Rapid Intramolecular Proton Exchange in the $B_3H_8^-$ Anion. A Molecular Orbital Study

Philip E. Stevenson

Contribution from the Department of Chemistry,
Worcester Polytechnic Institute, Worcester, Massachusetts 01609.
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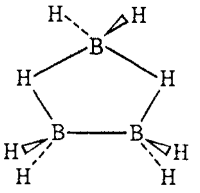
Abstract: Nonempirical molecular orbital (NEMO) calculations have been performed on a number of geometries of $B_3H_8^-$. These calculations give theoretical support to Lipscomb's pseudorotation mechanism for the equivalence of all the protons on the nmr time scale. The geometry calculated to have the lowest energy possesses one symmetric and one asymmetric bridge proton, while two transition states are 2.5 and 4.4 kcal/mol higher in energy. These results are in agreement with a recent low-temperature nmr study which placed an upper bound of about 6 kcal/mol on the barrier to proton exchange.

The crystal structure of $[(H_3N)_2BH_2^+][B_3H_8^-]$ was determined by Peters and Nordman,[1] who reported that $B_3H_8^-$ (I) consisted of a triangle of B atoms, two bridge H atoms, and six terminal H atoms.



I

The ^{11}B[2] and ^{1}H[3] nmr spectra of $B_3H_8^-$ in solution, however, indicate the presence of three equivalent borons and eight equivalent protons, thus ruling out a rigid structure such as I for the ion in solution. At room temperature these spectra are complicated by spin–spin coupling. The proton spectrum at low temperatures,[3a] however, shows a single sharp proton peak as a result of thernal decoupling of the nuclear spins, and this peak remains sharp even at −137°, indicating that a process of rapid proton exchange takes place, and that the upper bound on the barrier to this process is no more than 6 kcal/mol.

Lipscomb proposed a mechanism to account for the observed equivalence of the three borons and the eight hydrogens. The mechanism, which he called pseudorotation,[4] consists of a series of internal rotations of BH_3 units in such a way as to exchange bridge and terminal protons and to move the bridged positions about the ion. The name, pseudorotation, reflects the fact that the bridges appear to rotate about the ion with respect to the positions of the boron atoms.

In view of the fact that there has been no theoretical discussion of the new low-temperature data, it was decided to undertake an investigation of the pseudorotation mechanism using the nonempirical molecular orbital (NEMO)[5] method. Parameters for this work were obtained from the minimum basis set SCF calculation of B_2H_6.[6]

Geometry. The crystal geometry[1] of $B_3H_8^-$ shows the three boron atoms in nearly an equilateral triangle of edge 1.77 Å and that the protons are distributed: two on one of the borons and three each on the other two. Each proton, both bridge and terminal, is about 1.2 Å away from the nearest boron. The crystal structure does not indicate the out of plane distance of the terminal protons, but the local symmetry of each of the BH_3 groups seems to be nearly C_{3v}.

In this rigid crystal structure, there are three kinds of protons and two kinds of boron atoms, and if this rigidity persisted in solution, one would obtain a fairly complex nmr spectrum. Instead the nmr spectrum is characteristic of eight equivalent protons and three equivalent borons; so the ion must be undergoing a series of internal motions which bring about complete intramolecular proton exchange.

In most of the calculations, two of the borons were given three protons, each 1.20 Å distant, and the third boron was given the remaining two protons, also at distances of 1.20 Å. Each BH_3 group was assumed to have local C_{3v} symmetry, the BH bonds making an angle of 120° with the local threefold axis. The BH_2 group was placed so as to make the angle HBH be 100°. The plane of the BH_2 group was fixed perpendicular to the plane of the boron atoms and the protons set at equal distances above and below this plane. One such structure is shown in Figure 1b. In the remainder of the calculations there were two BH_2 groups and one BH_3 group with geometries as above. The one remaining proton was placed symmetrically with respect to the two BH_2 groups and 1.40 Å distant from each of the borons. See Figures 1a and 1c for examples.

Results

The most stable structure found was one with a single BH_3 group and two BH_2 groups with a symmetric bridge proton between them. The angle of the local C_{3v} axis with the unbridged boron–boron bond was 15°. One of the BH_3 hydrogens was in the plane of the boron atoms. This structure is pictured in Figures 1a and 1c. This curious structure is considerably

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[1] C. R. Peters and C. E. Nordman, *J. Amer. Chem. Soc.*, **82**, 5758 (1960).

[2] W. D. Phillips, H. C. Miller, and E. L. Muetterties, *ibid.*, **81**, 4496 (1959).

[3] (a) H. Beall, C. H. Bushweller, W. J. Dewkett, and M. Grace, *ibid.*, **92**, 3484 (1970); (b) D. Marynick and T. Onak, *J. Chem. Soc. A*, 1160 (1970).

[4] W. N. Lipscomb, *Advan. Inorg. Chem. Radiochem.*, **1**, 117 (1959).

[5] (a) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **88**, 2353 (1966); (b) F. P. Boer, M. D. Newton, and W. N. Lipscomb, *ibid.*, **88**, 2361 (1966).

