

Article

SOME SYSTEMATICS AND SURPRISES IN THE ENERGETICS AND STRUCTURAL PREFERENCES OF “FEW-BORON SPECIES” AND RELATED COMPOUNDS WITH CARBON AND NITROGEN

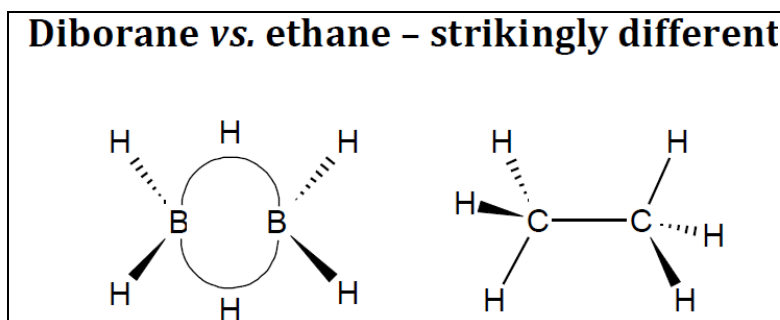
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ABSTRACT

This paper discusses the energetics and structural preferences of “some few-boron species”, BH_3 , B_2H_6 , $[\text{B}_3\text{H}_8]^-$ and B_3H_9 , B_4H_{10} and B_4H_{12} and the corresponding isoelectronic hydrocarbons CH_2 , C_2H_4 , C_3H_6 , C_4H_6 and C_4H_8 . Nitrogen hydrides are also briefly discussed as are substituted derivatives. Both systematics and surprises are found.



Keywords: boranes, hydrocarbons, nitrogen hydrides, isomer stabilities and preferences

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1. INTRODUCTION

Boron forms a large variety of binary species containing hydrogen. These substances are now generally called boranes, occasionally still called boron hydrides, and historically through the decades, almost never named hydroborons. By simply counting the number of SciFinder citations given for each compound of interest [1], we find the most thoroughly studied species so described are the neutral diborane(6) and decaborane(14), B_2H_6 and $B_{10}H_{14}$ with ca. 9000 and 2000 reference citations respectively (very often with the total hydrogen count, 6 and 14, ignored in the name), and the anionic borohydride (most often $[BH_4]^-$ but also quite commonly $[B_3H_8]^-$, $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$) with ca. 45000 reference citations respectively. The list of species containing only boron and hydrogen is extensive, although admittedly much shorter than that of binary species of carbon with hydrogen.

2. THE TWO BORON SPECIES, B_2H_6 , THE RELATED HYDROCARBON C_2H_4 , AND THEIR ONE-BORON AND ONE-CARBON MONOMERS

Isoelectronic with B_2H_6 is ethylene, C_2H_4 , which is among the simplest of all the hydrocarbons, and indeed, we are reminded of the early description of diborane(6) as having “a protonated double bond” [2]. Both diborane(6) and ethylene are highly stable as written and isolable as bulk, macroscopic samples, while neither species is isolable in the form of its corresponding isoelectronic one-carbon and one-boron monomer, CH_2 and BH_3 respectively, [3-6]. We note an immediate difference between CH_2 and BH_3 : they are respectively a ground state triplet and singlet. Among the earliest electron diffraction studies ever reported was an investigation of B_2H_6 [7] which incorrectly suggested a structure like that of ethane, C_2H_6 . For a discussion of the differing structures of diborane(6) and ethane within the molecular orbital framework, see [8-10] respectively. However, nearly two decades before the expressions “the STYX rules” and “3-center bonds” entered the chemist’s vocabulary [11] and just before the aforementioned electron diffraction study [7], there was a molecular orbital based discussion of B_2H_6 in which this species was assumed to have the ethane-like structure [12].

