



The story of the B₄H₄ 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 B₄H₄ molecule, namely, the highly symmetric geometrical configuration T_d (regular tetrahedron) and two isomers of planar C_s geometries tagged T_d(II), C_s(I), and C_s(III), respectively. Mostly for reasons of consistency the species BH(X¹Σ⁺, a³Π), BH₂(X̃²A₁), and H₂BBH₂(D_{2h}, D_{2d}) have also been examined at the same level of theory. It was reconfirmed that the global minimum of B₄H₄ is the planar C_s(I) *lower* by 6 kcal/mol than T_d(II), while C_s(III) is 13 kcal/mol *above* C_s(I). With an emphasis on the concept of chemical bond particularly for the three B₄H₄ isomers I, II, and III, we offer quantitative geometric and energetic results for all species studied.

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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 B_xH_y or B_xH_yⁿ⁻ is indeed staggering [2,3]. As a matter of fact the study of B_xH_y or B_xH_yⁿ⁻ (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 C_xH_y (hydrocarbons) is inevitable at this point. Recall that the ground state of carbon is ³P(2s²2p²) with a third excited state of symmetry ⁵S(2s¹2p³) 4.183 eV (=96.5 kcal/mol) higher [4], the ⁵S term being responsible for the immense field of organic chemistry, of course with the hydrocarbons included. It is interesting here to think that even CH₄ is a “hypervalent” molecule correlating directly to the ⁵S carbon term [5].

The boron atom has a ²P(2s²2p¹) ground state with the first excited state ⁴P 3.571 eV (= 82.3 kcal/mol) higher [4]. Now, the boron monohydride, BH(X¹Σ⁺), is isoelectronic to carbon with a first excited state of a³Π symmetry located 10,588 cm⁻¹ (30.3 kcal/mol) above its X state [6,7]. Take into account that there is no experimental a³Π-X¹Σ⁺ energy distance, the value given above is a very accurate ab initio result [7]. We would like as well to point out that the a³Π state of BH is analogous to the ³P of carbon, the symmetry of the former, however, being cylindrical instead of spherical. The valence bond-Lewis (vbl) diagram of BH (a³Π) shown below explains pictorially what is meant; see also Ref. [7] (see Scheme 1).

Although the focus of the present study is the elusive deltahe-dral B₄H₄ molecule (regular tetrahedron), it is more than useful to emphasize that the incredible variety of boranes (“hydroborons”) emanates from the motif BH(a³Π), in direct analogy to the hydrocarbons related to the ⁵S term of carbon, or equivalently to the ⁴Σ⁻ state of CH about 17 kcal/mol above its X²Π state [6,8].

Twenty-three years ago we published a theoretical ab initio study on the B₄H₄ system [9]. Till then the ground state of B₄H₄ was thought to be of T_d (X̃¹A₁) symmetry ([9] and references therein). Indeed the T_d configuration is well bound with respect to the four BH (a³Π or X¹Σ⁺) moieties and with no imaginary frequencies [9]. Yet, despite all efforts B₄H₄ has never been experimentally observed till now, whereas the tetrahedral derivatives B₄Cl₄, B₄Br₄, and B₄(Me₃C)₄ are well established, Refs. [10–13]. To our surprise it was found that the ground state of B₄H₄ was not of T_d configuration but rather of C_s-planar symmetry (¹A'), about 6 kcal/mol *lower* than the T_d symmetry. Notice that the zero point energy (ZPE) had not been taken into account.

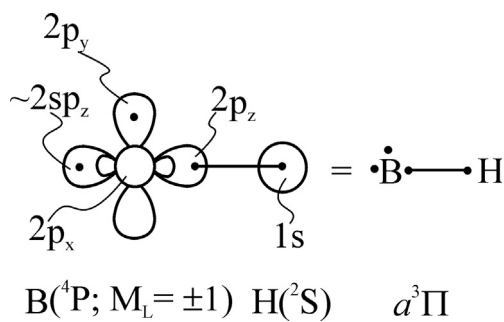
In 2011 Olson and Boldyrev through ab initio calculations confirmed beyond doubt that the ground state of B₄H₄ is a planar low symmetry C_s structure [14], the same one as in Ref. [9], confirmed as well by Böyükata et al. albeit at the DFT/B3LYP level [15]. It is surprising, however, that quantitative theoretical results on T_d B₄H₄ (a “black sheep” molecule according to Ref. [14]) and B₄H₄-C_s (planar) are lacking from the literature. It was then decided to revisit the very interesting system B₄H₄ 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

