Ab initio structural study of the B_4H_4 molecule. Asymmetric structure for a 'symmetric' system

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Abstract

Ab initio calculations on the B_4H_4 molecule using MP2, MP4, and CISD methodologies, reveal that the ground state of this system has a (planar) C_s instead of the highly symmetric T_d structure, the energy difference being approximately 6 kcal/mol. An attempt is made to rationalise this finding by invoking the excited a $^3\Pi$ state of the B–H unit.

1. Introduction

The closed deltahedral B_4H_4 system (canonical tetrahedron) has been the subject of a large number of theoretical investigations [1–7]. Although B_4H_4 has been declared bound with respect to four B–H ($X\,^1\Sigma^+$) species by ≈ 263 kcal/mol [5], the molecule is experimentally unknown, while the substituted analogues B_4Cl_4 and $(Me_3C)_4B_4$ (tetrakis (1,1-dimethylethyl)tetraborane(4)) are well established [8–10]. The reasons for the non-existence of the parent molecule B_4H_4 (or other analogous species, i.e. B_4F_4) are not yet clear, but are based mainly upon the high electron deficiency of this system. Rationalisations invoking back-donation from ligands into the boron cage are rather controversial and/or conflicting [4,11].

Despite the large number of calculational studies on the B_4H_4 system, post-Hartree–Fock studies are not abundant. One of the first is by Guest and Saunders based on antisymmetrized geminals [12], followed by the CISD and CPF (coupled-pair func-tional, closely related to CISD but size-consistent) study of Swanton and Ahlrichs [5], and also McKee's MP4/6-31G* calculations [6].

The upshot of the aforementioned work on B_4H_4 can be summarized as follows.

(i) The T_d structure is energetically the most stable configuration reported till now.

(ii) The D_{4h} structure reported to be a minimum in earlier works, e.g. Ref. [3], was found to be unstable with respect to D_{2d} relaxation [4,6], with the D_{2d} minimum being higher in energy than the T_d minimum by ≈ 59 kcal/mol at the MP4/6-31G*// SCF level [6].

(iii) The Swanton–Ahlrichs [5] calculations suggest that the D_{4h} structure is higher in energy by 54 kcal/mol than the T_d structure at the CPF level of theory; notice though that these researchers did not examine the Hessian of the D_{4h} structure.

Motivated by the fact that the D_{4h} structure is not electron deficient, according to traditional valence electron counting in boron skeleton, we decided to examine more thoroughly the path from T_d to D_{4h}.

To our surprise it was discovered that not only the D_{4h} structure possesses three imaginary frequencies, but in addition it deforms to a C_s planar (see below) structure, which competes strongly with the T_d structure, at being the global minimum of the B_4H_4 system. In what follows we present MP2, MP4 and CISD calculations on B_4H_4.

2. Computational approach – basis set

The computational methods employed in the present study are SCF, MP2, MP4 and CISD. For the CISD (+ Davidson correction(s)) calculations the program MELD [13] was used. The GAUSSIAN92 [14] set of codes was used only for MP2 gradient optimisations and frequency analysis. The rest of our calculations were performed by using the GAMESS [15] code.

In all MPn calculations the 6-31G* basis set [16] was used; occasionally the 6-31G** and 6-31+G* [16] sets were also employed. In the correlated CISD calculations and for B and H atoms the cc-pVTZ(10s5p2d/5s2p) basis sets of Dunning [17,18] were used, contracted to [4s3p2d/2s1p] according to Raffenetti [19]. The resulting [(4s3p2d)_4/(2s1p)_4] basis contains 120 Cartesian Gaussian functions. In all correlated calculations the four lowest MO corresponding to core 1s orbitals of B atoms were kept frozen.

Our calculations were done with the IBM RS/6000-350 computer of Comenius University in Bratislava, the Sun SPARC station 10 of the Physical Chemistry Laboratory of Athens University and the CONVEX 3820 computer of the NCSR DEMOKRITOS, Greece.

