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Ab Initio Characterization of a Triborane(9) Isomer with a Pentacoordinated Central Boron Atom

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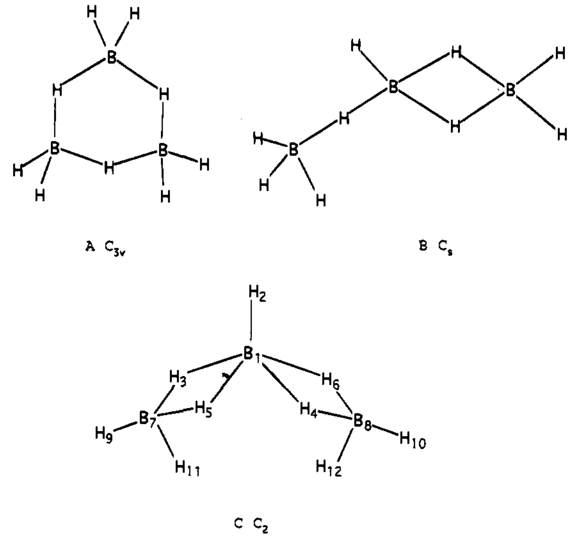
Abstract: A new isomer of triborane(9) has been characterised by ab initio molecular orbital theory at both the MP2 level and the CISD level. This isomer has C_2 symmetry with a pentacoordinated central boron atom, and it may play an important role in the mechanism of pyrolysis of diborane(6).

The important pyrolysis reaction of diborane(6) to give higher boranes such as tetraborane(10), pentaborane(9) and pentaborane(11) is believed to involve the unstable triborane(9) as an intermediate.[1] Several ab initio theoretical studies[2–7] have concluded that the most stable structure of triborane(9) is a C_{3v} symmetry ring (A of Figure 1) with the bridge hydrogen atoms about 0.46 Å above the plane of the boron atoms. A detailed ab initio study[7] of the early stages of diborane pyrolysis concentrated on this structure. However, Fehlner[9] suggested a structure (B of Figure 1) with a single bridge formed from the terminal H of B_2H_6 to BH_3. In an earlier study,[10] we found no local minimum for the Fehlner structure, but a genuine stationary state was found as one of the H atoms of the BH_3 moves in to the central boron atom to give a C_2 structure (C of Figure 1) with a pentacoordinated central atom. We designate this structure as p-B_3H_9. At the SCF level of theory with a double-ζ plus polarization basis set, this structure is a transition state with one negative eigenvalue of the second derivative matrix (one imaginary vibrational frequency).

At the configuration interaction with all single and double excitations (CISD) correlated level of theory, the evidence pointed very tentatively to the p-B_3H_9 structure being a local minimum and hence a second isomer of triborane(9). This point could not be established due to the inability to calculate the second derivative matrix for a molecule of this size at this level of theory. Recently it became possible to evaluate the second derivative matrix analytically at the Moller–Plesset (MP2) correlated level of theory and numerically at the CISD level using GAUSSIAN92.[11] As discussed earlier,[10] the presence of this p-B_3H_9 structure unravels some features of the kinetics of diborane pyrolysis not explained by Stanton et al.[8] Independently, p-B_3H_9 has been found to be a local minimum at the MP2/6-31+G* level of theory as part of a broad survey of B_3H_n (n = 3, 9) by Korkin et al.[12]



A C_{3v} B C_s C C_2

Figure 1.

Several basis sets were employed in this research, all giving similar qualitative results. Only results with the two largest basis sets are reported here. These are the Huzinaga[13]–Dunning[14] (B:9s5p/4s2p; H:4s/2s) double-ζ plus polarization basis set (α_d–B = 0.7; α_p–H = 0.75) (size, 93 functions), designated DZP, and the Pople 6-31G**[15] split valence plus polarization function basis set (size, 90 functions). Cartesian sets of six d–like polarization functions are used in both basis

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(1) Greenwood, N. N.; Greatrex, R. *Pure Appl. Chem.* **1987**, *59*, 857. Fridmann, S. A.; Fehlner, T. P. *J. Am. Chem. Soc.* **1971**, *93*, 2824. Fridmann, S. A.; Fehlner, T. P. *Inorg. Chem.* **1972**, *11*, 936.

(2) Ortiz, J. V.; Lipscomb, W. N. *Chem. Phys. Lett.* **1983**, *103*, 59.

