The B_6H_{14} Problem: Generation of a Catalogue of Conceivable Isomers

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ABSTRACT

The structure-generating feature of the computer program RAIN (reactions and intermediates networks) was used to produce the complete set of 48 conceivable B_6H_{14} isomers with twofold constitutional symmetry. The constitutional isomers are built from BH units and contain up to two closed BBB three-center bonds.

INTRODUCTION

Sixty years after Stock's fundamental work on borane chemistry [1], the theoretical studies on this interesting class of compounds found their first culmination, mainly associated with the name Lipscomb [2]. The completely unexpected structural principles required considerable extensions of MO theory and still pose unsolved questions.

The structures of neutral boranes B_nH_m and borane anions $B_nH_m^{x-}$ can be subdivided into five main classes. The groups of *closo*, *nido*, and *arachno* structures (as defined by Wade's rules [3,4]) were augmented by the *hypho* and *conjuncto* boranes [5,6]. *Hypho* boranes with $2n + 8$ framework electrons should have fairly open structures with considerable flexibility. One new member of this compound class, B_6H_{14}, could be obtained by dimerization of B_3H_7 and was characterized by its ^{11}B NMR spectrum [7]. However, until now, B_6H_{14} resisted all attempts to correctly elucidate its structure. Ab initio calculations [8–10] and combined ab initio/NMR simulations [11] could not explain the experimental results. For this reason, it is of considerable interest to have available a complete list of *all conceivable isomers*. This could be the foundation of further theoretical investigations.

METHODS

Since the mid-1980s, we developed the PC program RAIN (reactions and intermediates networks) [12–14]. It produces reaction pathways using a formal reaction generator [15], together with a reaction network management system. The possible applications of RAIN are numerous. Structure generation is one of the most interesting operating modes of RAIN [16]. RAIN's reaction generator produces isomeric ensembles of molecules (EM) [17] from a starting ensemble. It is guided by a set of formal constraints that mainly limit the complexity of electron redistribution and bond breaking/making processes. If all these constraints are set to an infinite value, RAIN generates the family of isomeric EM (FIEM) from a collection of atoms, multiatomic systems, or multivalent fragments. Any list of forbidden, allowed, or required substructures can be set up to control the generating process.

According to the underlying theory of the be- and r-matrices [17], RAIN and its structure generator can only handle integer bond orders of degree one to three. The exceptional borane structures therefore require the following special approach.

It is assumed that the constitutional isomers of B_6H_{14} can be constructed from BH—respectively BH_2—units without exception; i.e., $B_6H_{14} = (BH)_6H_8$. All but one of the isomers considered in the literature fulfill this requirement. The only exception is structure 2f in Ref. [11]. Figure 1 shows the con-

Dedicated to Prof. Dr. Heinrich Nöth on the occasion of his sixtieth birthday.

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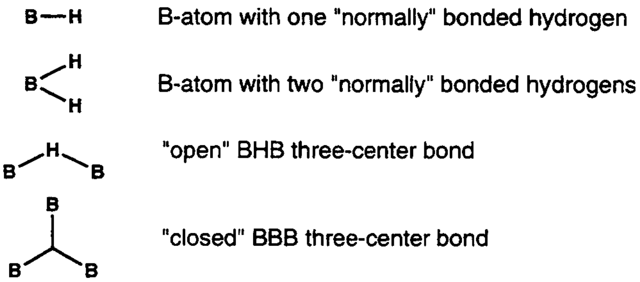


FIGURE 1 Building blocks used for the generation of B_6H_{14} isomers.

stitutional units of the B_6H_{14} isomers that were used in this study.

Each BH unit can contribute two electrons to skeletal bonds. A hydrogen atom naturally delivers one electron that can be located in a two-center MO or a three-center MO. In order to meet the requirement of bond orders being integers, all numbers of valence electrons and the bond orders of the BH—respectively H—(pseudo)atoms are formally multiplied by a factor of 2. Additional dummy atoms of valence 4 are defined that form the centers of closed BBB three-center bonds. Figure 2 shows the complete composition of the starting EM together with the allowed valence schemes of the building blocks. A representative example of a generated B_6H_{14} constitutional isomer is shown in Figure 3.

