The story of the $\text{B}_4\text{H}_4$ molecule told again

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ABSTRACT

Employing ab initio multireference and coupled-cluster methods along with correlation consistent basis sets we have studied three geometrical isomers of the (hydro)borane $\text{B}_4\text{H}_4$ molecule, namely, the highly symmetric geometrical configuration $\text{T}_d$ (regular tetrahedron) and two isomers of planar $\text{Cs}$ geometries tagged $\text{T}_d(\text{II})$, $\text{Cs}(\text{I})$, and $\text{Cs}(\text{III})$, respectively. Mostly for reasons of consistency the species $\text{BH}(\text{X}^1\Sigma^+)$, $\text{a}^2\Pi$, $\text{BH}_2(\text{X}^1\Sigma^+)$, and $\text{H}_2\text{BBH}_2(\text{D}_{\text{sa}}, \text{D}_{\text{ad}})$ have also been examined at the same level of theory. It was reconfirmed that the global minimum of $\text{B}_4\text{H}_4$ is the planar $\text{Cs}(\text{I})$ lower by 6 kcal/mol than $\text{T}_d(\text{II})$, while $\text{Cs}(\text{III})$ is 13 kcal/mol above $\text{Cs}(\text{I})$. With an emphasis on the concept of chemical bond particularly for the three $\text{B}_4\text{H}_4$ isomers I, II, and III, we offer quantitative geometric and energetic results for all species studied.

Although the focus of the present study is the elusive deltahedral $\text{B}_4\text{H}_4$ molecule (regular tetrahedron), it is more than useful to emphasize that the incredible variety of boranes (“hydroborons”) emanates from the motif $\text{BH}(\text{a}^2\Pi)$, in direct analogy to the hydrocarbons related to the $^3\Sigma^-$ term of carbon, or equivalently to the $^4\Sigma^-$ state of CH about 17 kcal/mol above its $^1\text{X}^1\Sigma^+$ state [6,8].

Twenty-three years ago we published a theoretical ab initio study on the $\text{B}_4\text{H}_4$ system [9]. Till then the ground state of $\text{B}_4\text{H}_4$ was thought to be of $\text{T}_d (\text{X}^1\text{A}_1)$ symmetry [9] and references therein. Indeed the $\text{T}_d$ configuration is well bound with respect to the four $\text{BH}(\text{a}^2\Pi$ or $\text{X}^1\Sigma^+)$ moieties and with no imaginary frequencies [9]. Yet, despite all efforts $\text{B}_4\text{H}_4$ has never been experimentally observed till now, whereas the tetrahedral derivatives $\text{B}_4\text{Cl}_4$, $\text{B}_4\text{Br}_4$, and $\text{B}_4(\text{Me}_3\text{C})_4$ are well established, Refs. [10–13]. To our surprise it was found that the ground state of $\text{B}_4\text{H}_4$ was not of $\text{T}_d$ configuration but rather of $\text{Cs}$-planar symmetry ($^1\text{A}^+$), about 6 kcal/mol lower than the $\text{T}_d$ symmetry. Notice that the zero point energy (ZPE) had not been taken into account.

In 2011 Olson and Boldyrev through ab initio calculations confirmed beyond doubt that the ground state of $\text{B}_4\text{H}_4$ is a planar low symmetry Cs structure [14], the same one as in Ref. [9], confirmed as well by Böyükata et al. albeit at the DFT/B3LYP level [15]. It is surprising, however, that quantitative theoretical results on $\text{T}_d$ $\text{B}_4\text{H}_4$ (a “black sheep” molecule according to Ref. [14]) and $\text{B}_4\text{H}_4-\text{C}_4$ (planar) are lacking from the literature. It was then decided to revisit the very interesting system $\text{B}_4\text{H}_4$ with the purpose of obtaining quantitative numerical results and to provide some new insights. To this end we performed multireference (MRCI) and single reference coupled-cluster (RCCSD(T)) calculations.