(3) Pepperberg, I. M.; Halgren, T. A.; Lipscomb, W. N. *Inorg. Chem.* **1977**, *16*, 363.

(4) McKee, M. L.; Lipscomb, W. N. *Inorg. Chem.* **1982**, *21*, 2846.

(5) McKee, M. L.; Lipscomb, W. N. *Inorg. Chem.* **1985**, *24*, 2317.

(6) Stanton, J. F.; Lipscomb, W. N.; Bartlett, R. J.; McKee, M. L. *Inorg. Chem.* **1989**, *28*, 109.

(7) Jemmis, E. D.; Subramanian, G.; Srinivas, G. N. *J. Am. Chem. Soc.* **1992**, *114*, 7939.

(8) Stanton, J. F.; Lipscomb, W. N.; Bartlett, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 5165.

(9) Fehlner, T. P. *Boron Hydride Chemistry*; Muetterties, E. L., Ed.; Academic Press: New York, 1975; p 175.

(10) Duke, B. J.; Liang, C.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1991**, *113*, 2884.

(11) GAUSSIAN92, Revision C; M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople; Gaussian, Inc.: Pittsburgh, PA, 1992.

(12) Korkin, A. A.; McKee, M. L.; von Schleyer, P. R. *Abstracts of "International Conference on Materials Science and Environmental Chemistry of Main Group Elements"* held in Kuala Lumpur, Malaysia, November 8–11, 1993, and a private communication, A. A. Korkin.

(13) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

(14) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.

(15) Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 4233. Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *66*, 217.

0002-7863/95/1517-7753$09.00/0

Table 1. Optimized Geometries of the Pentacoordinated B_3H_9 (Distances in Å and Angles in deg; Numbering System As in Structure C—See Text)

	DZP			6-31G**		
	SCF	MP2	CISD	SCF	MP2	CISD
$r(B_1-H_2)$	1.179	1.186	1.183	1.176	1.181	1.178
$r(B_1-H_3)$	1.293	1.381	1.331	1.287	1.337	1.317
$r(B_1-H_5)$	1.596	1.432	1.501	1.580	1.464	1.494
$r(B_7-H_3)$	1.354	1.278	1.304	1.333	1.275	1.287
$r(B_7-H_5)$	1.248	1.264	1.253	1.239	1.242	1.239
$r(B_7-H_9)$	1.189	1.188	1.188	1.186	1.183	1.183
$r(B_7-H_{11})$	1.190	1.187	1.188	1.187	1.183	1.183
$\angle H_2B_2H_3$	119.0	108.6	114.8	118.6	113.3	115.5
$\angle H_2B_1H_5$	98.5	103.8	100.4	99.0	101.5	100.4
$\angle H_3B_1H_5$	86.9	88.2	87.9	86.6	88.0	87.6
$\angle H_9B_7H_{11}$	122.8	124.6	123.9	122.4	123.1	122.8
$\angle B_1B_3B_7$	90.8	85.8	88.2	90.9	87.2	88.4
$\angle H_3B_7H_5$	100.3	100.8	100.7	100.4	101.4	101.0
$\angle B_1H_5B_7$	82.0	84.2	82.9	82.0	83.0	82.7
$\tau H_1B_1B_5H_9$	−26.5	−5.7	−17.6	−25.6	−14.1	−18.3
$\tau H_1B_1B_5H_{11}$	172.9	177.6	177.6	173.2	174.8	173.8
lowest vib freq	478i	69	184	495i	190	192

Table 2. Harmonic Frequencies (in cm^{-1}) and IR Intensities (in km mol^{-1}) for Pentacoordinated B_3H_9[a]

