(5) E. Cernia and A. Mazzei, *Inorg. Chim. Acta*, **10**, 249 (1974).
(6) A. R. Al-Karaghouli and J. S. Wood, submitted for publication in *Inorg. Chem.*; *J. Chem. Soc., Chem. Commun.*, 516 (1972).
(7) N. M. Karayannis, L. L. Pytlewski, and C. M. Mikulski, *Coord. Chem. Rev.*, **11**, 93 (1973), and references contained therein.
(8) D. M. Mehs and S. K. Madan, *J. Inorg. Nucl. Chem.*, **30**, 3017 (1968); W. V. Miller and S. K. Madan, *ibid.*, **31**, 1427 (1969).
(9) "International Tables for X-Ray Crystallography", Vol. 1, Kynoch Press, Birmingham, England, 1969, p 149.
(10) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(11) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(12) $R = (\sum||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.
(13) Supplementary material.
(14) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).
(15) S. P. Sinha, *Struct. Bonding (Berlin)*, **25**, 69 (1976).
(16) I. Bertini, D. Gatteschi, and L. J. Wilson, *Inorg. Chim. Acta*, **4**, 629 (1970).

Contribution from the Gibbs Chemical Laboratory,
Harvard University, Cambridge, Massachusetts 02138

Tautomerism in Monocarbahexaborane(7)

Susan K. Lambiris, Dennis S. Marynick,
and William N. Lipscomb*

Received July 8, 1978

Microwave studies[1] of monocarbahexaborane(7) indicate a structure which is best described as a distorted octahedron with C_s symmetry (Figure 1A). The molecule possesses a bridge hydrogen which, at normal temperatures, is known[2] to tautomerize rapidly, equating borons 2, 3, 4, and 5 on the NMR time scale. Speculation on the location of this bridge hydrogen in the static structure has tended to favor a four-center face bond, where the hydrogen is linked to borons 2, 3, and 6. Calculations by the CNDO method support this theory.[1]

Our calculations, using the partial retention of diatomic differential overlap (PRDDO) method,[3] indicate that the unique hydrogen is best described as participating in a slightly delocalized equatorial–equatorial bridge bond, which interacts only weakly with boron 6. Thus our results do not favor a four-center face bond. Calculations of the barrier, using an assumed intermediate (Figure 1B) with an equatorial–apical (B_6) bridge, produced values in reasonable agreement with the experimental barrier and showed that the transition from an equatorial–equatorial to an equatorial–apical bridge proceeds smoothly, without a metastable intermediate.

Both the ground state and the transition state were fully optimized by the PRDDO method, using the orbital exponents listed in Table I, with the exception of the terminal C–H and B–H distances, which were fixed at 1.09 and 1.19 Å, respectively. Energies of the two structures were also determined using ab initio 4-31G calculations[4] on the PRDDO-optimized coordinates.

Optimized (PRDDO) framework distances and overlap populations for the ground state are given in Tables IIa and IIIa. The unique hydrogen is 0.33 Å farther from boron 6 than from borons 2 and 3, and the H_b–B_6 overlap population is 0.09, compared with the H_b–B_2 overlap population of 0.34. These data indicate that the unique hydrogen interacts primarily with the equatorial borons and has only a very limited bonding interaction with the apical boron. The H_b–B_6 overlap, while too small to be considered part of a four-centered bond, may be a factor in the lowering of the barrier for tautomerism. Even more striking is the difference in the electron density plot. In marked contrast to the B_2–H_b–B_3 plot (Figure 2A), the B_2–H_b–B_6 plot (Figure 2B) shows an area of low electron density separating the hydrogen from the apical boron.

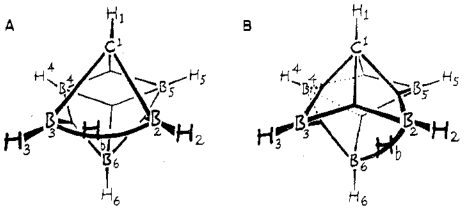

Figure 1. Localized valence structures using the Boys' criterion:[7-9] (A) for the ground state; (B) for the transition state. Dotted lines to B_4 represent electron populations from 0.45 to 0.52 e.

Table I. Orbital Exponents Used for All Calculations

	1s	2s	2p
C	5.67	1.6725	1.6725
B	4.68	1.375	1.375
H	1.24		

Table II. Framework Bond Lengths

atoms	*a*	*b*	*c*
C_1-B_2 (C_1-B_3)	1.59	1.60	1.60
C_1-B_4 (C_1-B_5)	1.65	1.63	1.63
B_2-B_3	1.865	1.87	1.87
B_2-B_5 (B_3-B_4)	1.68	1.70	1.70
B_4-B_5	1.71	1.72	1.72
B_2-B_6 (B_3-B_6)	1.90	1.89	1.89
B_4-B_6 (B_5-B_6)	1.68	1.70	1.70
H-B_2 (H-B_3)	1.41		
H-B_6	1.74		

atoms	*d*	atoms	*d*
C_1-B_2	1.61	B_3-B_6 (B_5-B_6)	1.81
C_1-B_3 (C_1-B_5)	1.58	B_4-B_6	1.69
C_1-B_4	1.63	H-B_2	1.37
B_2-B_3 (B_2-B_5)	1.79	H-B_3 (H-B_5)	2.30
B_2-B_6	1.85	H-B_6	1.35
B_3-B_4 (B_4-B_5)	1.68		

[a] Fully optimized geometry for ground state. [b] Geometry used to calculate potential surface in Figure 3. [c] Microwave geometry from ref 1. [d] Fully optimized transition state.

