Complexes Between Adamantane Analogues $B_4X_6\cdot X = \{\text{CH}_2, \text{NH}, \text{O}; \text{SiH}_2, \text{PH}, \text{S}\}$ - and Dihydrogen, $B_4X_6\cdot nH_2\ (n = 1–4)$

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Abstract: In this work, we study the interactions between adamantane-like structures $B_4X_6$ with $X = \{\text{CH}_2, \text{NH}, \text{O}; \text{SiH}_2, \text{PH}, \text{S}\}$ and dihydrogen molecules above the Boron atom, with ab initio methods based on perturbation theory (MP2/aug-cc-pVDZ). Molecular electrostatic potentials (MESP) for optimized $B_4X_6$ systems, optimized geometries, and binding energies are reported for all $B_4X_6\cdot nH_2\ (n = 1–4)$ complexes. All $B_4X_6\cdot nH_2\ (n = 1–4)$ complexes show attractive patterns, with $B_4O_6\cdot nH_2$ systems showing remarkable behavior with larger binding energies and smaller $B\cdot \cdot \cdot H_2$ distances as compared to the other structures with different $X$.

Keywords: hydrogen storage; boron; non covalent interactions; quantum chemistry

1. Introduction

Hydrogen storage is becoming an important issue regarding the energetic needs of our modern world [1,2]. Different methods are designed for hydrogen storage [3–5], including cryogenics, high pressures, and chemical compounds that reversibly release dihydrogen upon heating [6]. Among the different systems described in the literature, the metal organic frameworks (MOF) have been the most successful ones as hydrogen storage [7–11].

Related to the computational study in the chemical trapping of dihydrogen, non covalent interactions must be taken into account [12], given the relatively weak attracting force—mostly dispersive—derived from two neutral molecules, leading to general complexes with formula $Z\cdot nH_2$, where $Z$ is a neutral molecule and $n$ is the number of $H_2$ molecules attached to the $Z$ neutral system. A number of theoretical articles have been devoted to the interaction of dihydrogen with metallic systems [13–22].

The adamantane scaffold is widely used due to their steric [23,24], lipophilic [25] and rigid characteristics [26–30]. Derivatives that include heteroatoms have been synthesized, in addition to the well-known aza-AZADO and hexamethylenetetramine) [31–34] and oxo-derivatives (tetrodotoxin) [35]. Other derivatives involving C/As/O (arsenicin A) [36], C/N/S (tetramethylenedisulfotetramine) [37], P/S (phosphorus pentasulfide) [38], P/N [39], and C/P/S [40] have also been described.

For the study of dihydrogen complexes, we propose the use of adamantane analog systems where each CH tetrahedral vertex in adamantane is substituted by a Boron atom, and the remaining CH2 moieties is substituted by divalent X groups, with $X = \{\text{CH}_2, \text{NH}, \text{O}; \text{SiH}_2, \text{PH}, \text{S}\}$ thus leading to $B_4X_6$ tetrahedral molecules, as shown in Scheme 1.
As shown in Figure 1b, the large electronegativity of the three oxygen atoms bound to boron must have a stronger π-electron density (negative charge attractor) and surplus electron density (positive charge attractor) areas, respectively. Clearly, the electron density deficiency area above the Boron atoms in B₄X₆ could attract the electron density of the σ bond of the H₂ molecule. As shown in Figure 1b, the large electronegativity of the three oxygen atoms bound to boron must have a stronger effect on the attachment of H₂ molecules as a function of the π-hole values:

π-hole (au): 0.131 (O) >> 0.058 (NH) > 0.047 (SiH₂) > 0.034 (CH₂) > 0.025 (PH, S).
For O and SiH profiles. If we observe closely the curves from the zoom-in inset of Figure 3, the energy minima for CH profile zoom-in of the region 2.5 Å atom (of double-level, corresponding to energy minima for all cases. The cartesian coordinates for the B2.2. Geometries and Energies of B2020

Figure 1. (a) π-hole on the boron atom (a.u.) and (b) molecular electrostatic potential on the 0.001 au electron density isosurface for the B4O6 molecule. Red and blue colors indicate Molecular Electrostatic Potential (MESP) values < −0.015 and > +0.015 au, respectively. The location of the π-holes is indicated with a black dot.