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

B_4H_4 in a T_d -geometrical configuration is the simplest closo-borane, highly symmetric and aesthetically appealing. Recall that a regular tetrahedron, symmetry group 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 B-B bonds of equal length and four B-H bonds of equal length, each H atom attached to a B apex. Chemically, however, there is a snag: the BH moiety in its $a^3\Pi$ state can form two single bona fide $1/\sqrt{2}(\alpha\beta - \beta\alpha)$ B-B bonds, not three. The high symmetry of the T_d configuration comes to rescue, however, with the diagrams below clarifying our position.

In Fig. 1 dotted lines between pairs of 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 $B_4H_4-T_d$, shows



partial bonding (see below). We have three “resonance configurations” (a), (b), and (c) by symmetry, or adhering to the divalency of BH($a^3\Pi$) motif no more than one dotted line should originate from each B atom, that is $\binom{6}{2} - 4 \times \binom{3}{2} = 15 - 4 \times 3 = 3$ allowed “resonances”.

Clearly $B_4H_4-T_d$, structure (d) of Fig. 1, is electron deficient. Exempting the four well localized B-H covalent bonds, 8 electrons are shared among six B-B (partial) bonds, meaning in turn that each dashed line in Fig. 1(d) has a “bond index” of $2/3$ ($= 8 e^-/2 \times 6 e^-$) instead of 1, or that every B-B interaction is represented by $2 \times 2/3 = 4/3$ electrons instead of 2. Therefore it is safe to predict that B-B bonds in $B_4H_4-T_d$ would be significantly longer and weaker as compared to a single covalent B-B bond; and this is exactly what our calculations show (see below). Of course the voracity of $B_4H_4-T_d$ for electrons [14] and in fact the bewildering variety of boranes [2], traces its ancestry to the first excited state of BH, $a^3\Pi$. The $B_4H_4-C_s$ planar configuration (global minimum) and another one firstly mentioned in Ref. [14] will be discussed in Section 4.

3. Computational details

For both B and H the cc-pVnZ, $n=T, Q, 5$, ($= n\zeta$) correlation consistent basis sets of Dunning were used through the whole study [16]. The most extensive basis set employed (5ζ) is (14s8p4d3f2g1h/B 8s4p3d2f1g/H) generally contracted to [6s5p4d3f2g1h/B 5s4p3d2f1g/H] of order 91 and 55 for B and H atoms, respectively. Two calculational approaches were followed, the variational internally contracted MRCI ($=$ CASSCF + single + double replacements), and the single reference RCCSD(T) ($=$ restricted coupled-cluster single + double + perturbative connected triples) method [17–19]. The MRCI approach was used only to the highly symmetric $B_4H_4-T_d$ structure, whereas the coupled-cluster methodology was employed for both B_4H_4 geometries, T_d and C_s -planar (but see below). The reference CASSCF space was