Table III. Overlap Populations

atoms	*a*	atoms	*a*
C_1-B_2	0.584 19	B_2-B_6	0.288 43
C_1-B_4	0.482 53	B_4-B_6	0.601 95
B_2-B_3	0.204 31	H_b-B_2	0.339 30
B_2-B_5	0.508 99	H_b-B_6	0.088 31
B_4-B_5	0.447 40		

atoms	*b*	atoms	*b*
C_1-B_2	0.518 07	B_3-B_6	0.432 81
C_1-B_3	0.584 81	B_4-B_6	0.552 15
C_1-B_4	0.418 18	H_b-B_2	0.375 93
B_2-B_3	0.378 01	H_b-B_3	−0.011 63
B_2-B_6	0.306 37	H_b-B_6	0.374 44
B_2-B_4	0.513 89		

[a] Overlap populations over atoms for optimized ground-state structure. [b] Overlap populations over atoms for optimized transition-state structure.

A quadratic synchronous transit[5] using the ground state, the transition state, and an orthogonally optimized structure at path coordinate 0.5 produced a smooth energy profile which shows no sign of any intermediate between the ground state and the transition state. The calculated barriers (19.6 kcal mol^{-1} using PRDDO and 22.4 kcal mol^{-1} using 4-31G) are in reasonable agreement with the experimental value of 14 ± 0.5 kcal mol^{-1}.

In order to rule out the possibility that the unique hydrogen might flip onto the C_1–B_2–B_3 face, we calculated, using PRDDO, a potential surface for the movement of the unique hydrogen in the plane of symmetry. For this calculation we

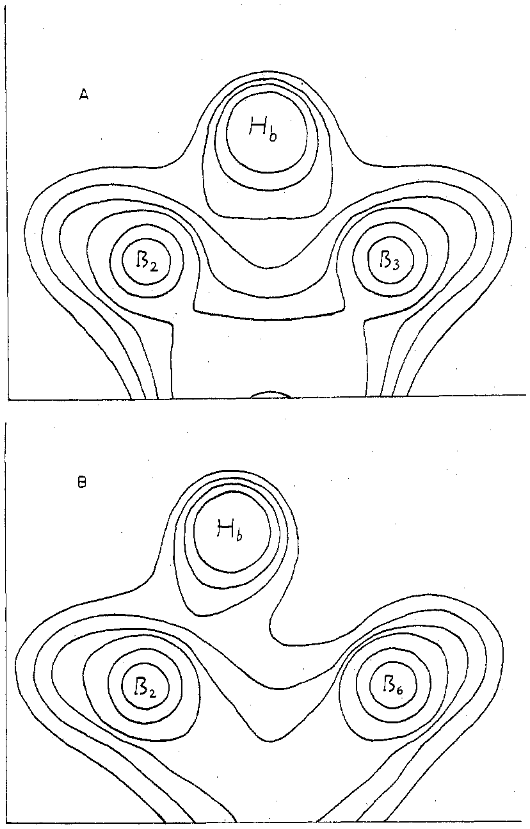

Figure 2. (A) Total electron density plot for the ground state in the B_2–H_b–B_3 plane. Contour levels are 0.07, 0.09, 0.11, 0.14, 0.50, and 3.0 e/au^3. (B) Total electron density plot for the ground state in the B_2-H_b-B_6 plane. Contour levels are 0.07, 0.09, 0.11, 0.14, 0.50, and 0.30 e/au^3.

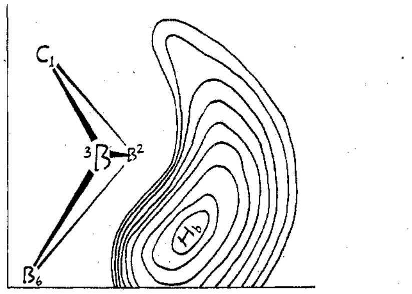

Figure 3. Energy surface for movement of H_b in the plane of symmetry. Contours are drawn with 10 kcal mol^{-1} spacing.

returned to a structure in essentially exact agreement with that obtained in microwave studies in order to remove any bias. The surface thus determined, shown in Figure 3, makes it extremely unlikely that such a structure is involved in the tautomerism.[6]

Our conclusions, therefore, are that the unique hydrogen is best described as an equatorial–equatorial bridge hydrogen in the static molecule and undergoes tautomerism at room temperature by passing through an equatorial–apical BHB bridge. While some small bonding interaction between the bridge hydrogen and boron 6 does occur, this interaction contributes very little to the ground-state valence structure.

