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A quantum-chemical study of carbon sandwich compounds

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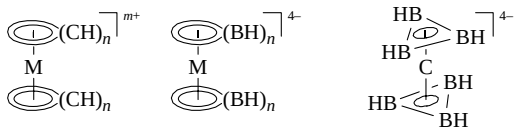
Ab initio **[MP2(fu)/6-311+G**] and DFT (B3LYP/6-311+G**) calculations predict highly symmetrical stable structures of sandwich compounds with a central carbon atom between three-, four- and five-membered $(BH)_n$ rings.**

Highly symmetrical sandwich structures **1** with alkali (M = Li, Na; $n = 5$)[1] or alkaline-earth metals (M = Mg, Ca, Ba; $n = 5$)[2,3] have been well studied, whereas the experimental or theoretical evidence of similar main-group element sandwich compounds is limited by X-ray determinations of D_{5d} structures of decamethylberyllocene[4] and decamethylsilicocene[5] **1** (M = Be, Si; $n = 5$, $m = 0$). Both of the structures are less energy favourable than isomeric η^1,η^5-half sandwich and η^2,η^5-bent sandwich forms of beryllocene[6] and decamethylsilicocene,[7] respectively, and the adoption of D_{5d} conformations is due to solely crystal packing effects. The less symmetrical bent sandwich structure is the principal stable conformation for the main group 14 elements (M = Si, Ge, Sn, Pb; $n = 5$, $m = 0$)[3] and the isoelectronic group 15 cations (M = P, As, Bi; $n = 5$, $m = 1$).[3,8] At the same time, no experimental or theoretical data are available on stable carbocenes **1** (M = C) or their organoelement analogues possessing sandwich structures with carbon, nitrogen or oxygen as the central element. Here, we report on the first computational finding of such compounds.



1 **2**, D_{nh} **3**, D_{3d}

The bonding schemes of main-group elements, in contrast to transition metals, are confined to the use of their valence *s*- and *p*-orbitals, which limits the number of bonding MOs, formed in main-group element sandwich compounds **1** by π- and π*-MOs of the basal rings and the valence orbitals of M, to four and, hence, the number of the 'interstitial' electrons in a stable main-group element sandwich structure to eight. According to these requirements (8 electron count rule[9,10]), one may expect that the simplest stable carbocenes (M = C) possessing a D_{nh} or D_{nd} structure must have large positive charges: $m = 2$ for the cyclopropenyl (**1**, $n = 3$), and $m = 4$ for the cyclobutadiene (**1**, $n = 4$) sandwiches. The validity of this expectation has been recently demonstrated by the B3LYP/6-311++G** calculations[11] of a silicon analogue, $C[(SiH)_3]_2^{2+}$, of carbocene **1** ($n = 3$, $m = 2$). We are exploring another way to satisfy the requirements of the 8e rule in carborane sandwich systems **2**, in which carbons in the basal rings of **1** are replaced by more electropositive boron atoms and the electron-deficient $(BH)_n$ rings leave more vacancies for electrons of the central carbon. The efficiency of this approach to the adjustment of main-group element polyhedral structures to the rigid requirements imposed by the electron count rules on the number of interstitial electrons in the closed shells has been recently demonstrated by computational findings of boron wheels containing hypercoordinated carbon and other main-group element centres.[9]

The orbital interaction diagram (Figure 1) shows the formation of the MOs of sandwich **2** ($n = 4$), and completely similar bonding schemes are characteristic of other members of this structural family. Filling all bonding MOs of the sandwiches $C[(BH)_n]_2$ with electrons forms a typical three-dimensional aromatic closed shell but gives rise to tetraanions **2** (M = C), which are, apparently, destabilised because of strong electrostatic repulsion between four extra charges even though delocalised