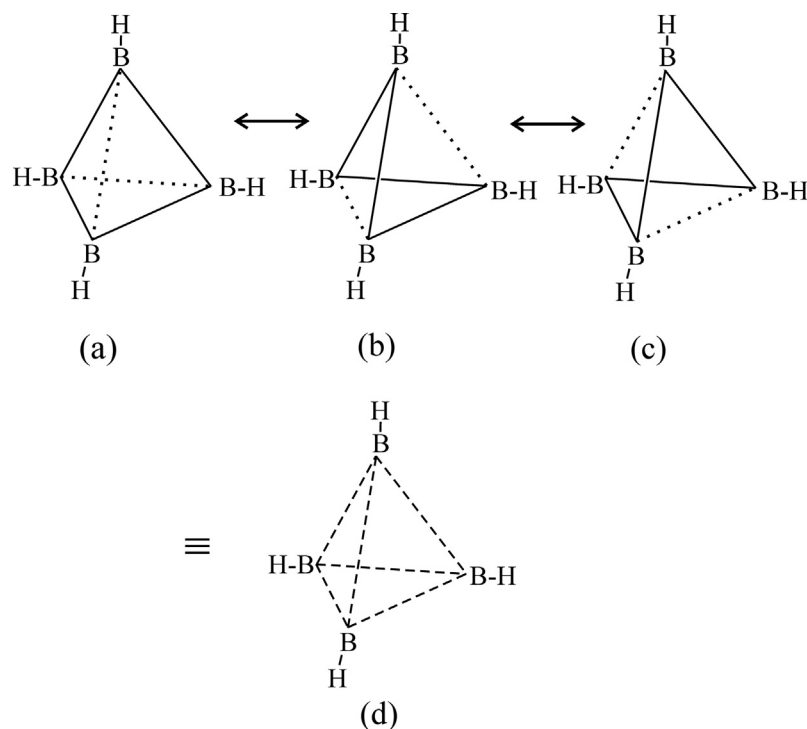


Fig. 1. “Resonance” structures (a), (b), (c) of $B_4H_4-T_d$; see text.

Table 1

Methods, total equilibrium energies E (E_h), equilibrium bond distances r_e (Å), and dissociation energies D_e and D_0 (kcal/mol) with respect to four BH ($X^1\Sigma^+$, $a^3\Pi$) species of B_4H_4 - T_d (II, regular tetrahedron) molecule.

Method	$-E$	r_e (B-H)	r_e (B-B)	$D_e^{X^1\Sigma^+}$ ^a	$D_e^{a^3\Pi}$ ^b	$D_0^{X^1\Sigma^+}$ ^{a,c}	$D_0^{a^3\Pi}$ ^{b,c}
MRCI/Q ζ	101.40016	1.185	1.685	322.9	443.9	305.2	427.7
MRCI + Q/Q ζ ^d	101.4526	–	–	331.6	452.6	313.9	436.4
RCCSD(T)/Q ζ	101.47226	1.184	1.685	333.8	456.0	316.1	439.8
RCCSD(T)/5 ζ ^e	101.47932	–	–	335.4	457.7	317.7	441.5

^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 ζ level.

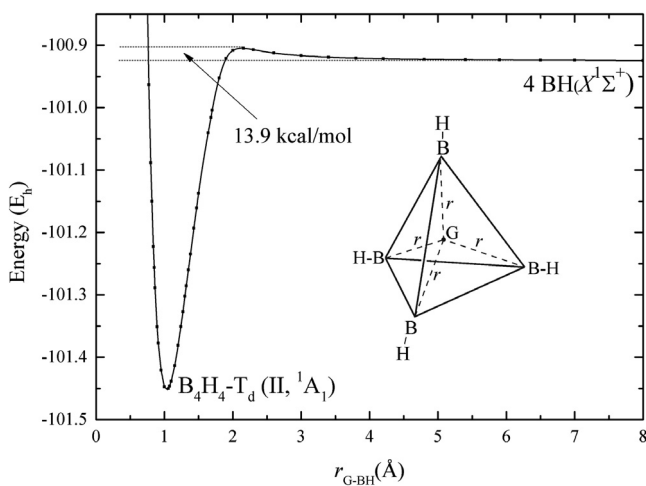


Fig. 2. MRCI+Q/Q ζ potential energy profile of tetrahedral B_4H_4 with respect to four BH units, G is the center of mass.