2.2. Geometries and Energies of B4X6:nH2 Complexes (n = 1–4)

Figure 2 shows the optimized geometries of the isolated B4X6 systems at MP2/aug-cc-pVDZ level, corresponding to energy minima for all cases. The cartesian coordinates for the B4X6 optimized structures are gathered in Table S1, with the MP2 method and basis sets aug-cc-pVDZ and aug-cc-pVTZ, of double-ζ and triple-ζ quality respectively, including diffuse and polarization functions.

In the computations, we first obtain the energy profile of a frozen H2 molecule approaching this B atom (d distance) along the corresponding local C3 axis, as shown in Figure 3 for the B4X6:H2 complexes.

From Figure 3 we can clearly observe that all energy profiles are attractive for an H2 molecule down to 3 Å, and then three different curve patterns emerge: (i) for X = CH2, NH, PH, S] the energy profile becomes repulsive when d < 3 Å (ii) for X = O, the energy minimum well is flatter and becomes repulsive shifting down to values of d ~ 1.7–2.0 Å; and finally (iii) for X = SiH2 the energy profile remains attractive down to 1.25 Å. The inset plot of Figure 3—upper right corner—shows an energy profile zoom-in of the region 2.5 Å < d < 3.3 Å in order to see more clearly the positions of the energy minima regions, for a given X. Clearly, the [CH2, NH], and [PH, S] curves show similar energy minima regions: We turn from an attractive to a repulsive system at d ≤ 2.1 Å (CH2), 2.2 Å (NH), 2.48 Å (PH), and 2.55 Å (S). As stated above, a zoom-in of the energy profile for 2.5 Å ≤ d ≤ 3.3 Å is included in order to unveil the effect of approaching a H2 molecule to the B4X6 system where several curves have similar profiles. If we observe closely the curves from the zoom-in inset of Figure 3, the energy minima for CH2, NH, PH, and S are located as follows: d_min(CH2) ~ 2.73 Å, d_min(NH) ~ 2.77 Å, d_min(PH) ~ 3.05 Å, d_min(S) ~ 3.06 Å. For O and SiH2 there are no minima within this region since the curves are always attractive.

Figure 2. Cont.
Once we choose the $d$ which corresponds to the energy minimum in Figure 3, we relax the nuclear coordinates in the whole complexes hence determining the energy minimum structure for the $B_4X_6:nh_2$ complexes.
systems. Due to the different behavior of the B₄(SiH₂)₆ system versus an H₂ molecule—permanent attractive profile for d down to 1.25 Å—as compared to the other complexes—Figure 3—and the lack of an energy minimum geometry for the B₄(SiH₂)₆:H₂ complex—a geometry optimization shows a bond breaking in the H₂ molecule and a rearrangement of the B₄(SiH₂)₆ adamantane structure—this system will be analyzed further in another work. The optimized structures for all B₄X₆:nH₂ complexes (n = 1–4) are depicted in Figure S2, except for B₄O₆:nH₂ (n = 1–4), the latter shown in Figure 4. In Table 1 we gather the average B···H₂ and H···H distances in the optimized geometries of the different B₄X₆:nH₂ complexes, all corresponding to energy minima at the MP2/aug-cc-pVDZ level of theory.