In his famous book about boron hydrides [2], Lipscomb gave a list of seven rules for the stability of boron hydride structures. The most important rule is: "... all known boron hydrides have at least a twofold element of symmetry ..." In order to select among all possible B_6H_{14} isomers those that fulfill this rule, a special filter module was constructed that takes care of the molecular symmetry. The application of the canonical numbering module [18], which is used for redundancy-free storage of structures, yields so-called equivalence indices. These indices are assigned to the individual atoms of a structure. If two atoms have the same index, they are constitutional equivalent. Structures with constitutional twofold symmetry can be recognized by the following rule: if there is any equivalence class that is occupied by exactly one single atom, the neighbors of this atom may only be assigned up to two different equivalence indices. It should be noted that this symmetry constraint is only an additional option to the constraints under which the RAIN structure generator operates. Of course, this option being switched off, RAIN is also able to deal with molecules lacking symmetry.

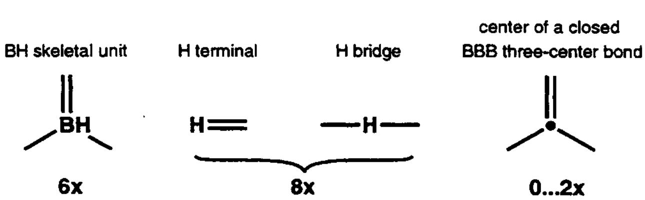


FIGURE 2 Starting ensemble for the structure generation.

RESULTS AND DISCUSSION

The structure generator of RAIN produced a total of 130 different constitutional isomers of B_6H_{14}. Among them, 48 structures were selected by the symmetry constraint module as described earlier. Figure 4 shows these 48 structures in a modified half-topological representation. A literature search yielded eight different B_6H_{14} isomers that have been considered by different authors up to now. The very first proposal was made by Lipscomb [2], of course without having any experimental data. Naturally, all constitutional isomers referenced in the literature that are built from BH units are contained in the complete set of structures compiled in Figure 4. Table I gives a cross-reference list of this subset and those numbers that were used by the different authors in their publications.

There still remain 40 constitutional isomers of B_6H_{14} that should be considered in further theoretical and experimental studies. However, the situation may be even more complicated, because B_6H_{14} seems to have a fluxional structure. Many of its isomers occupy points of similar energy on the potential energy hyper surface [11].