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 MRCI expansion contains 6×10^9 CFs reduced by three orders of magnitude after the internal contraction, namely 17×10^6 CFs. The 18 normal modes of B_4H_4 $\{\omega_i\}_{i=1}^{18}$ were determined as usual by diagonalizing the corresponding Hessian matrix. The size non-extensivity error of the MRCI 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]: B_4H_4 - C_s (I), B_4H_4 - T_d (II), B_4H_4 - C_s (III), refer to the global minimum (X^1A') [9], to the tetrahedral T_d configuration (1A_1), and to a new isomer of planar- C_s ($^1A'$) geometry higher in energy than B_4H_4 - T_d (II) discovered by the authors of Ref. [14], respectively. All three structures were optimized at the RCCSD(T)/T ζ 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 B_4H_4 - T_d (II) isomer is about 1 kcal/mol at the Q ζ 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 energies, geometries, and dissociation energies (D_e and D_0) of B_4H_4 - T_d (II) with respect to the ground ($X^1\Sigma^+$) and first excited state ($a^3\Pi$), of four BH fragments, $D_e^{X^1\Sigma^+}$ and

Table 2

Normal modes ω_i (cm^{-1}) symmetries s_i , and zero point energies ZPE (cm^{-1}) of the B_4H_4 - T_d (II) and B_4H_4 - C_s (I) species at the RCCSD(T)/T ζ level.

T_d (II)		C_s (I)	
ω_i	s_i	ω_i	s_i
605.7	E	231.6	A''
660.4	T_2	480.7	A'
788.9	T_1	562.4	A''
869.3	T_2	599.8	A'
901.5	E	704.3	A''
1062.8	A_1	761.6	A'
2692.3	T_2	764.0	A''
2723.8	A_1	802.7	A''
ZPE ^a = 10916.8 cm^{-1} (=31.21 kcal/mol)		811.6	A'
		868.3	A'
		924.1	A'
		1083.4	A'
		1280.6	A'
		1434.5	A'
		2258.0	A'
		2703.6	A'
		2757.4	A'
		2760.8	A'
		ZPE ^a = 10894.7 cm^{-1} (=31.15 kcal/mol)	

^a $ZPE = \sum_i \frac{\omega_i}{2} d_i$, where d_i is the degeneracy of the mode i , $d_i = 1, 2$, and 3 for A, E, and T, respectively.

$D_{e/0}^{a^3\Pi}$ respectively, at the MRCI/Q ζ and RCCSD(T)/Q ζ , 5 ζ levels of theory. The MRCI (or MRCI + Q) $D_e^{X^1\Sigma^+}$ 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 (MRCI + Q/Q ζ) on the PEP at 2.2 Å is a result of an avoided crossing between the repulsive (not shown) PEP $4 \times \text{BH}(X^1\Sigma^+) \rightarrow B_4H_4$ - T_d (II) and the strongly attractive (not shown) $4 \times \text{BH}(a^3\Pi) \rightarrow B_4H_4$ - T_d (II) PEPs. Clearly the four BH units within the B_4H_4 - T_d (II) species are in the $a^3\Pi$ state, meaning that *adiabatically* the B_4H_4 - T_d (II) correlates to four $\text{BH}(a^3\Pi)$ moieties coupled into a singlet (1A_1), thus (internal bond strength) $D_e^{a^3\Pi} = D_e^{X^1\Sigma^+} + 4 \times T_e(a^3\Pi - X^1\Sigma^+) = 443.9$ kcal/mol, where $T_e = 10,581$ cm^{-1} (= 30.25 kcal/mol) [7]. Corresponding $D_0^{X^1\Sigma^+}$ and $D_0^{a^3\Pi}$ values are calculated through the relation $D_0^{X^1\Sigma^+} = D_e^{X^1\Sigma^+} - ZPE = D_e^{X^1\Sigma^+} + [4 \times \frac{\omega_e}{2}(\text{BH}; X^1\Sigma^+) - \sum_i \frac{\omega_i}{2} d_i(B_4H_4 - T_d)] = 322.9 + 13.52 - 31.2 = 305.2$ kcal/mol, and similarly $D_0^{a^3\Pi} = 452.6 + 15.01 - 31.2 = 436.4$ kcal/mol, where the ω_e of X- and a-states of BH are 2366.7 and 2631 cm^{-1} , respectively [6,7], and the ZPE of B_4H_4 - T_d (II) along the normal modes $\{\omega_i\}$ is given in Table 2 at the RCCSD(T)/T ζ level; d_i is the degeneracy of the ω_i mode. The D_e or D_0 , values corrected by the Davidson correction (+Q), are practically the same as obtained at the RCCSD(T)/Q ζ , 5 ζ level, Table 1, but using $T_e(a^3\Pi - X^1\Sigma^+)$ values 10,685 (Q ζ) and 10,698