**OXYGEN.**

![Figure 4. Optimized geometries for the B₄O₆:nH₂ complexes (n = 1–4) with MP2/aug-cc-pVDZ computations. All geometries correspond to energy minima.](image)

| Molecules | B···H₂ | H-H |
|-----------|--------|-----|
| X         | 1:1    | 1:2  | 1:3  | 1:4  | 1:1    | 1:2    | 1:3    | 1:4    |
| CH₂       | 2.737  | 2.740 | 2.745 | 2.750 | 0.755  | 0.755  | 0.755  | 0.754  |
| NH        | 2.777  | 2.727 | 2.705 | 2.727 | 0.755  | 0.755  | 0.755  | 0.755  |
| PH        | 3.080  | 3.045 | 3.046 | 3.049 | 0.755  | 0.755  | 0.755  | 0.755  |
| O         | 1.624  | 1.687 | 1.766 | 1.850 | 0.774  | 0.770  | 0.766  | 0.763  |
| S         | 3.071  | 3.070 | 3.068 | 3.068 | 0.755  | 0.755  | 0.755  | 0.755  |

As regards to the B···H₂ distances (d) in the B₄X₆:nH₂ complexes, as gathered in Table 1, three groups can be clearly distinguished: (i) X = [CH₂, NH] with d distances of ~ 2.7 Å (ii) X = [PH, S] with d distances of ~ 3.0 Å and (iii) X = O, with shorter d distances down to ~ 1.6 Å. The case for B₄O₆ is quite remarkable. As more H₂ molecules are attached to B₄O₆, the d(B···H₂) distances are elongated steadily up to d ~ 1.85 Å, and the H···H molecules remain slightly stretched down to Δ ~ 0.016 Å. This behavior for the B₄O₆ systems is unique as compared to the other systems since in the latter the attachment of the H₂ molecules is quite farther to the B atom and the H₂ molecules remain practically unaltered. There is no clear tendency—as compared to B₄O₆—for the d distances as more H₂ molecules are added for X = [CH₂, NH, PH, S], with tiny differences for the series 1 ≤ n ≤ 4.

Turning now to the H-H distances in the complexes, as shown in Table 1, in the energy minimum structures of the complexes, the H-H distances are very similar as compared to the isolated H₂ molecule, 0.755 Å. However, there is an exception for the oxygen complexes: when one H₂ molecule is attached to the B₄O₆ system, the H···H bond is elongated by Δ ~ 0.02 Å. As further H₂ molecules are attached to the B₄O₆ system, this elongated H-H bond is shortened consecutively by ~ 0.004 Å, down to 0.763 Å in each H-H molecule of the B₄O₆:4H₂ complex, though still 0.008 Å longer than in the isolated H-H molecule.
Finally, we show the computed binding energies of the H2 molecules for the different complexes B4X6:nH2 (n = 1–4), as seen in Table 2 and displayed in Figure 5, where we also include the CBS extrapolated values. As expected from the computed MESP and energy profiles in B4X6:H2 complexes, the larger binding energy for one H2 molecule corresponds to the B4O6 system, with ΔE ~ 29 kJ/mol (ΔECBS ~ 22 kJ/mol). For comparative purposes, the electronic binding energy of the water dimer is ΔE[(H2O)2] ~ 21 kJ/mol [51].

Table 2. Binding energies (kJ/mol) in optimized (B4X6:nH2) complexes, X = [CH2, NH, PH, O, S] with MP2/aug-cc-pVDZ computations and the MP2 complete basis set (CBS) limit obtained by extrapolation of the HF energies calculated at aug-cc-pVdz, with k = D, T and Q, following Equations (1)–(3). ΔE(1:n) for a given X corresponds to the binding energy of the complex B4X6:nH2.

| X   | ΔE(1:1) MP2 CBS | ΔE(1:2) MP2 CBS | ΔE(1:3) MP2 CBS | ΔE(1:4) MP2 CBS |
|-----|----------------|----------------|----------------|----------------|
| CH2 | -6.6 – 2.8     | -13.3 – 5.4    | -20.1 – 8.0    | -26.8 – 10.7   |
| NH  | -5.8 – 2.5     | -12.9 – 6.1    | -20.0 – 9.7    | -25.8 – 12.2   |
| PH  | -6.2 – 1.6     | -13.3 – 3.9    | -19.9 – 6.1    | -26.4 – 7.7    |
| O   | -28.6 – 22.1   | -49.5 – 37.6   | -65.5 – 49.1   | -79.2 – 58.9   |
| S   | -7.9 – 3.3     | -15.8 – 6.7    | -23.4 – 10.1   | -31.6 – 13.5   |

Figure 5. Binding energies of the B4X6:nH2 complexes (n = 1–4) as function of attached H2 molecules. MP2/aug-cc-pVDZ computations (solid lines) and extrapolated MP2/CBS limit (dashed lines).