3. THE CORRESPONDING BH_3 AND CH_2 TRIMERS, TRIBORANE(9), CYCLOPROPANE, AND ALSO $[B_3H_8]^-$

The corresponding BH_3 and CH_2 trimers, B_3H_9 and C_3H_6 are recognized as cyclopropane and triborane(9) respectively. Indeed, long predating the conceptually useful alternative (but nowhere recommended) name of ethylene as “cycloethane” [13,14], in the late 19th and early 20th centuries cyclopropane and its derivatives were not uncommonly named “trimethylenes”. Indeed, occasionally the words “cyclopropanes” and “trimethylenes” were both used in the same article [e.g.15]. However, there is a profound distinction between C_3H_6 and B_3H_9 . While cyclopropane and numerous derivatives are isolable, see the monographs [16,17], the latter species triborane(9) is but a transient intermediate associated with processes such as the gas phase reaction of diborane(6) with BH_3 [18], the protonation of $[B_3H_8]^-$ salts [19-21] and

diborane(6) pyrolysis [22,23]. These studies suggest that 3-membered all-carbon rings are stable but 3-membered all-boron rings are not (by saying all-boron rings we neglect any bridging H's in the ring atom count). Ethylene and its substituted counterparts generally do not equilibrate or otherwise interconvert with the corresponding cyclopropanes.

The thermolysis reaction of the formally simplest case of cyclopropane



is endothermic [24], entropically favored (two molecules forming three), and unobserved in either direction. (At STP, this reaction may be readily calculated to have fortuitously close to a zero free energy change, and not surprisingly shows a significant temperature variation [25].) Corresponding reactions are also generally not seen for substituted derivatives of cyclopropane and ethylene. Among the few recorded cases [26,27] of thermolysis of a cyclopropane to form the corresponding ethylene is that of the perfluorinated hexafluorocyclopropane, a species known to be highly strained as discussed in [28-31]. (We exclude from our discussion of ethylene/cyclopropane and dimer/trimer interconversions, the extrusion of a carbene from a cyclopropane and the more common reverse addition reaction.)

Computational chemistry affirms the exothermicity of the transformation of triborane(9) into diborane [21,32-35].



We now remind the reader that B_3H_9 was taken as the hydrogen bridged 3-membered ring species $[\text{BH}_2(\mu\text{-H})]_3$ much as B_2H_6 is the hydrogen bridged $[\text{BH}_2(\mu\text{-H})]_2$. After all, there is another isomer of B_3H_9 , $\text{H}_2\text{B}(\mu\text{-H})_2\text{BH}-\text{BH}_2(\text{H}_2)$ which is computationally found [34,35] to be even less stable than the aforementioned species and has ignored in most discussions of the chemistry of boranes.. Additionally, solution-phase protonation of the well-known $[\text{B}_3\text{H}_8]^-$ anion results in complexes of B_3H_7 [20] and of BH_3 [19]. As found in numerous salts, it is well-established crystallographically that $[\text{B}_3\text{H}_8]^-$ has the 3-membered ring structure $[(\text{BH}_2)_2(\mu\text{-H})_2\text{BH}_2]^-$ accompanied in the solid by diverse cations: $[(\text{H}_3\text{N})_2\text{BH}_2]^+$ [36]; $[\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{CH}_3)_3]^+$, [37]; Cs^+ [38]; $[(\text{C}_6\text{H}_5)_4\text{P}]^+$ [39]; $[\text{NH}_4]^+$, [40]; Na^+ [41]. The $[\text{B}_3\text{H}_8]^-$ isomer with the structure $[\text{H}_2\text{B}(\mu\text{-H})_2\text{BH}-\text{BH}_3]^-$ remains experimentally unknown, and computationally is found to be less stable than $[(\text{BH}_2)_2(\mu\text{-H})_2\text{BH}_2]^-$ [34,35].