	DZP		6-31G**	
symmetry	MP2	CISD	MP2	CISD
A	2807 (141)	2806 (200)	2815 (131)	2816 (188)
B	2803 (20)	2800 (35)	2813 (29)	2812 (40)
A	2752 (49)	2786 (21)	2779 (31)	2805 (1)
A	2686 (4)	2692 (33)	2714 (30)	2718 (33)
B	2681 (114)	2687 (132)	2708 (108)	2713 (119)
A	2374 (22)	2389 (29)	2437 (18)	2446 (24)
B	2365 (37)	2388 (99)	2439 (54)	2446 (78)
B	2274 (165)	2203 (81)	2294 (116)	2256 (91)
A	2199 (0)	2133 (0)	2236 (1)	2190 (0)
A	1764 (59)	1862 (68)	1855 (41)	1925 (51)
B	1643 (181)	1863 (511)	1810 (330)	1919 (456)
A	1436 (1)	1433 (5)	1461 (1)	1460 (3)
B	1371 (922)	1288 (503)	1319 (409)	1306 (297)
A	1178 (10)	1198 (12)	1229 (14)	1243 (15)
B	1167 (48)	1190 (17)	1222 (35)	1239 (16)
B	1147 (32)	1169 (155)	1203 (124)	1216 (183)
B	1108 (165)	1112 (223)	1139 (188)	1146 (261)
A	1088 (0)	1129 (0)	1150 (0)	1181 (1)
A	961 (0)	989 (2)	1006 (3)	1041 (7)
B	951 (2)	977 (2)	1006 (7)	1031 (9)
B	916 (1)	950 (9)	969 (4)	988 (7)
B	862 (52)	889 (0)	881 (14)	897 (1)
A	813 (0)	846 (0)	847 (0)	870 (0)
B	772 (110)	584 (261)	644 (240)	568 (167)
A	733 (0)	742 (0)	748 (0)	756 (0)
A	651 (1)	593 (1)	635 (1)	604 (2)
B	512 (10)	392 (68)	480 (77)	385 (27)
B	384 (23)	366 (196)	369 (15)	322 (323)
A	197 (8)	248 (0)	220 (0)	285 (0)
A	69 (0)	184 (9)	190 (8)	192 (9)

[a] Frequencies are in decreasing order for DZP/MP2 and then in decreasing order within each symmetry group for the other columns.

Table 3. Relative Energies of B_3H_9 Structures (Energies in Hartree and Relative Energy to Cyclic Structure in kcal mol^{-1})

method	cyclic C_{3v}	pentacoordinated	$B_2H_6 + BH_3$
SCF/DZP[a]	−79.19529	−79.18895 (4.0)	−79.20903 (−8.6)
CISD/DZP[a]	−79.54113	−79.53540 (3.6)	−79.53489 (3.9)
CCSD/DZP// CISD/DZP[a]	−79.58535	−79.57981 (3.5)	−79.57494 (6.5)
MP2/DZP	−79.57262	−79.56714 (3.4)	−79.55548 (10.7)
MP4SDQ/DZP// MP2/DZP	−79.63217	−79.62687 (3.3)	−79.62013 (7.5)
QCISDT/DZP// MP2/DZP	−79.64348	−79.63813 (3.3)	−79.62873 (9.2)

[a] Reference 9. Korkin et al.[12] give the pentacoordinated structure 3.7 kcal mol^{-1} above the cyclic structure.

sets. Optimum geometries were obtained using the SCF method, the Moller−Plesset perturbation method of order two (MP2)[16] method (with explicit consideration of all electrons), and the CISD method with core orbitals excluded from the configuration interaction expansion. Analytic first derivatives were used at all three levels of theory. The convergence criteria was the GAUSSIAN OPT=TIGHT criteria (e.g. root mean square of forces less than 1.0×10^{-5}). Vibrational frequencies were estimated using analytic second derivatives for the SCF and MP2 methods and numerical second derivatives for the CISD method. Energies were also evaluated at the DZP/MP2 optimized geometry using the Moller−Plesset perturbation method of order four using the space of single, double, and quadruple substitutions (MP4SDQ)[17] and the quadratic configuration interaction method including single and double substitutions with a triples contribution to the energy (QCISDT).[18]

In Table 1 we present the optimized geometries at the stationary point. The SCF/DZP and CISD/DZP results agree closely with those reported previously. The lowest harmonic vibrational frequency (in cm^{-1}) is also listed. Both SCF stationary points are transition states with one imaginary frequency, while both MP2 and CISD stationary points are local minima. The large change in the geometry of the stationary state from SCF/DZP to CISD/DZP was one of the factors that suggested a local minimum at the CISD level. It is clear from Table 1 that changes from SCF to MP2 are even more marked. The sensitivity of other triborane(9) structures to the level of correlated theory has been noted by Stanton et al.[6] We note that the addition of polarization functions to the basis set is critically important. Both the 6-31G and the DZ basis set (identical to 6-31G** and DZP respectively but with the polarization functions removed) at the MP2 level of theory give one imaginary vibrational frequency.