The maximum binding energy for the complexes corresponds to B4O6:4H2 with a value of 79 kJ/mol (CBS extrapolation 60 kJ/mol). However, the binding energy of one H2 molecule attached to the other B4X6 systems is remarkably smaller in comparison, especially when the CBS extrapolation is added. The addition of more H2 molecules to the complexes shows practically additive relations for all X. As displayed in Figure 5, when extrapolated to the CBS limit, we can see several features regarding the binding energies in B4X6:nH2 (n = 1–4) complexes as compared to the MP2/aug-cc-pVDZ energies: (1) the CBS extrapolated binding energies are smaller for a given X and n (2) the (absolute value of the) slope of ΔE versus n (number of H2 molecules decreases for CBS extrapolated values (3) both CBS extrapolated and non-extrapolated binding energies follow a similar linear trend, except for X = O, the latter with clearly larger (CBS) binding energies, from 20 kJ/mol (n = 1) to 60 kJ/mol (n = 4).

We should notice that for X = O, though the CBS extrapolated slope is smaller than the non-extrapolated one, yet this slope is larger (in absolute value) as compared to the other Xs hence the...
peculiar behavior of $B_4O_6:nH_2$ as compared to complexes with different Xs. We should also emphasize the small differences (less than $\sim 5$ kJ/mol) between binding energies for different Xs for a given number $n$ of attached $H_2$ molecules, with the exception of $X = O$ with larger binding energies.

3. Computational Method

All geometries of the $B_4X_6$ systems and the corresponding $B_4X_6:nH_2$ ($n = 1-4$) complexes were optimized with second-order Møller-Plesset perturbation theory (MP2) [52] and a double-$\zeta$ basis set including polarization and diffuse functions [53], such as aug-cc-pVDZ. The interactions between $B_4X_6$ systems and $H_2$ molecules are clearly of noncovalent nature, weaker than conventional chemical bonds, given the closed-shell nature of the species involved and the lack of any further singlet coupling between unpaired electrons. We search for stable complexes $B_4X_6:nH_2$ and dispersive corrections are important given the neutral and spin-zero nature of the involved systems, hence the use of MP2 theory in computations. This theory improves on the Hartree–Fock (a mean-field—molecular-orbital—theory of electronic structure) method by adding electron correlation effects by means of Rayleigh–Schrödinger perturbation theory (RS–PT).

The quantum-chemical computations in this work were carried out at the MP2 level of theory with the scientific software Gaussian09 (Gaussian Inc, Wallingford, CT, USA) [54], and the molecular electrostatic potential (MESP) for the $B_4X_6$ systems was computed with the DAMQT program [55,56], also at the MP2 level of theory. Frequency computations were performed in order to check the energy minimum nature in all $B_4X_6$ systems and $B_4X_6:nH_2$ complexes ($n = 1-4$). The binding energies for the $B_4X_6:nH_2$ complexes are computed as $\Delta E = E(B_4X_6:nH_2) - E(B_4X_6) - n\cdot E(H_2)$, and reported in kJ/mol. Further geometry optimizations of all $B_4X_6$ complexes were carried out with the MP2/aug-cc-pVTZ computational model—with a triple-$\zeta$ basis set—in order to check the validity of the optimized geometries (see Supplementary Information). A single-point energy profile (MP2) versus $B⋯H_2$ distance in the complex $B_4(CH_2)_nH_2$ was computed using both basis sets: aug-cc-pVDZ and aug-cc-pVTZ (see Supplementary Information), double-$\zeta$ and triple-$\zeta$ respectively. As shown in Figure S1, the results show similar profiles along the local $\tilde{C}_3$ axis of rotation on the B atom and therefore we can confirm the validity of the MP2/aug-cc-pVDZ computational model for geometries and binding energies.