3. Results and discussion

Table 1 presents absolute energies at the SCF and MP levels for the B_4H_4 molecule in T_d, D_{2d}, S_4, $C_s(1)$ and $C_s(2)$ symmetries, Fig. 1. Symmetries S_4 and $C_s(1)$ are transition structures of first order (see Table 1), located between the D_{2d} and T_d minima, and D_{2d} and $C_s(2)$ minima respectively. Schematically we can write
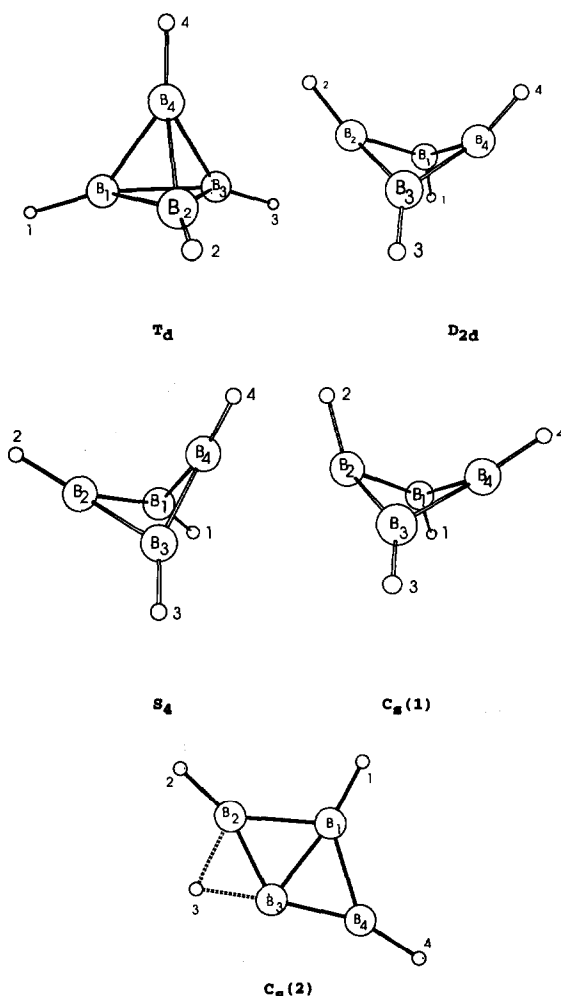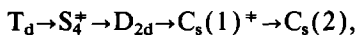

Fig. 1. Perspective drawings of the T_d, D_{2d}, S_4, $C_s(1)$ and $C_s(2)$ structures of the B_4H_4 molecular system.

$$T_d \rightarrow S_4^+ \rightarrow D_{2d} \rightarrow C_s(1)^+ \rightarrow C_s(2),$$

as calculations of intrinsic reaction coordinate [20] indicate. From Tables 1 and 2 it can be deduced that the D_{2d} structure is a minimum, though a shallow one at all levels of theory. By adding the MP2 zero-point energies to the S_4, D_{2d} and $C_s(1)$ structures (28.0, 28.6 and 28.5 kcal/mol) it is clear that the D_{2d} minimum practically disappears. Energetically, both transition structures are almost degenerate at MP2 and MP4 levels and this is reflected in their geometrical parameters which are similar, Table 4.

However, what really surprised us was the $C_s(2)$

Table 1
Absolute energies, E (hartree) of the B_4H_4 molecule in point groups T_d, D_{2d}, S_4, $C_s(1)$ and $C_s(2)$, as obtained from the SCF, MP2 and MP4 methods, at SCF or MP2 (in parentheses) optimized geometries using the 6-31G* basis set

Symmetry	E			nif [a]
	SCF	MP2	MP4	
T_d	−100.92570	−101.27142	−101.32328	0
		(0.27149)	(0.32342)	
D_{2d}	−100.88955	−101.17221	−101.22975	0
		(0.17423)	(0.23146)	(0)
S_4	−100.87483	−101.18549	−101.24366	1
		(0.17309)	(0.23040)	(1)
$C_s(1)$	−100.88847	−101.17259	−101.23001	1
		(0.17398)	(0.23114)	(1)
$C_s(2)$	−100.94409	−101.27761	−101.32799	0
		(0.27844)	(0.32884)	(0)

[a] Number of imaginary frequencies at the SCF (MP2) level of approximation.

Table 2
Absolute energies in hartree, E(SCF, CISD, CISD+Q, CI-F) in T_d and $C_s(2)$ symmetries of the B_4H_4 molecule at MP2/6-31G* geometries [a]

Symmetry	E			
	SCF	CISD [b]	CISD+Q [c]	CI-F [d]
T_d	−100.95158	−101.3235	−101.3759	−101.3969
$C_s(2)$	−100.97207	−101.3376	−101.3881	−101.4073

[a] The basis set used is the cc-pVTZ[4s3p2d/2s1p], see text.
[b] CISD=SCF plus single and double replacements (SCF+1+2). A perturbation selection scheme with energy thresholds 1×10^{-6} and 2.9×10^{-6} for T_d and $C_s(2)$ cases respectively was applied; this amounts to an estimated energy loss ≈ 0.004 hartree for T_d and ≈ 0.040 hartree for $C_s(2)$ symmetries. The above reported CISD values have been corrected to the complete CISD-space energies. The number of SACs finally involved are 51172 and 52435.
[c] The Davidson correction for the effects of unlinked quadruples, $\Delta E_Q = (1 - C_0^2)(E_{CISD} - E_{SCF})$ has been employed, Ref. [21].
[d] The Davidson extrapolation to the 'full' CI, $E_{CI-F} = E_{SCF} + (E_{CISD} - E_{SCF})(C_0^2/2C_0^2 - 1)$ has been used, Ref. [22].