1. Introduction

Despite its biological ‘absence’, boron is one of the most interesting and versatile elements of the periodic table [1]. Its ability to form boron hydrides, neutral or negatively charged, that is compounds of the general form $\text{B}_n\text{H}_m$ or $\text{B}_n\text{H}^-_m$ is indeed staggering [2,3]. As a matter of fact the study of $\text{B}_4\text{H}_4$ or $\text{B}_4\text{H}_4^-$ (boranes) opened a whole new field of chemistry whereas the bonding of boranes is still a challenge; see Ref. [2] and references therein. The comparison with the corresponding carbon hydrides $\text{C}_n\text{H}_m$ (hydrocarbons) is inevitable at this point. Recall that the ground state of carbon is $\text{3P}(2s^22p^2)$ with a third excited state of symmetry $^3\text{S}(2s^22p^3)$, 4.183 eV (= 96.5 kcal/mol) higher [4], the $^3\text{S}$ term being responsible for the immense field of organic chemistry, of course with the hydrocarbons included. It is interesting here to think that even CH$_4$ is a “hypervalent” molecule correlating directly to the $^3\text{S}$ carbon term [5].

The boron atom has a $^2\Pi(2s^22p^1)$ ground state with the first excited state $^4\text{P}$ 3.571 eV (= 82.3 kcal/mol) higher [4]. Now, the boron monohydride, $\text{BH}(\text{X}^1\Sigma^+)$, is isoelectronic to carbon with a first excited state of $^2\Pi$ symmetry located 10,588 cm$^{-1}$ (30.3 kcal/mol) above its $\text{X}^1\Sigma^+$ state [6,7]. Take into account that there is no experimental $^2\Pi-\text{X}^1\Sigma^+$ energy distance, the value given above is a very accurate ab initio result [7]. We would like as well to point out that the $^2\Pi$ state of BH is analogous to the $^3\text{P}$ of carbon, the symmetry of the former, however, being cylindrical instead of spherical. The valence bond-Lewis (vbl) diagram of BH ($^2\Pi$) shown below explains pictorially what is meant; see also Ref. [7] (see Scheme 1).
employing correlation consistent basis sets. The following two Sections refer to some insights and computational details, respectively. Section 4 concerns results and discussion and we close with a summary in Section 5.

2. Insights

\( \text{B}_4\text{H}_4 \) in a \( \text{T}_d \)-geometrical configuration is the simplest closo-borane, highly symmetric and aesthetically appealing. Recall that a regular tetrahedron, symmetry group \( \text{T}_d \), is composed of four equilateral triangles and has six edges of equal length, the simplest of the five (convex) Platonic polyhedrons. In our case it means six \( \text{B-B} \) bonds of equal length and four \( \text{B-H} \) bonds of equal length, each \( \text{H} \) atom attached to a \( \text{B} \) apex. Chemically, however, there is a snag: the \( \text{BH} \) moiety in its \( \alpha^3\Pi \) state can form two single bona fide \( \frac{1}{\sqrt{2}}(\alpha^2 \beta - \beta \alpha) \) \( \text{B-B} \) bonds, not three. The high symmetry of the \( \text{T}_d \) configuration comes to rescue, however, with the diagrams below clarifying our position.

In Fig. 1 dotted lines between pairs of \( \text{B} \) atoms in the structures (a), (b), and (c) represent absence of bonding, while dashed lines in the structure (d), a more realistic representation of \( \text{B}_4\text{H}_4\text{-T}_d \), shows partial bonding (see below). We have three “resonance configurations” (a), (b), and (c) by symmetry, or adhering to the divalency of BH(\( \alpha^3\Pi \)) motif no more than one dotted line should originate from each \( \text{B} \) atom, that is \( \left( \frac{6}{2} \right) - 4 \times \left( \frac{3}{2} \right) = 15 - 4 \times 3 = 3 \) allowed “resonances”.