By contrast, propene, simply describable as CH_2CHCH_3 (as well as speaking of it as a simply substituted derivative of ethylene), is 33 kJ mol^{-1} more stable than the likewise isolable cyclopropane [24]. Comparable differences of enthalpies of formation differences are found for the four methylpropenes (isomeric butenes) and methylcyclopropane [24], and for the vinylpropenes (isomeric methylbutadienes and pentadienes) and vinylcyclopropane [42,43]. Relatedly using the enthalpy of formation data in [24], the isomeric cyanopropenes, whether the species chosen is the (*E*)-1-, (*Z*)-1-, and 3-derivative, are some $30\text{--}50 \text{ kJ mol}^{-1}$ more stable than cyanocyclopropane. (There are seemingly no experimental thermochemical data on the 2-derivative, a species more commonly known as methacrylonitrile.) This difference is more than doubled to 110 kJ mol^{-1} for the formally related species with two vinyl and cyclopropane moieties apiece as found in 1,3-butadiene, $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$, and bicyclobutane, $\text{CH}_2(\text{CH})_2\text{CH}_2$, and almost doubled for the species with one double bond and one cyclopropane, namely methylenecyclopropane [24].

4. TETRABORANE(10) AND BICYCLOBUTANE, THEIR ISOMERS, DERIVATIVES AND SUBSTITUENT EFFECTS

We have earlier said that B₃ rings are unstable compared to 2-boron species as found in the comparison of B₂H₆ and B₃H₉, but more stable as found for the two isomers of the 3-boron [B₃H₈]⁻ e.g. [32,34]. So, what is the case for B₄H₁₀? The 4-boron tetraborane(10) has been experimentally shown by electron diffraction and microwave spectroscopy [44,45] to have a structure related to that of bicyclobutane, cf. BH₂(μ-H)₂(BH)₂(μ-H)₂BH₂ and CH₂(CH)₂CH₂. Computational theory [46-49] shows BH₂(μ-H)₂BH–BH(μ-H)₂BH₂ to be slightly less stable than BH₂(μ-H)₂(BH)₂(μ-H)₂BH₂, where we remember the former had been earlier suggested for B₄H₁₀ [2]. (Still earlier electron diffraction measurements suggested a BH₃–BH₂–BH₂–BH₃ butane-like structure [50, cf. 7].) In other words, C₄H₆ prefers the 1,3-butadiene structure with two ethylenes and not two 3-membered rings, i.e., CH₂=CH–CH=CH₂ and not bicyclobutane, CH₂(CH)₂CH₂ while B₄H₁₀ prefers the structure BH₂(μ-H)₂B₂(μ-H)₂BH₂ with two 3-membered rings and not BH₂(μ-H)₂BH–BH(μ-H)₂BH₂.

Substituents have been shown to significantly affect the strain energies of the derivatives of ethylene (cf. the aforementioned cycloethane), cyclopropane and bicyclobutane [14]. In that the last cited paper dealt with substituent effects and strain energies, we accordingly wonder what will be found for the related derivatives of B₂H₆, [B₃H₈]⁻ and B₄H₁₀? How will the energies and enthalpies of formation of substituted diborane(6) derivatives, B₂H₅X, both H₂B(μ-H)(μ-X)BH₂ and H₂B(μ-H)₂BHX, compare with those of the ethylene-based vinyl derivatives, CH₂CHX? The last decade has seen a renaissance in thermochemical studies of vinyl derivatives. Along with many examples [24] for vinyl species, e.g. X = H and diverse alkyl, phenyl and other hydrocarbon substituents, we now have enthalpies of formation for the vinyl species: X = Cl [51], Br [52], I [51], CHO [53], COOH [54], CN [55]. This is not the case for the monosubstituted diboranes. Reliable structures have been reported, but these studies are without corresponding energetics data whether it be as enthalpies of formation. We have “merely” relative isomer stabilities from which it is assumed that the observed isomer is the more stable. Examples include X = CH₃ [56], NH₂ [57], SCH₃ [58], Cl [59], Br [60].