structure, Fig. 1. Notwithstanding the aesthetic appeal of the platonic symmetry of the T_d structure, the $C_s(2)$ structure of B_4H_4 with the minimal symmetry of a molecular plane, is lower in energy than the T_d structure. Table 1 shows that the $C_s(2)$ geometry is the most stable in all levels of theory reported in this table. In particular, the energy differences are 11.5, 4.4 and 3.4 kcal/mol at SCF, MP2 and MP4 6-31G* levels of theory respectively, in favour of $C_s(2)$ symmetry. The picture remains essentially the same at SCF and MP2/6-31G**, with differences of 12.2 and 4.3 kcal/mol respectively. At the CCSD (coupled clusters singles and doubles) 6-31+G* level [14], the $C_s(2)$ structure is more stable than the T_d structure by 5.7 kcal/mol.

In order to confirm the above results concerning

the T_d and $C_s(2)$ structures we employed a much larger basis set, namely the cc-pVTZ of Dunning (vide supra), in conjunction with the CISD methodology. Our results are summarized in Table 2; notice that the geometries used are those obtained from the MP2/6-31G* calculations. Our SCF energy of the T_d structure is the lowest so far reported, being lower by ≈ 0.004 hartree than the best calculation of Swanton and Ahlrichs [5]. From Table 2 it can be seen that the $C_s(2)$ structure is 8.8 kcal/mol more stable than the T_d structure at the CISD level, with this difference diminishing by $\approx 1-2$ kcal/mol as we apply the Davidson correction for unlinked quadruples (CISD+Q) and extrapolation to 'full' CI (CI-F) [21,22].

All our energy differences for all symmetries are

conveniently condensed in Table 3. The optimized geometrical parameters of the $C_s(2)$ structure are collected in Table 5. We observe that the B–B distances vary from 1.530 to 1.705 Å at the SCF level or from 1.529 to 1.709 Å at MP2, and this should be contrasted with the B–B bond length of the T_d structure which is 1.686 Å, Table 4. These large differences are indicative of the different character of bonding in the B–B skeleton between $C_s(2)$ and T_d symmetries. The B–H bond distances of the $C_s(2)$ structure do not differ significantly from those of the T_d structure, with the exception of the bridging hydrogen H_3, with bond distances of 1.279 Å (B_3–H_3) and 1.346 Å (B_2–H_3), Table 5, Fig. 1.

The natural question to be asked is why this $C_s(2)$ highly distorted geometry, competes successfully in stability with the highly symmetric T_d structure. We reason as follows. We imagine that B_4H_4 is assembled from four B–H units, $B_4H_4 = (B-H)_4$. The B–H species has a $^1\Sigma^+$ ground state [23] and a low-lying a $^3\Pi$ state, approximately 1.4 eV above X $^1\Sigma^+$ [24]. The valence-bond picture of the $^3\Pi$ wavefunction can be represented as
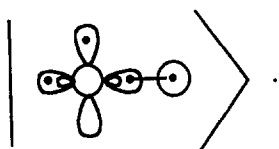
We can now imagine that four such BH (a $^3\Pi$) units

Table 3
Relative energies, ΔE (kcal mol^{-1}) [a] of the B_4H_4 system in different symmetries and with different methods

| Method	ΔE				
	T_d	D_{2d}	S_4	$C_s(1)$	$C_s(2)$
SCF//SCF [b]	11.5	34.2	43.3	34.9	0.0
MP2//MP2 [b]	4.4	65.4	66.1	65.5	0.0
MP4//MP2 [b]	3.4	61.1	61.7	61.3	0.0
SCF//MP2 [c]	12.9	–	–	–	0.0
CISD//MP2 [c,d]	8.8	–	–	–	0.0
CISD+Q [d]	7.7	–	–	–	0.0
CI-F [d]	6.5	–	–	–	0.0

[a] $\Delta E = E(X) - E(C_s(2))$, $X = T_d$, D_{2d}, S_4, $C_4(1)$ and $C_s(2)$.
[b] Basis set employed, 6-31G*.
[c] Basis set employed, cc-pVTZ[4s3p2d/2s1p].
[d] See footnotes b, c and d of Table 2.

interact accordingly resulting in the formation of the B_4H_4 molecule as the following icon shows
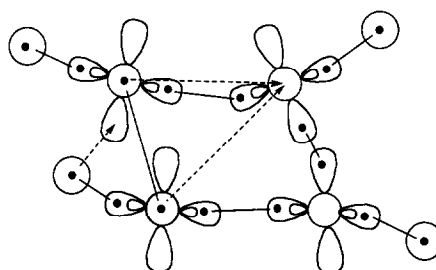
In other words, we are claiming that the in situ B–H units in the $C_s(2)$ structure can be thought as being in the $^3\Pi$ excited state. The excitation energy of four B–H fragments which amounts to ≈ 130 kcal/mol is by far compensated by the formation of four B–B nominal bonds in the B_4H_4 ($C_s(2)$) molecule. From the above picture the following conclusions can be drawn.