Clearly \( \text{B}_4\text{H}_4\text{-T}_d \) structure (d) of Fig. 1, is electron deficient. Exempting the four well localized \( \text{B-H} \) covalent bonds, 8 electrons are shared among six \( \text{B-B} \) (partial) bonds, meaning in turn that each dashed line in Fig. 1(d) has a “bond index” of \( \frac{2}{3} \) (= \( 8 \text{ e}^{-} \div 2 \times 6 \text{ e}^{-} \)) instead of 1, or that every \( \text{B-B} \) interaction is represented by \( 2 \times \frac{2}{3} = \frac{4}{3} \) electrons instead of 2. Therefore it is safe to predict that \( \text{B-B} \) bonds in \( \text{B}_4\text{H}_4\text{-T}_d \) would be significantly longer and weaker as compared to a single covalent \( \text{B-B} \) bond; and this is exactly what our calculations show (see below). Of course the voracity of \( \text{B}_4\text{H}_4\text{-T}_d \) for electrons [14] and in fact the bewildering variety of boranes [2], traces its ancestry to the first excited state of BH, \( \alpha^3\Pi \). The \( \text{B}_4\text{H}_4\text{-Cs} \) planar configuration (global minimum) and another one firstly mentioned in Ref. [14] will be discussed in Section 4.

3. Computational details

For both \( \text{B} \) and \( \text{H} \) the cc-pVnZ, \( n = \text{T}, \text{Q}, 5, (= n \nu) \) correlation consistent basis sets of Dunning were used through the whole study [16]. The most extensive basis set employed (5\( \nu \)) is \( \{14s8p4d3f2g1h/8s4p3d2f1g\text{/h}\} \) generally contracted to \( \{6s5p4d3f2g1h/5s4p3d2f1g\text{/h}\} \) of order 91 and 55 for \( \text{B} \) and \( \text{H} \) atoms, respectively. Two calculational approaches were followed, the variational internally contracted MRCl (= CASSCF + single + double replacements), and the single reference RCCSD(T) (= restricted coupled-cluster single + double + perturbative connected triples) method [17–19]. The MRCl approach was used only to the highly symmetric \( \text{B}_4\text{H}_4\text{-T}_d \) structure, whereas the coupled-cluster methodology was employed for both \( \text{B}_4\text{H}_4 \) geometries, \( \text{T}_d \) and \( \text{Cs} \)-planar (but see below). The reference CASSCF space was...
constructed by allotting the 16 valence electrons to 12 orbitals resulting to a CASSCF wavefunction of 18,153 configuration functions (CF). The ensuing configuration interaction uncontracted MRCl expansion contains $6 \times 10^{6}$ CFs reduced by three orders of magnitude after the internal contraction, namely $17 \times 10^{4}$ CFs. The 18 normal modes of $\text{B}_4\text{H}_4$ ($\omega_i$) were determined as usual by diagonalizing the corresponding Hessian matrix. The size nonextensivity error of the MRCl calculations was ameliorated by applying the Davidson correction (+Q) [20].

Henceforth, and for reasons of easy comparison and clarity, we adopt the symbolism of Olson and Boldyrev [14]: $\text{B}_4\text{H}_4\text{-C}_1$ (I), $\text{B}_4\text{H}_4\text{-T}_d$ (II), $\text{B}_4\text{H}_4\text{-C}_s$ (III), refer to the global minimum ($X^1A^1$) [9], to the tetrahedral $T_d$ configuration ($^1A_1$), and to a new isomer of planar-$C_4$ ($^1A'$) geometry higher in energy than $\text{B}_4\text{H}_4\text{-T}_d$ (II) discovered by the authors of Ref. [14], respectively. All three structures were optimized at the RCCSD(T)/T$_0$ level. During all calculations and for all chemical species examined the core 1s$^2$-boron electrons were kept doubly occupied.

Finally the basis set superposition error (BSSE) for the $\text{B}_4\text{H}_4\text{-T}_d$ (II) isomer is about 1 kcal/mol at the $Q_0$ level, thus was not taken into consideration any further.

All computations were performed by the MOLPRO2015.1 code [21].