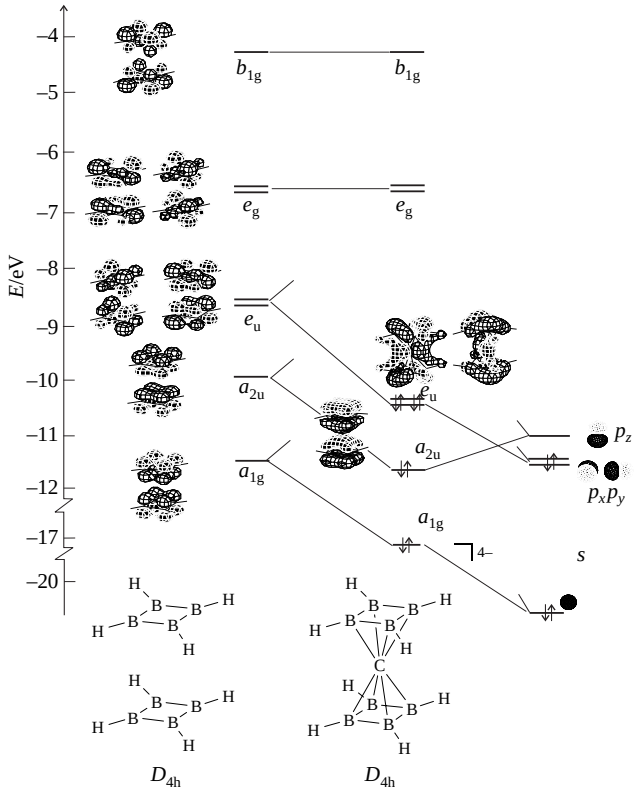
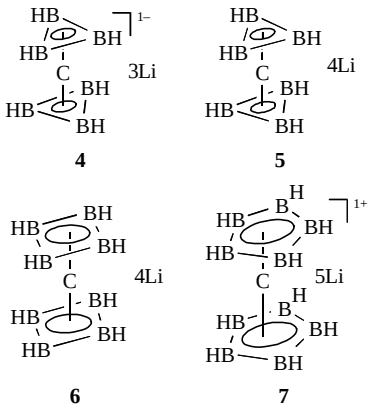


Figure 1 Correlation diagram of the interaction of carbon *s*- and *p*-valence orbitals with π- and π*-molecular orbitals of the four-membered boron ring in D_{4h} symmetry (taken in the same geometry as in **6**) in the sandwich structure of **6** with D_{4h} symmetry without lithium atoms. The shapes and energies of MOs are taken from EHMO calculations. The shapes and energy order of MOs levels in this figure fully coincided with those in the MP2 calculations of **6**.

over the ligands. Indeed, according to the B3LYP/6-311+G** calculations, the sandwich structure of **3** with the closed electron shell corresponds to a two-dimensional hill (two negative force constants) rather than to a minimum on the potential energy surfaces (PESs).

The experimentally observed main-group element sandwiches are stabilised as solvated and ate-type complexes with the environment of solvent molecules and counter ions, which provide for the delocalization of electric charge at the central ion.[1–3] In order to fully or partially neutralise the excessive negative charge in anions **2**, they may be surrounded by an appropriate number of counter ions, *e.g.*, Li^+. We found that, in the complexes with π-ligands, the role of such counter ions is not reduced to the electrostatic stabilization, but it also includes charge-transfer effects leading to the formation of a closed electron shell of the complex.[9] We performed an *ab initio* [MP2(fu)/6-311+G**] and DFT (B3LYP/6-311+G**) computational study of stable lithiocarboranes **4**–**7**, which exemplify a new structural type of sandwich compounds containing highly hypercoordinate central carbon atoms.

According to the calculations, the D_{nh} structures of ion clusters **4**, **6** and **7** correspond to energy minima ($\lambda = 0$; hereafter, λ designates the number of negative hessian eigenvalues) on



the respective PESs. No such a minimum has been located for the D_{nh} structure of **5**, instead of which three less symmetric isomeric structures, **5a**, **5b** and **5c**, corresponding to minima and transition state structure **5d**, corresponding to a saddle point, have been found for the $Li_4C[(BH)_3]_2$ cluster. The optimised geometries of these systems found by the calculations are shown in Figures 2 and 3. The energy characteristics are given in Table 1.