(5 ζ) cm⁻¹ as shown in Table 3. Therefore the mean binding energy \bar{D}_e per formal B–B single bond (not per BH unit), say at the RCCSD(T)/Q ζ level, is $\bar{D}_e^{X^1\Sigma^+} = 333.8/6 = 55.6$ kcal/mol and $\bar{D}_e^{a^3\Pi} = 456.0/6 = 76.0$ kcal/mol. The same results are obtained within 3 kcal/mol using the MRCI+Q values. Corresponding \bar{D}_0 values are $\bar{D}_0^{X^1\Sigma^+} = 52.7$ and $\bar{D}_0^{a^3\Pi} = 73.3$ kcal/mol.

Recall, however, that B₄H₄-T_d (II) is electron deficient (Lewis acid) the “bond order” of B–B being 2/3 instead of 1; see Section 2. Thus it would be of interest to calculate the binding energy of a “genuine” single B–B bond as contrasted to a B–B binding energy of B₄H₄-T_d (II).

Table 3 gives the total energy and geometry of the \tilde{X}^2A_1 state of the BH₂ radical at the RCCSD(T)/Q ζ level including experimental results [22]. Small discrepancies from experiment, $\delta r_e \approx +0.01$ Å and $\delta(\angle HBH) \approx -2^\circ$ are rather due to core effects not included to our calculations (vide infra). The vBL diagram of the \tilde{X}^2A_1 state of BH₂ (Scheme 2) is predicting clearly a bent structure of C_{2v} symmetry and the possibility to form the H₂B–BH₂ molecule through a single B–B bond. Indeed, the H₂B–BH₂ 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 ζ level, are shown in Fig. 3.

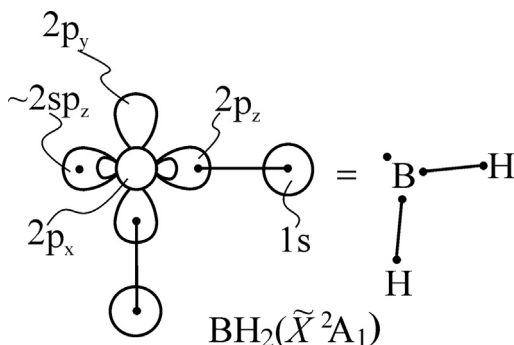
The most stable configuration is the staggered D_{2d} with an astonishing large barrier-to-rotation of 12.5 kcal/mol. Our results are in agreement with previous calculations; for details see Ref. [23] and references therein. The unexpected and capricious behavior of H₂B–BH₂ can be understood by referring to the vBL diagram of the BH₂(\tilde{X}^2A_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 H₂B–BH₂ with respect to two BH₂(\tilde{X}^2A_1) radicals at the RCCSD(T)/Q ζ level (see also Table 3 and

Table 3
Total equilibrium energies E (E_h), geometries r_e (Å) and the angle $\angle HBH$ (degrees), and energy separation T_e (cm⁻¹) of the BH and BH₂ species at the RCCSD(T) level.

State/Basis set	$-E$	r_e (B–H)	$\angle HBH$	T_e
<i>BH</i>				
X ¹ Σ ⁺ /Q ζ	25.235064	1.233		0.0
X ¹ Σ ⁺ /5 ζ	25.236212	1.233		0.0
a ³ Π/Q ζ	25.186380	1.192		10685
a ³ Π/5 ζ	25.187469	1.191		10698
<i>BH₂</i>				
\tilde{X}^2A_1 /Q ζ	25.868894	1.188	128.9	0.0
Expt. ^a		1.18 ₁	131	0.0

^a Experimental spectroscopic results, Ref. [22].



Scheme 2.