### 4. Results and discussion

Table 1 lists total energy, geometries, and dissociation energies ($D_e$ and $D_0$) of $\text{B}_4\text{H}_4\text{-T}_d$ (II) with respect to the ground ($X^1\Sigma^+$) and first excited state ($a^3\Pi$), of four BH fragments, $D_{1/0}^{a^3\Pi}$ and $D_{1/0}^{a^3\Pi}$, respectively, at the MRCl/$Q_0$ and RCCSD(T)/$Q_0$, $S_0$ levels of theory. The MRCl (or MRCl + Q) $D_{1/0}^{a^3\Pi}$ value has been obtained by pulling in $T_d$ fashion to infinity (20 bohr) the four BH units, maintaining the B–H bond distances fixed at 1.185 Å. The potential energy profile (PEP) of this process is shown in Fig. 2. The hump of 13.9 kcal/mol with respect to the asymptote (MRCl + Q,$Q_0$) on the PEP at 2.2 Å is a result of an avoided crossing between the repulsive (not shown) PEP $4 \times BH(X^1\Sigma^+)$ to $\text{B}_4\text{H}_4\text{-T}_d$ (II) and the strongly attractive (not shown) $4 \times BH(a^3\Pi)$ to $\text{B}_4\text{H}_4\text{-T}_d$ (II) PEPs. Clearly the four BH units within the $\text{B}_4\text{H}_4\text{-T}_d$ (II) species are in the $a^3\Pi$ state, meaning that diabatically the $\text{B}_4\text{H}_4\text{-T}_d$ (II) correlates to four BH($a^3\Pi$) monomers coupled into a singlet ($^1A_1$), thus (internal bond strength) $D_{1/0}^{a^3\Pi} = D_{1/0}^{a^3\Pi} + 4 \times D_{1/0}^{a^3\Pi}$ = 443.9 kcal/mol, where $T_d = 10.581$ cm$^{-1}$ = (30.25 kcal/mol) [7].

![Fig. 2. MRCl+$Q_0$ potential energy profile of tetrahedral $\text{B}_4\text{H}_4$ with respect to four BH units, $G$ is the center of mass.](image)

### Table 1

<table>
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<th>Method</th>
<th>$\tilde{E}$</th>
<th>$r_e$(B-H)</th>
<th>$r_e$(B-B)</th>
<th>$D_{1/0}^{a^3\Pi}$</th>
<th>$D_{1/0}^{X^1\Sigma^+}$</th>
<th>$D_{1/0}^{a^3\Pi}$</th>
<th>$D_{1/0}^{X^1\Sigma^+}$</th>
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<td>MRCl/$Q_0$</td>
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<td>1.685</td>
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<td>443.9</td>
<td>305.2</td>
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<td>–</td>
<td>–</td>
<td>331.6</td>
<td>452.6</td>
<td>313.9</td>
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<td>456.0</td>
<td>316.1</td>
<td>439.8</td>
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<tr>
<td>RCCSD(T)/$S_0$</td>
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<td>–</td>
<td>–</td>
<td>335.4</td>
<td>457.7</td>
<td>317.7</td>
<td>441.5</td>
</tr>
</tbody>
</table>

$^a$ With respect to the $X^1\Sigma^+$ state of BH.

$^b$ With respect to the $a^3\Pi$ state of BH.

$^c$ $D_0 = D_e - ZPE$; see text.

$^d$ +Q refers to the Davidson correction.

$^e$ Geometry at the RCCSD(T)/T$_0$ level.

$^f$ $D_{1/0}^{\Sigma^+}$ is about 1 kcal/mol at the Q$_0$ level.

$^g$ Corresponding $\omega_0$ values are calculated through the relation $\omega_0 = \sum_{\text{CF}} d_i (\text{B}_4\text{H}_4 - T_d)_i$.

$^h$ +Q, respectively, at the MRCl/$Q_0$ and RCCSD(T)/$Q_0$, $S_0$ levels of theory.
Table 3 gives the total energy and geometry of the $\bar{X}A_1$ state of the BH$_2$ radical at the RCCSD(T)/Q$_c$ level including experimental results [22]. Small discrepancies from experiment, $\delta E = \pm 0.01$ Å and $\delta (\angle \text{HHB}) = \pm 2^\circ$ are rather due to core effects not included to our calculations (vide infra). The vbl. diagram of the $\bar{X}A_1$ state of BH$_2$ (Scheme 2) is predicting clearly a bent structure of C$_{2v}$ symmetry and the possibility to form the H$_2$B=BH$_2$ molecule through a single B–B bond. Indeed, the H$_2$B=BH$_2$ molecule has been observed in 1989 [23]. An ethylene-like D$_{2h}$ configuration and a D$_{2d}$ staggered one, both completely optimized at the RCCSD(T)/Q$_c$ level, are shown in Fig. 3.

