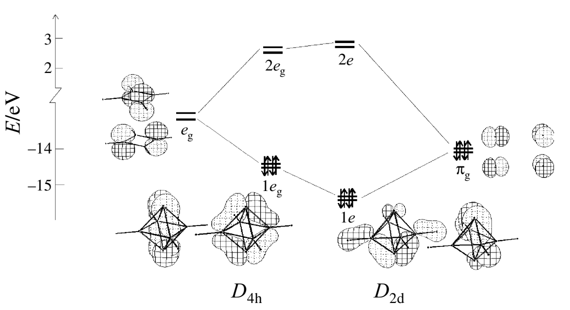


Figure 3 Diagram of formation of bonding molecular orbitals in **4** and **6**.

In conclusion, the MP2 and DFT calculations on hypothetical diaza-*closo*-boranes **5** and **6** indicate that these compounds, which are isoelectronic to dicarbo-*closo*-hexaboranes **1** and **3**, respectively, possess stable highly symmetric structures. Compound **6** was predicted to be susceptible to undergo the low-energy barrier B_4 ring puckering rearrangement **6a** $\rightleftarrows$ **4** $\rightleftarrows$ **6b**.

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