(a) The B_3–H_3–B_2 bridging bond can be rationalised as a σ-type interaction between H_3 and the empty pσ orbital of the B_2 atom. As there is only one such empty p orbital of appropriate symmetry, only one hydrogen bridge can be formed. This bridging interaction can be considered as the cause, at least in part, of the asymmetrical, low energy $C_s(2)$ structure.

(b) There are two π electrons delocalized mainly among the B_1, B_2 and B_3 atoms. This suggests a partial two-electron π bond between B_2 and B_3 and a partial one-electron π bond between B_3 and B_1 atoms.

(c) The structure proposed above along with its rationalisation, does not suffer from the common 'disease' of severe electron deficiency of the boron skeleton.

4. Concluding remarks

The present study proposes a planar, highly asymmetrical structure of the B_4H_4 molecular system, which seems to be the global minimum of this molecule; that is, the $C_s(2)$ structure has a lower energy than the T_d structure. The cause of such a geometry can be traced to hydrogen bridging between two boron atoms and a π-delocalized 'aromatic' two-electron system. The existence of this structure can possibly explain why the T_d structure of B_4H_4 has not yet been observed experimentally.

Table 4
Equilibrium geometrical parameters (Å, deg) of the B_4H_4 molecule in point groups T_d, D_{2d}, S_4 and $C_s(1)$, as obtained from SCF and MP2 (in parentheses) methods, in the 6-31G* basis set. The numbering of atoms is according to Fig. 1

Geometrical parameter	T_d	D_{2d}	S_4	Geometrical parameter	$C_s(1)$
$r(B-B)$	1.686 (1.685)	1.709 (1.680)	1.677 (1.671)	$r(B_2-B_3)$	1.657 (1.648)
$r(B-H)$	1.182 (1.188)	1.185 (1.190)	1.181 (1.189)	$r(B_3-B_4)$	1.760 (1.713)
$\angle B_1B_2B_3B_4$		121.7 (116.5)	100.3 (110.6)	$r(B_1-H_1)$	1.183 (1.189)
$\angle B_2B_1H_1$		134.4 (134.0)	155.5 (145.9)	$r(B_2-H_2)$	1.197 (1.197)
$\angle B_4B_1H_1$			128.2 (127.1)	$r(B_4-H_4)$	1.184 (1.188)
				$\angle B_1B_2B_3B_4$	121.8 (115.8)
				$\angle H_4B_4L$ [a]	170.6 (164.0)
				$\angle H_2B_2L$ [a]	137.9 (143.5)
				$\angle H_1B_1B_3$	138.6 (128.1)
				$\angle H_1B_1B_3B_2$	126.4 (127.3)

[a] L is the (imaginary) line bisecting the angle $\angle B_1B_4B_3$, or $\angle B_1B_2B_3$.

Table 5
Equilibrium geometrical parameters (Å, deg) of the planar $C_s(2)$ structure of B_4H_4 molecule, as obtained from SCF and MP2 methods in the 6-31G* basis set. The numbering of atoms is according to Fig. 1

Bond length	SCF	MP2	Bond angle	SCF	MP2
B_1-B_2	1.677	1.646	$\angle B_1B_2B_3$	59.8	59.8
B_2-B_3	1.564	1.595	$\angle B_2B_3B_1$	63.6	61.6
B_3-B_4	1.530	1.529	$\angle B_1B_3B_4$	65.5	65.5
B_1-B_3	1.618	1.616	$\angle B_3B_4B_1$	59.7	59.7
B_1-B_4	1.705	1.701	$\angle B_2B_1H_1$	112.9	117.7
B_1-H_1	1.180	1.185	$\angle B_1B_2H_2$	139.9	144.3
B_2-H_2	1.172	1.180	$\angle B_2B_3H_3$	55.5	55.8
B_2-H_3	1.346	1.371	$\angle B_3B_2H_3$	51.5	50.2
B_3-H_3	1.279	1.274	$\angle B_3B_4H_4$	159.0	160.5
B_4-H_4	1.174	1.180			

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