The Existence of a Direct Bond between Borons of Diborane

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The study of boron hydrides has a long and interesting history. Although the corresponding halides of boron have a monomer structure, BX_3, the simple substance, BH_3, has not yet been prepared; instead, diborane (B_2H_6) has been found to be the simplest boron hydride. The fundamental difficulty in the structural problem is that there does not seem to be enough valence electrons in the molecule to fill the molecular orbitals. Various interpretations have been proposed in attempts to elucidate the structure of this molecule.[1] Ogawa and Miyazawa[2,3] have recently calculated the normal vibrations of diborane and showed several characteristics of the bond in the bridge. They concluded that some type of bond existed between two boron atoms through the analysis of the potential function, but they proposed no detailed explanation of the bond character.

The LCAO calculations of diborane have been carried out by several authors,[4-7] but, in all the treatments hitherto reported, electrons have been treated as σ electrons and the calculated transition energies have not been satisfactory for assigning the observed bands. In the present study, the electronic structure of diborane is calculated by a LCAO-SCF procedure so as to discuss the bonding in the bridge of diborane.

Results and Discussion

Two bridge hydrogen atoms are treated as a united atom which has a pseudo σ orbital, χ_0, and a pseudo π orbital, χ_1:

$$\chi_0 = 1/\{2(1+S_0)\}^{1/2}(a_1+a_2)$$

$$\chi_1 = 1/\{2(1-S_0)\}^{1/2}(a_1-a_2)$$

where a_1 and a_2 are 1s orbitals of the bridge hydrogen atoms. Each boron atom is regarded as having sp^2 hybrid orbitals and a vacant $2p\pi$ orbital since the terminal ∠HBH angle is 122° and the B–B distance (1.775 Å) is approximately equal to the sum (1.77 Å) of Pauling's tetrahedral covalent radii.[8] Two sp^2 orbitals of borons make a B–B

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1) See, W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York (1963).

2) T. Ogawa, K. Hirota, T. Imanaka, K. Fukushima and T. Miyazawa, "Proceedings of the International Symposium on Molecular Structure and Spectroscopy," Science Council of Japan, Tokyo (1962), A 309.

3) T. Ogawa and T. Miyazawa, *Spectrochim. Acta*, **20**, 557 (1964).

4) W. C. Hamilton, *Proc. Roy. Soc.*, **A235**, 395 (1956).

5) M. Yamazaki, *J. Chem. Phys.*, **27**, 1401 (1957).

6) R. Hoffman and W. N. Lipscomb, *ibid.*, **37**, 2872 (1962).

7) L. Burnelle and J. J. Kaufman, *ibid.*, **43**, 3540 (1965).

8) L. Pauling, "The Nature of Chemical Bond," Cornell University Press, New York (1960), p. 246.

bond, with which the χ_0 orbital of the bridge hydrogen atoms will interact; they make a bonding σ orbital and an antibonding σ orbital. The remaining sp^2 orbitals of boron make B–H bonds with terminal hydrogen atoms, which are considered to be sufficiently localized to separate them from the remaining part of the molecule.(4)

There are four electrons in these bridge bonds; two come from borons and two from bridge hydrogens. These four electrons are situated in the lowest and the second lowest orbitals. The lowest orbital must be the lowest bonding σ orbital, $B-H_2-B$. The second lowest orbital is concluded not to be the second σ orbital, but a bonding π orbital, since the findings of Hamilton(4) and the results of the non-empirical calculation by Yamazaki(5) show the π-like orbital ϕ_7 (in Yamazaki's notation) to be very stable energetically. That is to say, in the bridge of diborane two electrons lie in the σ orbital, and the remaining two electrons, in the π orbital; the situation is very similar to that of ethylene.

The energies of these π electrons are calculated by a LCAO-SCF approximation. The integrals were mostly calculated non-empirically on the basis of Slater orbitals,(9) although some of them were evaluated by making some approximations. The details of calculations will be published elsewhere.(10) Both the calculated and the observed transition energies and oscillator strengths are given in Table 1. The symmetry of the first excited states is A_{1g}; the transition to this excited state is forbidden by the symmetry selection rule. The observed first transition(10,11) is weak and diffuse, and it corresponds well to the calculated results. The transition to the second excited state is possible, and the calculated results are in good agreement with the observed data.(12) The electronic spectrum of diborane can be interpreted well by considering a bond between boron atoms.

TABLE 1. THE TRANSITION ENERGIES AND OSCILLATOR STRENGTHS

	Calcd.		Obs.(10,11)	
	Energies eV	f	Energies eV	f
I	6.74	0	6.9	0.0005
II	10.55	0.9	9.2	0.3

Since Pitzer(13) advocated the protonated double bond model of diborane, the existence of this bond has been a matter of discussion. Glockler(14) analyzed the thermochemical data of diborane, derived linear relations between bond energies and their corresponding internuclear distances, and concluded that the heat of the formation of diborane could be well interpreted by considering a bond between boron atoms. The calculated value of the B–B force constant(3) of 2.72±0.21 md/Å corresponds well to this bond. The facts that the calculated value of the bridge B–H stretching constant was about half as great as that of the terminal stretching constant and that the value of the bridgeangle deformation constant was set at zero probably result from this π bonding nature of the bridge. Together with these results, it may be concluded that the bonding in the central part of diborane hasa direct B–B bond.

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9) C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951).

10) T. Ogawa and K. Hirota, *J. Mol. Spectroscopy*, **21**, 29 (1966).

11) E. Blum and G. Herzberg, *J. Phys. Chem.*, **41**, 91 (1937).

12) W. C. Price, *J. Chem. Phys.*, **16**, 894 (1948).

13) K. S. Pitzer, *J. Am. Chem. Soc.*, **67**, 1126 (1945).

14) G. Glockler, *Trans. Faraday Soc.*, **59**, 1080 (1963).