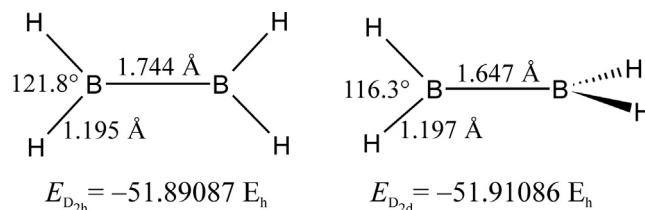


Fig. 3. Equilibrium geometries and total energies of the D_{2h} and D_{2d} structures of the H₂BBH₂ molecule.

Fig. 3) is D_e^0 (B–B) = 108.6 kcal/mol, a remarkably strong single bond equal to $D_e^0(X^1\Sigma^+) = 109.5$ kcal/mol of H₂ [6]. As was reported before the mean binding B–B bond energy of B₄H₄-T_d (II) at the same level of theory is $\bar{D}_e^{a^3\Pi} = 76.0$ kcal/mol. Therefore the ratio $\frac{\bar{D}_e^{a^3\Pi}}{\bar{D}_e^0(B-B)} = \frac{76.0}{108.6} = 0.70 \approx \frac{2}{3}$ is in complete agreement with the “bond order” of 2/3 deduced in Section 2 by a completely different, non-energetic, way of reasoning.

We turn now to the B₄H₄-C_s (I) low symmetry configuration, suggested to be the global minimum of B₄H₄ more than twenty years ago [9]. 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 B₄H₄ and B₄H₄” [14]. It was found at the highest level of theory, CCSD(T)/CBS limit, that the B₄H₄-C_s (I) structure is 6.6 kcal/mol lower than B₄H₄-T_d (II); the corresponding value found in Ref. [9] lies between 5 and 6 kcal/mol. Unfortunately, besides energy differences among the three isomers of B₄H₄, 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 B₄H₄ has a C_s (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 ζ level, using as an initial guess the geometry of Ref. [9]. Total energies and energy differences $\Delta E_{II,I} = E_{Td(II)} - E_{Cs(I)}$ are given in Table 5. At the RCCSD(T)/5 ζ /RCCSD(T)/T ζ level $\Delta E_{II,I} = 5.9$ 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_s (I) and T_d (II), Table 2, has a null effect to the energy difference $\Delta E_{II,I}$ given above.

At the Hartree-Fock/T ζ level the permanent electric dipole moment of the global minimum B₄H₄-C_s (I) is $\mu_{Cs(I)} = (\mu_y^2 + \mu_z^2)^{1/2} = [(-0.456)^2 + (1.600)^2]^{1/2} = 1.63D$, obtained as an expectation value. The corresponding finite field value at the RCCSD(T)/T ζ level is $\mu_{Cs(I)}^{FF} = [(-0.447)^2 + (1.375)^2]^{1/2} = 1.45D$; field strength 5×10^{-5} a.u.

We have also examined the structure B₄H₄-C_s (III) discovered by Olson and Boldyrev [14] and shown in Fig. 4. Although B₄H₄-C_s (I) and B₄H₄-C_s (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 ζ level, while Table 5 gives total energies and energy differences ΔE at the RCCSD(T)/Q ζ , 5 ζ levels. Observe that at the RCCSD(T)/Q ζ /RCCSD(T)/T ζ level the B₄H₄-C_s (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 ζ the ZPE of B₄H₄-C_s (III) isomer is 31.2 kcal/mol identical to the ZPEs of C_s (I) and T_d (II), thereby its effect to energy differences $\Delta E_{III,I}$ or $\Delta E_{III,II}$ is none. The dipole moment of the B₄H₄-C_s (III) isomer is

$$\mu_{Cs(III)} = (\mu_y^2 + \mu_z^2)^{1/2} = [(1.585)^2 + (0.213)^2]^{1/2} = 1.60D, \text{ and}$$