The most stable configuration is the staggered D$_{2d}$ with an astonishing large barrier-to-rotation of 12.5 kcal/mol. Our results are in agreement with previous calculations; for details see Ref. [23] and references therein. The unexpected and capricious behavior of H$_2$B=BH$_2$ can be understood by referring to the vbl diagram of the BH$_2(\bar{X}A_1)$ electron deficient radical. Notice the significant B–B bond shortening by 0.10 Å of D$_{2d}$ as compared to the D$_{2h}$ ethylene-like configuration.

Now, the binding energy of H$_2$B=BH$_2$ with respect to two BH$_2(\bar{X}A_1)$ radicals at the RCCSD(T)/Q$_c$ level (see also Table 3 and Fig. 3) is $D^e_B$ (B–B) = 108.6 kcal/mol, a remarkably strong single bond equal to $D^e_B(\bar{X}^1\Sigma^+)$ = 109.5 kcal/mol of H$_2$ [6]. As was already mentioned this rather surprising result was confirmed recently by Olson and Boldyrev who used an “unbiased search for the global minimum of B$_4$H$_4$ and the BH$_4$" [14]. It was found at the highest level of theory, CCSD(T)/CBS limit, that the B$_4$H$_4$-C$_3$ (I) structure is 6.6 kcal/mol lower than B$_4$H$_4$-Td (II); the corresponding value found in Ref. [9] lies between 5 and 6 kcal/mol. Unfortunately, besides energy differences among the three isomers of B$_4$H$_4$, I, II, and III, numerical details like geometries or bond energies are not given in Ref. [14].

In the present work it was reconfirmed that the global minimum of B$_4$H$_4$ has a C$_3$ (I) planar configuration as shown in Fig. 4. The equilibrium geometrical parameters displayed in Table 4 were obtained by complete optimization at the RCCSD(T)/T$_{cc}$ level, using as an initial guess the geometry of Ref. [9]. Total energies and energy differences $\Delta E_{\text{full}} = E_{\text{full}}(\text{II}) - E_{\text{full}}(\text{I})$ are given in Table 5. At the RCCSD(T)/T$_{cc}$/RCCSD(T)/T$_{cc}$ level $\Delta E_{\text{full}}$ is 5.9 kcal/mol in good agreement with the results of Ref. [14] and those of Ref. [9]. Note that the ZPE being the same for both structures, C$_3$ (I) and T$_d$ (II), Table 2, has a null effect to the energy difference $\Delta E_{\text{full}}$ given above.

At the Hartree-Fock/T$_{cc}$ level the permanent electric dipole moment of the global minimum B$_4$H$_4$-C$_3$ (I) is $\mu_{\text{HF}} = (\mu^2 + \mu^2_\perp)^{1/2} = [(-0.456)^2 + (1.600)^2]^{1/2} = 1.63$ D, obtained as an expectation value. The corresponding finite field value at the RCCSD(T)/T$_{cc}$ level is $\mu_{\text{FF}} = [(-0.447)^2 + (1.375)^2]^{1/2} = 1.45$ D; field strength 5 $\times$ 10$^{-8}$ a.u.

We have also examined the structure B$_4$H$_4$-C$_3$ (III) discovered by Olson and Boldyrev [14] and shown in Fig. 4. Although B$_4$H$_4$-C$_3$ (I) and B$_4$H$_4$-C$_3$ (III) are deceptively similar they are not the same. Fig. 4 clearly depicts the difference. Table 6 lists equilibrium bond lengths and angles at the RCCSD(T)/T$_{cc}$ level, while Table 5 gives total energies and energy differences $\Delta E$ at the RCCSD(T)/T$_{cc}$, 5$^c$ levels. Observe that at the RCCSD(T)/5$^c$/RCCSD(T)/T$_{cc}$ level the B$_4$H$_4$-C$_3$ (III) structure is located 11.5 kcal/mol above the global minimum, becoming 12.8 kcal/mol at the quintuple basis set as contrasted to 7.0 kcal/mol of Olson and Boldyrev [14]. Take into consideration that at the RCCSD(T)/T$_{cc}$/ the ZPE of B$_4$H$_4$-C$_3$ (III) isomer is 31.2 kcal/mol identical to the ZPEs of Cs (I) and Td (II), thereby its effect to energy differences $\Delta E_{\text{full}}$ or $\Delta E_{\text{full}}$ is none. The dipole moment of the B$_4$H$_4$-C$_3$ (III) isomer is