As can be seen in Figures 2 and 3, the B–B bond lengths in the $(BH)_n$ rings of all lithiocarboranes fall into the range of typical single bonds of this type,[12] whereas the C–B distances, which monotonically increase with the ring size, are longer than the normal C–B bonds (~1.6 Å).[12] Of special interest are the C–Li distances, which in the smallest clusters of **4** and **5** have the same value as the covalent C–Li bond in MeLi (1.959–2.10 Å).[13] The B–Li distances are also close to the sum of the B and Li covalent radii (2.03 Å). These structural characteristics indicate the importance of covalent factors contributing to the stabilization of the sandwich structures of lithiocarboranes. The isomeric structures of the D_{4h} and D_{5h} structures of **6** and **7** have not been investigated. In **6**, the C–Li and C–B distances are only 0.2–0.3 Å longer than the normal C–Li and C–B bonds. Therefore, the sandwich of **6** may be regarded as a compound with the most highly hypercoordinate (twelve-coordinate) carbon atom in an electrically neutral cluster system. The sandwich of **7** is perhaps not thermodynamically stable because of the very low first harmonic frequency (55 cm^{-1}) corresponding to shifting central carbon outward the central position. The central carbon atoms in the cage structures of **4**, **5a**, **5b**, **6** bear large Mulliken positive charges of +2.0e in **5a** and +1.0e in **6**, every lithium has a positive charge of about +0.3e in both compounds **5a** and **6**, all negative charge distributed equally on BH groups. This provides for the decrease in the effective size of the central atom and reduces steric strain caused by its encapsulation into the rigid lithioboron framework.

Table 1 *Ab initio* [MP2(fu)/6-311+G**] and DFT (B3LYP/6-311+G**) data for sandwich structures **4**–**7**.[a]

Structure	Method	E_{tot}	λ	ΔE	ΔE_{ZPE}	$\omega_1/i\omega_1$
4, D_{3h}	DFT	–213.462666	0	0	0	162 (*E′*)
	MP2	–212.761208	0	0	0	161 (*E′*)
5a, C_{3v}	DFT	–220.981309	0	0	0	131 (*E*)
	MP2	–220.239154	0	0	0	133 (*E*)
5b, C_{2v}	DFT	–220.955061	0	16.5	16.5	107
	MP2	–220.212249	0	16.9	16.7	90
5c, C_{2v}	DFT	–220.964621	0	10.5	10.8	14
C_s	MP2	–220.222586	0	10.4	10.8	107
5d, C_{2v}	DFT	–220.961523	1	12.4	12.9	i123
	MP2	–220.218048	1	13.2	13.7	i163
6, D_{4h}	DFT	–271.881973	0	0	0	140
	MP2	–271.008638	0	0	0	160
7, D_{5h}	DFT	–330.156580	0	0	0	55

[a] E_{tot} (in a.u.) and ΔE are the total and relative energies, respectively (1 a.u. = = 627.5095 kcal mol^{-1}); λ is the number of negative hessian eigenvalues; ZPE (in a.u.) is the harmonic zero-point correction; ΔE_{ZPE} (in kcal mol^{-1}) is the relative energy with account for harmonic zero-point corrections; $\omega_1/i\omega_1$ (in cm^{-1}) are the lowest or imaginary harmonic vibration frequencies.

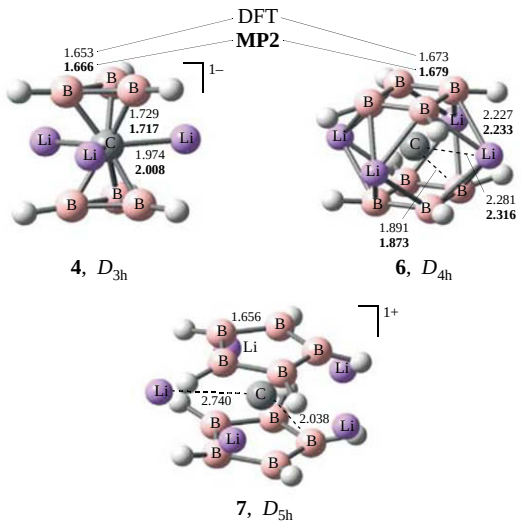


Figure 2 Geometry parameters of sandwich compounds **4**, **6** and **7** calculated by DFT (B3LYP/6-311+G**) and *ab initio* [MP2(full)/6-311+G**] methods. The bond lengths and angles are indicated in angstrom units and degrees, respectively.