$$\mu_{Cs(III)}^{FF} = [(1.569)^2 + (0.153)^2]^{1/2} = 1.58D$$

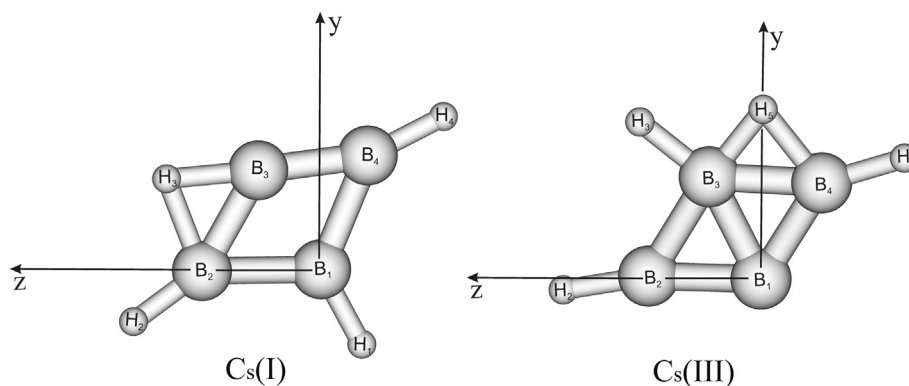


Fig. 4. Geometric configurations of the C_s structures $B_4H_4-C_s$ (I) (global minimum) and of $B_4H_4-C_s$ (III).

Table 4

Equilibrium bond lengths r_e (Å) and angles θ (degrees) of the $B_4H_4-C_s$ (I) molecule at the RCCSD(T)/ $T\zeta$ level.^a

Bond	r_e	Angle	θ
B_1B_2	1.654	$B_2B_1B_4$	113.2
B_2B_3	1.599	$B_1B_2B_3$	60.0
B_3B_4	1.537	$B_2B_3B_4$	126.8
B_4B_1	1.704	$H_4B_4B_1$	140.0
B_1B_3	1.627	$H_1B_1B_4$	130.1
B_1H_1	1.183	$H_2B_2B_1$	143.6
B_2H_2	1.177	$H_2B_2H_3$	106.1
B_4H_4	1.177	$H_3B_3B_2$	55.6
B_2H_3	1.370	$H_3B_3B_4$	177.7
B_3H_3	1.280	$H_4B_4B_3$	160.0

^a The numbering of the B and H atoms refers to Fig. 4.

Table 5

Total E (E_h) of the C_s (I), T_d (II), C_s (III) and energy differences $\Delta E_{II,I}$ ($=E_{Td(II)} - E_{Cs(I)}$), $\Delta E_{III,I}$ ($=E_{Cs(III)} - E_{Cs(I)}$) in kcal/mol of B_4H_4 at the RCCSD(T)/ $T\zeta$, $Q\zeta$, 5ζ level.

Basis set	$-E_{Cs(I)}$ ^a	$-E_{Td(II)}$ ^b	$-E_{Cs(III)}$ ^a	$\Delta E_{II,I}$	$\Delta E_{III,I}$
$T\zeta$	101.45481	101.44675	101.44453	5.1	6.5
$Q\zeta$	101.48146 ^c	101.47226	101.46308 ^c	5.8	11.5
5ζ	101.48869 ^c	101.47932 ^d	101.46837 ^c	5.9	12.8

^a Geometry optimization at the RCCSD(T)/ $T\zeta$ only.

^b Geometry optimization at the RCCSD(T)/ $T\zeta$ and $Q\zeta$; see Table 1.

^c RCCSD(T)/ $Q\zeta$ or 5ζ //RCCSD(T)/ $T\zeta$.

^d RCCSD(T)/ 5ζ //RCCSD(T)/ $Q\zeta$.

Table 6

Equilibrium bond lengths r_e (Å) and angle θ (degrees) of the $B_4H_4-C_s$ (III) molecule at the RCCSD(T)/ $T\zeta$ level.^a

Bond	r_e	Angle	θ
B_1B_2	1.509	$B_1B_2B_3$	60.0
B_2B_3	1.800	$B_2B_3B_1$	51.3
B_3B_4	1.721	$B_1B_3B_4$	55.1
B_4B_1	1.571	$B_3B_1B_4$	63.9
B_1B_3	1.675	$B_1B_2H_2$	175.6
B_2H_2	1.180	$B_2B_3H_3$	109.1
B_3H_3	1.180	$H_3B_3H_5$	95.7
B_4H_4	1.180	$H_5B_4B_3$	49.8
B_3H_5 ^b	1.329	$H_5B_4H_4$	151.6
B_4H_5 ^b	1.308	$H_4B_4B_1$	147.5

^a The numbering of the B and H atoms refers to Fig. 4.

