A Diborane Story**

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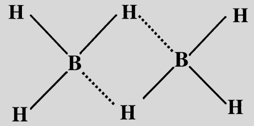
Just as with ferrocene,[1] the formula first written for diborane B_2H_6 was orthodox, conforming with the usual paradigmatic rules regarding molecular structure. However, it was wrong. Correcting the mistake showed an extremely unusual bonding picture for the molecule. Just as in the ferrocene case, it opened up a whole new chapter of chemistry, later recognized with the award of a Nobel prize to William N. Lipscomb in 1976 for "his studies on the structure of boranes illuminating problems of chemical bonding."

I shall highlight here only a few episodes from the diborane story. Act 1: In 1937, a former student of Linus Pauling, Simon H. Bauer—an outstanding physical chemist still very much active in research at Cornell at the age of 88—applied the technique of electron diffraction, a tool that he had learned to use at Caltech with Pauling, to diborane. He found and reported a structure analogous to that of ethane, which he therefore wrote as $H_3B{-}BH_3$.[2] In 1942 Bauer reiterated his contention of the ethane-like structure for diborane.[3]

At the same time of the early 1940s, H. I. Schlesinger, a chemistry professor at the University of Chicago, was also working on boron compounds. One of the reasons was his involvement in the Manhattan Project: it was thought that separation of the isotopes of uranium could be devised using such derivatives. In any case, Schlesinger was very much interested in the structure of diborane.

Thus Schlesinger wrote a letter to Linus Pauling at Caltech on January 3 1941.[4] Let me quote:

> As a result of our work on the metallo borohydrides I definitely feel that a structure for diborane quite different from those generally proposed, would aid in correlating many of the observations we have made. … Curiously enough I have just now received a reprint of a Russian article on hydrides of boron… I gather from some of the formulae in the article that the author has come to a conclusion very similar to mine.
> The structure I have in mind is a bridge structure, in which the two boron atoms are joined to each other through an unusual type of hydrogen bond, perhaps best represented by the following formula



From hindsight we know this Schlesinger formula to be the correct one. Also, he ought to have shared in the recognition for proposing such a bridged structure. End of Act II.

Act III was brief. Pauling wrote back by return mail (January 7 1941)[4]

> I do not feel very friendly toward the structure which you mention in your letter for the diborane molecule. So long as the suggested structure remains vague and indefinite, it is not easy to say that it is eliminated by electron diffraction data or other data. However, the force constant for the B–B vibration is I think much stronger than would be expected for a structure of this type, in which there is no direct B–B bond.

In other words, at this point Pauling, with his considerable insider knowledge of structural chemistry, not only shot down the correct structure that Schlesinger had come up with, but he also indirectly convinced him not to bring it into print. What a shame![5] When Schlesinger did publish his review, he had summarized the chemical and physical properties of boron hydrides in terms of an ethane-like structure containing electron-deficient boron–hydrogen bonds.[6]

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Act IV occurred soon afterwards. An undergraduate student by the name of H. Christopher Longuet-Higgins was at Balliol College, in Oxford. He was only in his second year of study when he became interested in this question of the diborane structure. He too came up with the same bridged structure after examining all the physical evidence and after thinking out an adequate theoretical description. His paper, signed jointly with one of the professors of chemistry from Balliol, R. P. Bell (a reputed physical chemist), appeared in 1943 in the *Journal of the Chemical Society*.[7] Longuet-Higgins would go on to become one of the worlds leading chemical theoreticians.

There was even a precursor found (as is almost invariably the rule with science discoveries[8]): Dilthey had anticipated the bridged structure as early as 1921[9] and this was revived by Russian scientists in the early 1940s[10, 11] (Schlesinger was referring to them in his letter to Pauling).

Act V saw the consolidation of the bridged structure of Schlesinger, Longuet-Higgins, and others (such as Dilthey and the Russian scientists). In 1947–48 Price confirmed the earlier (1940, 1941) infrared spectroscopic evidence by Stitt[12, 13] and interpreted it in favor of the bridged structure.[14, 15] Shoolery brought to bear clinching nmr evidence.[16] Three different theorists (Mulliken, Pitzer, and Walsh) gave molecular-orbital and valence-bond descriptions of the bridged structure in 1946 and 1947.[17–19] In 1951 Hedberg and Schomaker did another electron-diffraction study, which showed that the data ruled out the open structure and was consistent with the bridged structure only.[20]

Yet, in the second edition of *The Nature of the Chemical Bond*, which came out in 1945, Linus Pauling devoted a full 3.5 pages to presenting diborane as an ethane-like structure on the strength of both G. N. Lewis's conceptualization[21] of this molecule with "six electron pair bonds resonating amongst seven positions" and of S. H. Bauer's electron diffraction work.[22] True, his influence on structural chemistry was on the wane: in the felicitous wording of Mary Jo Nye, his valence-bond approach to molecular structure "earned most chemists' allegiance, at least up until 1940."[23]

Both stories, that of ferrocene[1] and that of diborane, have a strong resemblance. They both bear out an account of scientific revolutions in the style of Kuhn.[24] Both compounds were anomalies within the existing paradigms. Their representations disobeyed "conventional wisdom" to make use of the expression pioneered by Galbraith.[25] Accordingly, they suffered from a birth defect. Both were incorporated into existing knowledge, at a high cost. Their formulas were inconsistent with some of the experimental evidence, some of the data had been inadvertently misread because of the paradigmatic bias.