Acknowledgment. This work was supported in part by Grant CHE-7719889 from the National Science Foundation.

Registry No. Monocarbahexaborane(7) (A), 25301-90-0; monocarbahexaborane(7) (B), 55188-36-8.

References and Notes

(1) G. L. McKown, B. P. Don, R. A. Beaudet, P. J. Vergamini, and L. H. Jones, *J. Chem. Soc., Chem. Commun.*, 765 (1974).
(2) E. Groszek, J. B. Leach, G. T. F. Wong, C. Ungermann, and T. Onak, *Inorg. Chem.*, **10**, 2770 (1971).
(3) T. A. Halgren and W. N. Lipscomb, *J. Chem. Phys.*, **58**, 1569 (1973).
(4) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, program GAUSSIAN 70, available from QCPE, Indiana University, Bloomington, Indiana.
(5) T. A. Halgren and W. N. Lipscomb, *Chem. Phys. Lett.*, **49**, 225 (1977).
(6) It is possible that, had we reoptimized the geometry at every point on the surface, a local metastable minimum near the C_1–B_2–B_3 face might have been found. However, the calculated surface makes it clear that this local minimum, if it exists, would be less stable than the ground-state structure by about 50 kcal mol^{-1}.
(7) S. F. Boys, *Rev. Mod. Phys.*, **32**, 296 (1960).
(8) J. M. Foster and S. F. Boys, *Rev. Mod. Phys.*, **32**, 300 (1960).
(9) S. F. Boys, "Quantum Theory of Atoms, Molecules, and the Solid State", P.-O. Löwdin, Ed., Academic Press, New York, N.Y., 1966, p 253.

Contribution from the Department of Chemistry,
University of Arizona, Tucson, Arizona 85721

A Boron-11 NMR Study of the Methanolysis of Sodium Dimethylamide–Bis(borane) and Some Related Boron–Nitrogen Compounds[1]

Coriolan R. Balulescu and Philip C. Keller*

Received November 3, 1977

Although the literature contains numerous studies on the solvolysis of diborane, alkali metal borohydrides, and amine–boranes,[2] little is known of the solvolytic behavior of derivatives of diborane and the borohydrides. This work is a qualitative boron-11 NMR study of the methanolysis of $Na(CH_3)_2N{\cdot}2BH_3$[3] and μ-$(CH_3)_2NB_2H_5$. In the course of this investigation it became of interest to examine the methanolysis of $K(CH_3)_2N{\cdot}BH_3$, $(CH_3)_2NH{\cdot}BH_3$, and $(CH_3)_2NH{\cdot}BH_2Cl$ under similar conditions; these observations are also included.

Results

$Na(CH_3)_2N{\cdot}2BH_3$. Solutions of $Na(CH_3)_2N{\cdot}2BH_3$ in methanol are stable at 25 °C for months, but acidification causes rapid solvolysis according to eq 1.[4] When the acid

$$Na(CH_3)_2N{\cdot}2BH_3 + 6CH_3OH + 2HCl \rightarrow (CH_3)_2NH_2Cl + 2B(OCH_3)_3 + 6H_2 + NaCl \quad (1)$$

methanolysis is followed by boron NMR at −60 °C (the solutions were usually diluted with $(C_2H_5)_2O$ to overcome low-temperature viscosity problems), signals characteristic of starting material, μ-$(CH_3)_2NB_2H_5$, $HB(OCH_3)_2$, and $B(OCH_3)_3$ are readily detected. An additional weak resonance, barely resolvable as a triplet, is also found under these conditions at −3.9 ppm (Figure 1). We have tentatively assigned this signal to the unisolated compound $(CH_3)_2NH{\cdot}BH_2OCH_3$ (see below). At −40 °C the $Na(CH_3)_2N{\cdot}2BH_3$ and μ-$(CH_3)_2NB_2H_5$ signals rapidly disappear. Warming to 25 °C causes the disappearance of all signals except that of the ultimate methanolysis product, $B(OCH_3)_3$, within ca. 2 min.

In separate parallel low-temperature boron NMR experiments genuine μ-$(CH_3)_2NB_2H_5$ was found to undergo acid methanolysis in exactly the above manner. As in Figure 1 the bridge hydrogen coupling was not resolved at −60 °C.

$K(CH_3)_2N{\cdot}BH_3$. The acid methanolysis of $K(CH_3)_2N{\cdot}BH_3$ is slower and requires higher temperature than $Na(CH_3)_2N{\cdot}2BH_3$. At −20 °C boron NMR shows only the spectrum of the starting material. At 0 °C the coupling constant of the quartet increases from 85 to 99 Hz indicating protonation of the anion to form $(CH_3)_2NH{\cdot}BH_3$ (the chemical shifts of the two quartets differ by only 1.2 ppm).[5] Complete methanolysis requires 15–20 min at 25 °C. Parallel NMR experiments

0020-1669/78/1317-3707$01.00/0