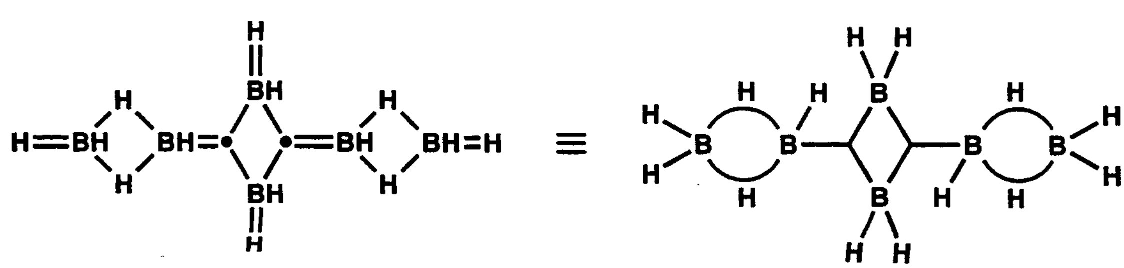
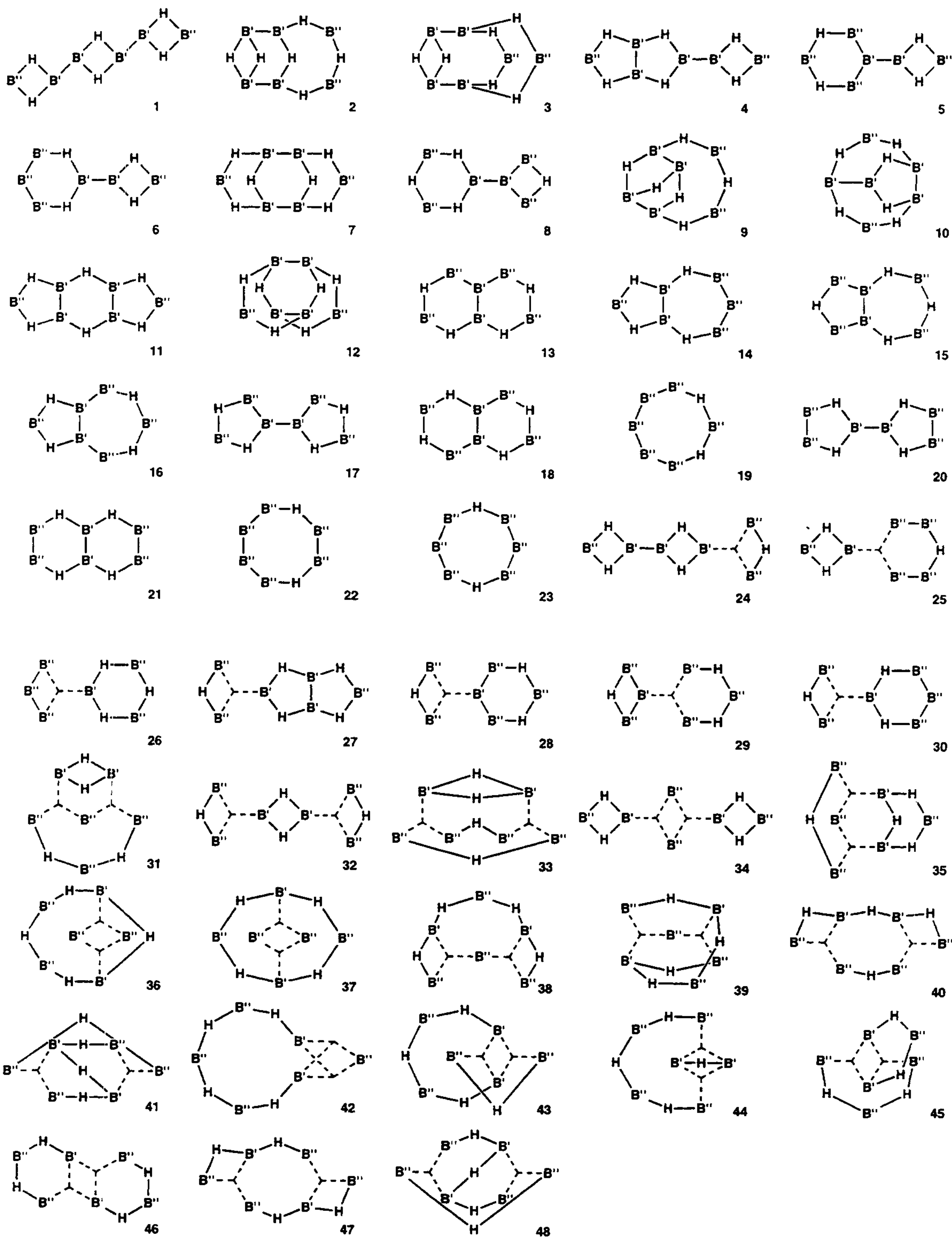


FIGURE 3 Example of generated B_6H_{14} structure.



B' = BH B'' = BH$_2$

B–H–B = open BHB three-center bond

B–B–B = closed BBB three-center bond

FIGURE 4 Set of conceivable B_6H_{14} isomers.

TABLE 1 Cross Reference List of Isomers (Figure 4) That Were Considered in the Literature

Number	*Structure Number or Styx Notation of Corresponding Isomer in the Literature*					
	Ref. [2]	*Ref.* [7]	*Ref.* [8]	*Ref.* [9]	*Ref.* [10]	*Ref.* [11]
1	—	—	2a	1	1a	2a
11	—	6022	2b	2	1b	2b/2d
24	—	—	2c	—	1c	—
32	—	—	2d	3	1d	2c
34	—	—	2e	—	1e	—
38	—	—	—	—	—	2e
46	4204	—	—	—	—	2g
47	—	4204	—	—	—	—

EXPERIMENTAL

The structure generation was carried out with RAIN Version 2.0 on an IBM PC with an 80486/33MHz processor. The elapsed CPU time was 11.5 hours. The graphical output of the generated structures was manually reprocessed for better clarity.

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