The structure is clearly bonded by four hydrogen bridges from a pentacoordinated boron atom, with no significant nonbonded interactions. At the DZP/CISD level of theory the B_1-B_7 distance is 1.834 Å, only slightly larger than in diborane. The outer boron atoms are well separated at 3.269 Å. The closest nonbonded H−H distance is H_3-H_9 at 1.952 Å, while the H_9-H_{11} distance is 2.095 Å. The two bridge regions are well separated with the closest H−H distance being H_3-H_6 at 1.889 Å. The $H_{11}-H_{12}$ distance is 3.302 Å. The bridge regions are highly asymmetric with H_3 being 1.253 Å from B_7 and 1.501 Å from B_1. In contrast H_5 is more central being 1.304 and 1.331Å from B_7 and B_1, respectively.

In Table 2 we present the MP2 and CISD vibrational frequencies and IR intensities for p-B_3H_9. Agreement between the various methods and basis sets is only qualitative, but all suggest prominent IR features in the 1300−1400 and 1640−1920 cm^{-1} regions. In contrast our previous work[10] suggests that the cyclic structure will show its largest peaks above 2200 cm^{-1}.

Table 3 gives some estimates for the energy difference between the pentacoordinated and cyclic structures and the dissociation products, B_2H_6 and BH_3. The pentacoordinated structure lies only 3 kcal mol^{-1} above the cyclic structure, while both structures are stable with respect to dissociation to diborane and borane.

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(16) Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(17) Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91. Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.

(18) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

These results strongly suggest that p-B_3H_9 is a second isomer of triborane(9). Previous work[10] suggests that the barrier to its formation from BH_3 and B_2H_6 will be small, while the barrier to the cyclic structure is expected to be large. Several attempts were made, all without success, to locate a transition state for the formation of p-B_3H_9 from B_2H_6 and BH_3. It is possible that the barrier for step II is zero. These results are consistent with the previously proposed mechanism:[9,19]

$$B_2H_6 \rightleftarrows 2BH_3 \qquad \text{(I)}$$

$$BH_3 + B_2H_6 \rightarrow B_3H_9 \qquad \text{(II)}$$

$$B_3H_9 \rightarrow B_3H_7 + H_2 \qquad \text{(III)}$$

with step II fast and step III slow, with one small modification. Step II is replaced by step IIa:

$$BH_3 + B_2H_6 \rightarrow \text{p-}B_3H_9 \qquad \text{(IIa)}$$

and step III is replaced by steps IIIa and IIIb:

$$\text{p-}B_3H_9 \rightarrow \text{cyclic } B_3H_9 \qquad \text{(IIIa)}$$

$$\text{cyclic } B_3H_9 \rightarrow B_3H_7 + H_2 \qquad \text{(IIIb)}$$

Step IIa will be fast, followed by a slow step IIIa. In contrast, Stanton et.[8] suggest that step II will be slow and step III (our step IIIb) will be fast. A fast step IIIb is not, of course, inconsistent with the evidence if step IIIa is slow. It is also possible that p-B_3H_9 dissociates slowly to B_3H_7 and H_2 directly without going through the cyclic structure. These results differ from the conclusion of Lipscomb et al.,[20] who find a transition state for the attack of a BH_3 on the bridge hydrogen atom of diborane with a barrier over 13 kcal mol^{-1}. Attack on the terminal hydrogen, giving p-B_3H_9, appears to occur with a lower barrier. Lipscomb et al.[19] also suggest that the direct reaction

$$B_2H_6 + BH_3 \rightarrow B_3H_7 + H_2$$

is a possible mechanism.

Further experimental work is required to investigate whether this second isomer of triborane(9) can be characterized and whether it is indeed involved in the pyrolysis reaction. Our theoretical characterization of this isomer does not resolve the controversy regarding the mechanism for the pyrolysis reaction of diborane, but the pentacoordinate structure does appear to be a likely candidate for inclusion in the mechanism.

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(19) Enrione, R. E.; Schaeffer, R. *Inorg. Chem.* **1961**, *8*, 103. Brennan, G. L.; Schaeffer, R. *Inorg. Nucl. Chem.* **1961**, *20*, 205.

(20) Lipscomb, W. N.; Stanton, J. F.; Connick, W. B.; Magers, D. H. *Pure Appl. Chem.* **1991**, *63*, 335.