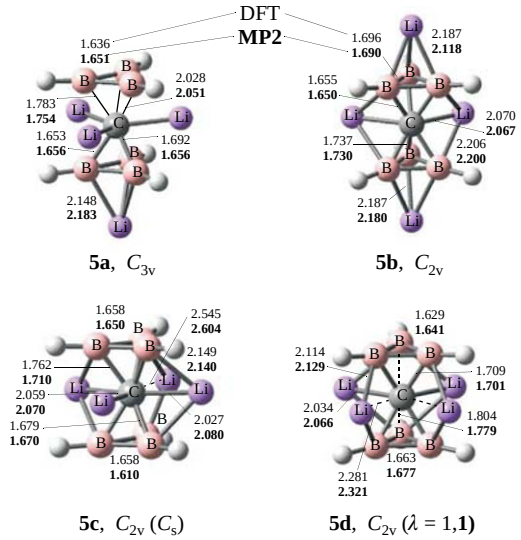


Figure 3 Geometry parameters of sandwich compounds **5a**–**c**, corresponding to the minima and **5d** corresponding to the saddle point calculated by DFT (B3LYP/6-311+G**) and *ab initio* [MP2(full)/6-311+G**] methods. The bond lengths and angles are indicated in angstrom units and degrees, respectively.

To evaluate the thermodynamic stability of electrically neutral sandwich clusters **5a** and **6** with respect to their decay to fragments, well studied both experimentally and by calculations for various borane and carborane cluster systems, we calculated the heats of the following reactions.

5a → $CLi_4 + 2B_3H_3$ – 239.9 (MP2) or 214.2 (DFT) kcal mol^{-1};

5a → $CLi_2 + B_6H_6{\cdot}Li_2$ – 110.5 (MP2) or 96.6 (DFT) kcal mol^{-1};

6 → $CLi_4 + 2B_4H_4$ – 210.5 (MP2) or 179.0 (DFT) kcal mol^{-1};

6 → $CLi_2 + B_8H_8{\cdot}Li_2$ – 86.5 (MP2) or 70.6 (DFT) kcal mol^{-1}.

The high endothermicity of these dissociation reactions points to the stability of the sandwich structures of the lithiocarboranes. Table 2 contains the energy characteristics of the components of these reactions.

In conclusion, the calculations demonstrated that clusters **4**–**7** represent a new structural type of stable sandwich compounds containing highly hypercoordinate carbon atoms centered between two hydroboron rings and closely surrounded by lithium counter ions.

The calculations were carried out using the Gaussian 98[14] and GAMESS[15] program packages with 'tight' optimization criteria (~10^{-5} a.u./bohr of maximum gradient).

Table 2 *Ab initio* [MP2(fu)/6-311+G**] and DFT (B3LYP/6-311+G**) data for structures **8**–**14** appeared in equations for the estimation of the thermodynamic stability of sandwiches **5** and **6**.

Structure	Method	E_{tot}	E_{ZPE}	ω_1
8, B_3H_3, C_s	DFT	–76.256444	–76.221140	306
	MP2	–76.000993	–75.965118	286
9, B_4H_4, T_d	DFT	–101.734835	–101.685327	609 (*E*)
	MP2	–101.409193	–101.358536	617 (*E*)
10, B_4H_6, D_{2d}	DFT	–102.982293	–102.911053	265
	MP2	–102.632716	–102.560046	113
11, $B_6H_6Li_2$, D_{3h}	DFT	–167.911383	–167.830557	123 (E_u)
	MP2	–167.351200	–167.269379	139 (E_u)
12, $B_8H_8Li_2$, C_2	DFT	–218.853519	–218.743788	204
	MP2	–218.158921	–218.047879	180
13, CLi_4, T_d	DFT	–68.127077	–68.118835	170 (T_2)
	MP2	–67.854861	–67.847275	136 (T_2)
14, CLi_2, C_{2v}	DFT	–52.916011	–52.911273	300
	MP2	–52.711822	–52.706693	288

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