How does the enthalpy of formation difference of (BH₂(μ-H))₂BHX and its isomer with bridging X depend on the group X? What about the isomeric substituted tetraboranes wherein the substituent may be on boron 1, boron 2 (both endo- and exo-) or replace one of the bridging hydrogens? Almost nothing is known from either experiment or computational theory: thermodynamic and kinetic data are almost totally absent as to the role of substituents in their diverse positions on the stability of boranes. Among the few relevant observations include methyl diborane is known from experiment [61] to methylate tetraborane, but from the results of quantum chemical calculations [14] we may deduce the related trans-methylation reaction of propene and bicyclobutane to form ethylene and (either 1- or 2-(exo))methylbicyclobutane is significantly endothermic. Monomeric trimethylboron exchanges hydrogen and methyl groups with diborane to form methyl diboranes [62] – does this tell us that methylation stabilizes a plausible triborane(9) intermediate.

5. TETRABORANE(12) AND CYCLOBUTANE

We close with a brief discussion of the experimentally still unknown B₄ species, tetraborane(12) for which the structure [BH₂(μ-H)]₄ is plausible [22,63]. This species is a formal dimer of diborane(6). However, the reaction



has not been observed experimentally although B₂H₆ and its isotopomers shuffle borons and hydrogens [64,65]. Indeed, the dimerization of diborane is seriously endothermic [33,35] according to calculational theory, and is clearly entropically disfavored as well. (We now acknowledge that the original experimentalists suggested the exchange reaction proceeds through the intermediacy of BH₃.)

We recognize [BH₂(μ-H)]₄ as analogous to cyclobutane (what other structures could we have [66,67]. None of this is surprising. Ethylene and olefins in general are much more common than cyclobutane and its corresponding substituted derivatives [68]. The dimerization reaction



for the parent hydrocarbons is not observed, and for substituted counterparts the reaction is rarely observed without catalysts or photochemical excitation. However, this last reaction of two ethylenes is enthalpically favorable. This nonreaction is unquestionably fortuitous – had the double bonds in so many biomaterials, such as the nucleobases uracil and thymine, unsaturated fatty acids and related triglycerides, the steroidal cholesterol, progesterone, testosterone and the multiple forms of vitamin D, vitamin A and the carotenoids, chosen to dimerize, life would be unrecognizable if not unrealized.

6. STILL OTHER FEW-BORON CONTAINING SPECIES

There are yet other few-boron containing species. These include the nominally homologous series B₂H₂, B₃H₃ and B₄H₄. Are they truly homologous and so reminiscent of the per-aza-cycloalkanes N_xH_x diimide, triaziridine, tetrazetidine and their acyclic counterparts [69]. The first species B₂H₂ has been observed [70] in a cryogenic matrix to be the linear triplet H–B=B–H with a pair of degenerate singly occupied π orbitals. What about the still unknown isomer H₂B–B? We are reminded of diimide and its substituted counterparts, azo compounds, and their fragile and much less stable isomers H₂N–N and aminonitrenes [71]?

The existence of B₃H₃ has been inferred from the presence of its parent ion via mass spectrometry [72]. As such, it remains experimentally unknown whether neutral B₃H₃ is either of the 3-membered ring species, the B–B or B(H) bridged (BH)₃ and [B(H)]₃ respectively, or perchance a BH₂ derivative of B₂H₂, H–B=B–BH₂. Triaziridines and triazenes, cyclo-(NR)₃ and R–N=N–NR₂ respectively, are both established classes of compounds) although their enthalpy of formation difference remains unavailable [73]. From experiment, we know of the enthalpy of formation of few triazenes (e.g. diphenyltriazene [24]) and no triaziridine at all. The inherent complexity of B₄H₄ is demonstrated by highly colored tetraamino derivatives, the blue and yellow diisopropylamino and tetramethylpiperidino species with their nonplanar central rings [74] and the tetrahedral mixed halo and tetra-tert-butyl species [75]. So, what about N₄H₄ and its derivatives? The

enthalpy of formation of some tetrazenes is available from experimental measurements but no tetrahedral assemblage of nitrogens including N_4 is known for comparison. So, what about yet another B_4H_4 isomer, $BH_2-B=B-BH_2$? There are seemingly few related species, much less relevant data. Indeed, only its 1,4-dioxo derivative B_4O_2 [76] and its radical anion come to mind. Barring meaningful comparisons, discussion of all of these species in this concluding section of the current article will thus be deferred.

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