In order to assess the dependency of the binding energies on basis set incompleteness, we also computed the binding energies of all complexes in the extrapolated complete basis set (CBS) limit. The CBS energy has been calculated by extrapolation of the HF energies calculated at aug-cc-pVQZ, with $k = D, T$ and $Q$, and Equation (1) and the correlation part with Equation (2). The sum of the two components (HF and correlation) (Equation (3)) provides the MP2(CBS) energy.

$$E_{HF,k} = E_{HF,lim} + Ae^{-bk}$$  \hspace{1cm} (1)

with $k = 2, 3$ and $4$ for aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ basis sets, respectively [57,58].

$$E_{corr,k} = E_{corr,lim} + Ak^{-3}$$  \hspace{1cm} (2)

with $k = 3$ and $4$ for aug-cc-pVTZ and aug-cc-pVQZ basis sets, respectively [59]. Finally, we have

$$E_{MP2}(CBS) = E_{HF,lim} + E_{corr,lim}$$  \hspace{1cm} (3)

4. Conclusions

From the results obtained in this work we can conclude with the following points:

1) The MESP in the adamantane-like structures $B_4X_6$, with $X = \{CH_2, NH, O; SiH_2, PH, S\}$, show $\pi$-holes above the B atom with electron (density) attraction forces largest for $B_4O_6$ and lowest for $B_4(PH)_6$ and $B_4(SH)_6$.

2) The energy profiles of one $H_2$ molecule approaching along a $C_{3v}$ axes the B atom of $B_4X_6$ systems show attractive patterns up to certain values for all systems where it turns to repulsive below
~ 2.1 Å for B\(_4\)(CH\(_2\))\(_6\) and B\(_4\)(NH)\(_6\) and below ~ 2.5 Å for B\(_4\)(PH)\(_6\) and B\(_4\)S\(_6\), except for B\(_4\)(SiH)\(_6\) where the profile is always attractive with H\(_2\) bond breaking and cage rearrangement. For B\(_4\)O\(_6\), there is a flat energy minimum region within 1.7–2.0 Å.

3) The attraction strength for electron density towards boron atoms in B\(_4\)X\(_6\) is also shown in the energy profiles of the B\(_4\)X\(_6\):H\(_2\) complexes as a function of the B–H\(_2\) distance \(d\). The \(d\) distances in the energy minima structures coincide with the predicted distances from the energy profiles.

4) The binding energies of the B\(_4\)X\(_6\):H\(_2\) complexes — \(n = 1–4\) — follow a similar linear additive pattern (in magnitude and direction) for all X, except X = O, with larger binding energies. CBS extrapolation shows a significant decrease in the binding energies.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/1420-3049/25/5/1042/s1, Figure S1: Plot of \(\Delta E\) (kJ/mol) versus \(d\) (Å) for the complex \([B_4(CH_2)_6]:H_2\) for a range of distances 1.25 Å \(\leq d \leq 4.0\) Å and a step \(\Delta d = 0.25\) Å. MP2/aug-cc-pVDZ (red solid line) and MP2/aug-cc-pVTZ (green dashed line) computations. Figure S2: Optimized structures of the B\(_4\)X\(_6\):H\(_2\) complexes (\(n = 1–4\)), X = [CH\(_2\); NH; PH; S] with MP2/aug-cc-pVDZ computations. All geometries correspond to energy minima, Table S1: Cartesian coordinates (Å) of MP2/aug-cc-pVDZ (left column) and MP2/aug-cc-pVTZ (right column) optimized geometries corresponding to energy minima of the adamantane analogue systems B\(_4\)X\(_6\) with X = [CH\(_2\); SiH\(_2\); NH; PH; O; S]. All molecules have \(T_\text{d}\) symmetry except B\(_4\)X\(_6\) with X = [NH, PH] which have C\(_1\) symmetry.

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