Both stories are inconsistent with the notion, central to a sociologist of science such as Bloor, of a Symmetry Principle.[26] According to this methodological edict the historian or the sociologist of science should give equal footing to the two types of theories of nature, whether they are winners or losers. There is, to the contrary, blatant dissymmetry in both the ferrocene[1] and the diborane case. Their first investigators could not bring themselves to see, let alone accept, the correct structure because the existing knowledge did not allow it. In order to make room for the correct formulation, two moves had to occur: a theoretical description for the novel entity had to be provided, and those parts of the experimental evidence earlier glossed over because they did not jibe with the postulated structure had to be retrieved from the waste basket. As an empirical natural philosopher, I must credit Thomas Kuhn with an operationally valid description, and I must beg to disagree with Bloor's symmetry principle: in both cases, the difference between the winning side and the losing side was not historically contingent and socially determined.

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[1] P. Laszlo, R. Hoffmann, *Angew. Chem.* **2000**, *112*, 127; *Angew. Chem. Int. Ed.* **2000**, *39*, 123.

[2] S. H. Bauer, *J. Am. Chem. Soc.* **1937**, *59*, 1096.

[3] S. H. Bauer, *Chem. Rev.* **1942**, *31*, 46.

[4] This letter is held in the Pauling Archive at Oregon State University, in Corvallis.

[5] The more so that valence-bond theory provides a fine description of diborane, accounting nicely for the strong boron–boron bond. Pauling was also mistaken in one comment: the force field is overdetermined and the molecular vibrations can be fit without a B–B bond. I am grateful to Roald Hoffmann for this clarification.

[6] H. I. Schlesinger, A. B. Burg, *Chem. Rev.* **1942**, *31*, 1. Alfred Stock's dogma of an ethane-like structure for diborane also cast its long shadow.

[7] H. C. Longuet-Higgins, R. P. Bell, *J. Chem. Soc.* **1943**, 250.

[8] Here is an example: Bernal and Kauffman have shown (including experimentally!) that Edith Humphrey had prepared enantiomerically pure crystals during her Ph.D. in Alfred Werner's Zürich laboratory, which Werner never bothered to make polarimetric measurements on. Had he done so, he would have been provided with an unequivocal proof of the soundness of his coordination theory, for which he won the Nobel Prize: I. Bernal, G. B. Kauffman, *J. Chem. Educ.* **1987**, *67*, 604; I. Bernal, *The Chemical Intelligencer* **1999**, 28–31. For priority and multiple discoveries, see P. Laszlo, *La découverte scientifique*, PUF, Paris, **1999**.

[9] W. Dilthey, *Z. Angew. Chem.* **1921**, *34*, 596.

[10] B. V. Nekrassov, *J. Gen. Chem. URSS* **1940**, *10*, 1021; B. V. Nekrassov, *J. Gen. Chem. URSS* **1940**, *10*, 1156.

[11] Y. K. Syrkin, M. E. Dyatkina, *Acta Physicochim. URSS* **1941**, *14*, 547. These insightful and brave scientists suffered much as a consequence of the infamous 1951 resonance theory conference and scandal (Roald Hoffmann, private communication).

[12] F. Stitt, *J. Chem. Phys.* **1940**, *8*, 981.

[13] F. Stitt, *J. Chem. Phys.* **1941**, *9*, 780.

[14] W. C. Price, *J. Chem. Phys.* **1947**, *15*, 614.

[15] W. C. Price, *J. Chem. Phys.* **1948**, *16*, 894.

[16] J. N. Shoolery, *Discuss. Faraday Soc.* **1955**, *19*, 215.

[17] R. S. Mulliken, *Chem. Rev.* **1947**, *41*, 207.

[18] K. S. Pitzer, *J. Am. Chem. Soc.* **1946**, *67*, 1126.

[19] A. D. Walsh, *J. Chem. Soc.* **1947**, 89.

[20] K. Hedberg, V. Schomaker, *J. Am. Chem. Soc.* **1951**, *73*, 1482.

[21] G. N. Lewis, *J. Chem. Phys.* **1933**, *1*, 17.

[22] L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, NY, USA, **1945**, p. 259.

[23] M. J. Nye, *Before Big Science. The Pursuit of Modern Chemistry and Physics 1800–1940*, Twayne & Prentice Hall International, New York, **1996**, p. 184.

[24] T. S. Kuhn, *The Structure of Scientific Revolutions*, University of Chicago Press, **1996**.

[25] J. K. Galbraith, *The Affluent Society*, Houghton Mifflin, Boston, MA, USA, **1958**.

[26] D. Bloor, *Knowledge and Social Imagery*, University of Chicago Press, Chicago, **1976** (2nd edition with a new foreword, **1991**).