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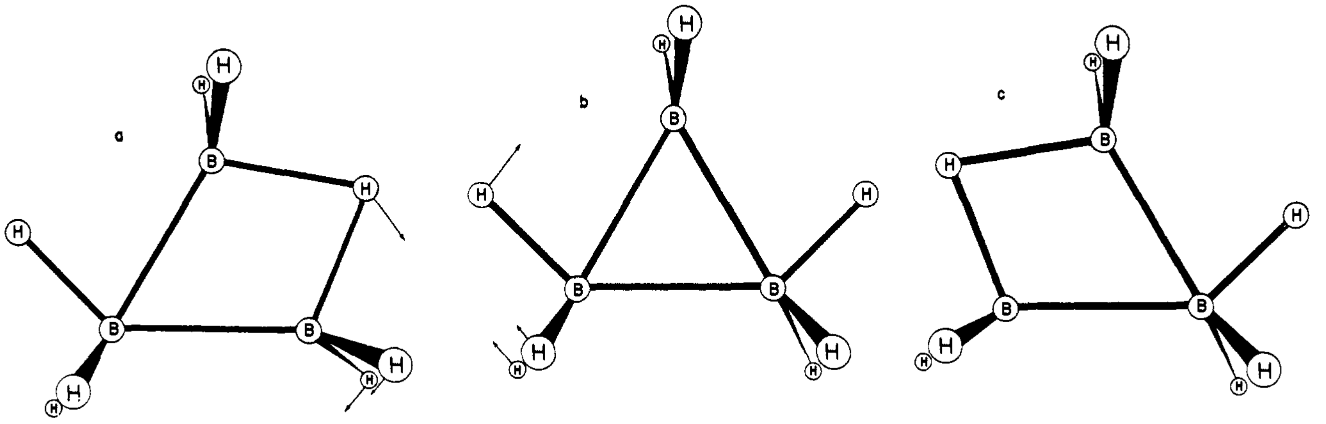

Figure 1. The swapping process. Two equivalent forms of the most stable structure are shown in (a) and (c). The transition structure, closely resembling the crystal structure, is shown in (b). Its energy is 4.38 kcal/mol above the most stable structure. The local threefold axes make 15° angles with the line connecting the unbridged pair of borons.

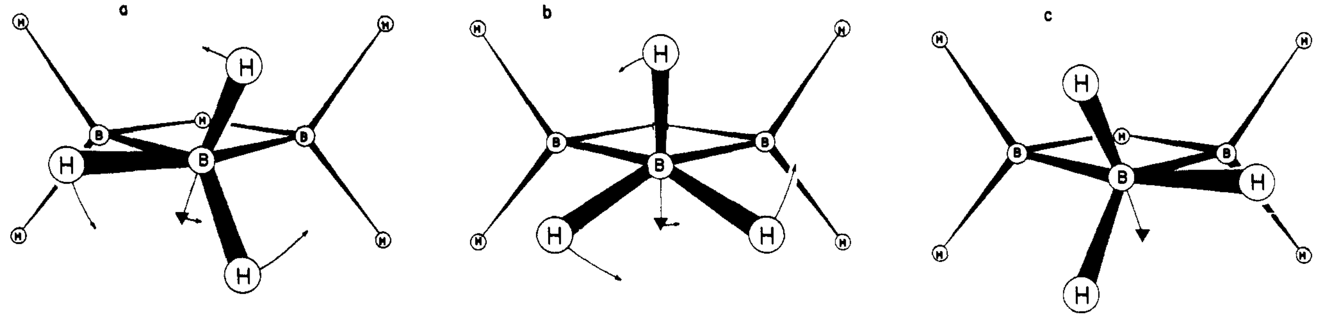

Figure 2. The pivot-rotation process. Two equivalent forms of the most stable structure are shown in (a) and (c). The transition structure is shown in (b). Its energy is 2.49 kcal/mol above the most stable structure. The local threefold axis is drawn in. With it fixed in the position of (b), nearly free rotation of the BH_3 group is possible.

different from the $B_3H_8^-$ crystal structure (which is similar to Figure 1b), but it rather resembles the crystal structure of $NH_3B_3H_7$.[7]

Two low-energy transition structures were found. One, pictured in Figure 1b, has two BH_3 groups, both with 15° angles between their local C_{3v} axes and the bond joining the two BH_3 borons. It lies 4.38 kcal/mol above the most stable structure according to the NEMO calculations.[8] The other transition structure, pictured in Figure 2b, arises from the most stable structure through a 30° rotation about the local C_{3v} axis combined with an increase of the angle between the boron–boron bond and the rotation axis from 15 to 30°. This motion is pictured in Figures 2a and 2b. The energy of this structure is 2.49 kcal/mol above that of the most stable structure. It should be noted also, that this transition structure has a very low additional sixfold rotation barrier of 0.20 kcal/mol when the local threefold axis is fixed at a 30° angle to both of the boron–boron bonds involving the BH_3 group. No other low-energy transition structures were found.

Each of the above transition structures is associated with a process that can exchange protons. Pictured in Figures 1a to 1c is a "swapping" process (with a 4.38 kcal/mol barrier) that interchanges the positions of the symmetric and asymmetric bridges and moves the position of the BH_3 group. Pictured in Figures 2a to 2c is a "pivot-rotation" process (with a 2.49 kcal/mol barrier) that exchanges bridge and terminal protons and moves the asymmetric bridge to the originally unbridged pair of boron atoms.

A pseudorotation process can be built from alternating swaps and pivot rotations. Swapping moves the location of BH_3 around the ring and exchanges BH_3, BH_2, and symmetric bridge protons. Pivot-rotation exchanges bridge and terminal protons, and the two processes together move the locations of the symmetric and asymmetric bridges around the ring.

The net effect is that each proton spends, on the average, the same amount of time in each proton position, thus making the protons equivalent, and the BH_3 groups and the positions of the symmetric and asymmetric bridges are shared equally among the borons, thus making them equivalent as well. Moreover the transition energies of 2.49 and 4.38 kcal/mol are low enough that the exchange process takes place at a rate which is rapid compared to the nmr time scale, even at −137°. Thus these calculations indicate that the pseudorotation mechanism, as proposed by Lipscomb,[4] can account for the observed rapid proton exchange in $B_3H_8^-$.

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(7) C. E. Nordman and C. Reimann, *J. Amer. Chem. Soc.*, **81**, 3538 (1959).

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