^b H_5 is the bridging H atom; there is no H_1 .

at the HF/ $T\zeta$ and RCCSD(T)/ $T\zeta$ level, respectively; field strength 5×10^{-5} a.u. Although the total dipole moments for both isomers, C_s (I) and C_s (III) are almost the same, their individual components, μ_y and μ_z , are entirely different. As a result the dipole vector lies practically along the z axis in C_s (I) but along the y axis in C_s (III), see Fig. 4.

A last observation: despite the fact that both the “unicorn” molecule of organic chemistry C_4H_4 (tetrahedrane) and $B_4H_4-T_d$ (II) are regular tetrahedrons and both are composed of four excited state units $CH(a^4\Sigma^-)$ and $BH(a^3\Pi)$, respectively, the reason for their non-observation (or very short lifetimes) is entirely different. For one thing $B_4H_4-T_d$ (II) is strongly electron deficient by 4 electrons, but this is not the case for C_4H_4 . 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 $BH_2(\tilde{X}^2A_1)$, H_2BBH_2 (B_{2d} or D_{2h}), in the three isomers of B_4H_4 (I, II, III) and of course in the vast variety of boranes B_xH_y , is in its first excited 4P (or $a^3\Pi$) state. For details see Ref. [5] and references therein.

5. Conclusions

From the vast field of boranes B_xH_y we have investigated by ab initio MRCI and RCCSD(T) methods three isomers of B_4H_4 , namely $B_4H_4-C_s$ (I) [planar, $^1A'$], $B_4H_4-T_d$ (II) [regular tetrahedron, 1A_1], and $B_4H_4-C_s$ (III) [planar, $^1A'$]. The geometrical arrangements of the two planar C_s species (I and III) are shown in Fig. 4. For reasons of necessity and/or completeness we have also examined the species $BH(X^1\Sigma^+, a^3\Pi)$, $BH_2(\tilde{X}^2A_1)$, and the two conformers of H_2BBH_2 (D_{2h} , D_{2d}). Our findings are summarized below.

- It has been reconfirmed that the global minimum of B_4H_4 has a C_s (I) geometry (Fig. 4). This is indeed significant as to the conceptual development and meaning of the chemical bond.
- Our results leave no doubt that isomer T_d (II) (regular tetrahedron) is located 6 kcal/mol above C_s (I) and certainly no more than 6.5 kcal/mol. $B_4H_4-T_d$ (II) is a singlet (1A_1) energetically stable geometrical arrangement in the B_4H_4 potential energy hypersurface, more or less of the same binding energy with respect to four $BH(a^3\Pi)$ units as the C_s (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 T_d (II) and C_s (I) is low, the former can “slip” to the latter which in turn can polymerize due to its $2 - e^- \pi_x$ system (see iii).
- The binding mode of $B_4H_4-C_s$ (I) can be rationalized through a vBL diagram diagram shown on p. 472 of Ref. [9] composed of four $BH(a^3\Pi)$ moieties, indicating a $2 - e^- \pi_x$ system carried by the B_2 and B_3 atoms bridged by H_3 ; see Fig. 4.

- (iv) The isomer $B_4H_4-C_s$ (III), Fig. 4, is located about 13 kcal/mol above the global minimum C_s (I). It is a stable local minimum on the B_4H_4 hypersurface and of course never observed experimentally.
- (v) The normal modes of $B_4H_4-C_s$ (I) and $B_4H_4-T_d$ (II) as well as their electrical dipole moments have been reported for the first time, whereas zero point energies are identical for all three B_4H_4 isomers, ZPE = 31.2 kcal/mol.

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