$$\mu_{\text{HF}} = (\mu^2 + \mu^2_\perp)^{1/2} = [(1.585)^2 + (0.213)^2]^{1/2} = 1.60$$ D, and

$$\mu_{\text{FF}} = [(1.569)^2 + (0.153)^2]^{1/2} = 1.58$$ D.
A last observation: despite the fact that both the “unicorn” molecule of organic chemistry C₄H₄ (tetrahedrane) and B₄H₄-Td (II) are regular tetrahedrons and both are composed of four excited state units CH(a^3Σ⁺) and BH(a^3Π), respectively, the reason for their non-observation (or very short lifetimes) is entirely different. For one thing B₄H₄-Td (II) is strongly electron deficient by 4 electrons, but this is not the case for C₄H₄. Nevertheless their Platonic aesthetic attraction remains the same over the years galvanizing the minds of researchers. Needless to say that aside from the BH diatomic species, the rest of the molecules examined in the present work are hypervalent: The B atom (or the BH motif) in BH₂(X²A₁), H₂BBH₂ (B₂ or D₂h), in the three isomers of B₄H₄ (I, II, III) and of course in the vast variety of boranes BₓHy, is in its first excited ²P (or a³Π) state. For details see Ref. [5] and references therein.

5. Conclusions

From the vast field of boranes BₓHy we have investigated by ab initio MRCI and RCCSD(T) methods three isomers of B₄H₄, namely B₄H₄-C₃ (I) [planar, ¹A₁], B₄H₄-Td (II) [regular tetrahedron, ¹A₁], and B₄H₄-C₃ (III) [planar, ¹A₁]. The geometrical arrangements of the two planar Cs species (I and III) are shown in Fig. 4. For reasons of necessity and/or completeness we have also examined the species BH(X¹Σ⁺), a²Π), BH₂(X²A₁), and the two conformers of H₂BBH₂ (D₂h, D₂d). Our findings are summarized below.

(i) It has been reconfirmed that the global minimum of B₄H₄ has a C₃ (I) geometry (Fig. 4). This is indeed significant as to the conceptual development and meaning of the chemical bond.

(ii) Our results leave no doubt that isomer Td (II) (regular tetrahedron) is located 6 kcal/mol above Cs (I) and certainly no more than 6.5 kcal/mol. B₄H₄-Td (II) is a singlet (¹A₁) energetically stable geometrical arrangement in the B₄H₄ potential energy hypersurface, more or less of the same binding energy with respect to four BH(a³Π) units as the Cs (I), yet never observed. It has six B–B equivalent (by symmetry) bonds but of “order” 2/3 instead of 1 and certainly is strongly electron deficient. This is perhaps the reason of its “chemical instability” that prohibits its observation. Alternatively, if the energy barrier between Td (II) and Cs (I) is low, the former can “slip” to the latter which in turn can polymerize due to its 2 – e⁻πₓ system (see iii).

(iii) The binding mode of B₄H₄-C₃ (I) can be rationalized through a vbl. diagram diagram shown on p. 472 of Ref. [5] composed of four BH(a³Π) moieties, indicating a 2 – e⁻πₓ system carried by the B₂ and B₃ atoms bridged by H₂; see Fig. 4.

Fig. 4. Geometric configurations of the Cs structures B₄H₄-Cs (I) (global minimum) and of B₄H₄-Cs (III).
(iv) The isomer $\text{B}_4\text{H}_4$-$\text{Cs}$ (III), Fig. 4, is located about 13 kcal/mol above the global minimum $\text{Cs}$ (I). It is a stable local minimum on the $\text{B}_4\text{H}_4$ hypersurface and of course never observed experimentally.

(v) The normal modes of $\text{B}_4\text{H}_4$-$\text{Cs}$ (I) and $\text{B}_4\text{H}_4$-$\text{Td}$ (II) as well as their electrical dipole moments have been reported for the first time, whereas zero point energies are identical for all three $\text{B}_4\text{H}_4$ isomers, ZPE = 31.2 kcal/mol.

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