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A Theoretical Study of the Lewis-Base Adducts of Triborane(7)

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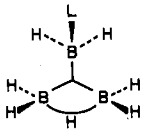
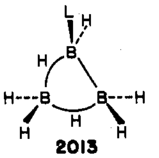
The Lewis-base adducts of B_3H_7 were studied using the PRDDO, STO-3G, and STO-4-31G methods. Bases used were NH_3, H_2O [as a model for $(CH_3)_2O$], $(CH_3)_2O$, and CO. Six possible structures were studied. In all cases the preferred geometry resembled the crystal structure of $B_3H_7 \cdot CO$ with one BHB bond and C_s symmetry. The weaker the base, the stronger this preference appears. The other structures did not appear to lie in local energy minima; they collapsed to the preferred geometry by a pseudorotation process. Comparison is made to the triborate ions and fluxional processes are discussed. Localized molecular orbitals, bond indices, atomic charges, and dipole moments are reported.

Introduction

The crystal structure of $B_3H_7 \cdot NH_3$ was determined by Nordman and Reimann[1] not long after the Lewis-base adducts of triborane(7) were first reported.[2] More recently, the crystal structure of $B_3H_7 \cdot CO$ was reported by Glore, Rathke, and Schaeffer.[3a] In ammonia–triborane, the boron framework is noticeably asymmetric, and the structure is intermediate in styx notation[4] between 1104 and 2013. In $B_3H_7 \cdot CO$ a 1104 structure is found,[3] whereas in $B_3H_8^-$ a 2013 structure is known from x-ray diffraction.[5] Many boron hydrides are known to be fluxional, including the octahydrotriborate ion and several triborane(7) adducts.[6] The mobility of the hydrogens, as observed by NMR, further complicates the structural picture for these compounds.



1104



2013

A theoretical study was therefore undertaken to explore the energetics and bonding patterns in the various styx-allowed isomers of the Lewis-base adducts of B_3H_7 including an investigation of the rotation of the BH_2L group in the 1104 structure. The effect of ligand strength on the different structures was investigated, and likely pathways for structural rearrangement were explored.

Computational Methods

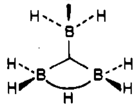
Most wave functions used in this research were obtained using the PRDDO method, an SCF-LCAO-MO procedure which gives results comparable to ab initio calculations at the minimum basis set level.[7] Except where noted, Slater exponents and a hydrogen exponent of 1.2 were used. A few calculations were carried out using Pople's standard molecular exponents,[8] SCF optimized exponents from B_2H_6,[9] NH_3,[10] and H_2O,[10] and PRDDO refined exponents. Additional wave functions were obtained using Pople's STO-3G[8] and STO-4-31G[11] methods.

Starting geometries were obtained from crystal structures.[1a,b,3a,5] Considerable geometric refinement was carried out by varying individual bond distances and angles for what were felt to be important parameters. Geometries were not truly optimized but were refined in a relatively even-handed manner. Table I summarizes bond lengths for several structures which are illustrated in Figure 1.[12] Extensive use was also made of the method of synchronous transits, in which internuclear distances in a molecular rearrangement vary essentially linearly or quadratically between limiting structures.[13] This method allows a smooth and chemically reasonable transition between isomers and is extremely helpful in investigating energy surfaces for molecules which have complicated geometries, such as boron hydrides. For pathways involving considerable geometric rearrangement, geometries were refined at a constant position on the path coordinate defined by the linear synchronous transit (orthogonal optimization),[13] and three-point interpolations (quadratic synchronous transits)[13] were then used in defining the rearrangement path.

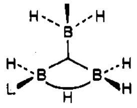
Molecular orbitals were localized using the method of Boys[14] to relate the canonical molecular orbitals to the localized orbitals of three-center bond theory.[4a,15] Bond indices and valencies were computed using the method of Armstrong, Perkins, and Stewart.[16]

Four Styx Structures

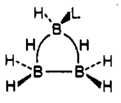
For Lewis bases L = NH_3, H_2O (as a model for ethers), and CO four styx-allowed isomers were investigated. Structures I and III have a plane of symmetry.



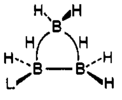
I



II



III



IV

For L = NH_3 all four geometries were extensively refined. For L = H_2O and CO structure I was refined extensively, and the boron framework for structures II–IV was taken from the corresponding NH_3 adduct. This procedure saved considerable computation time and appears to result in an error no greater than about 1 kcal/mol.[17]

Table II shows the relative energies of the four structures with the three different bases. In each case, structure I is the

Table I. Selected Interatomic Distances, Overlap Populations, and Bond Indices[a]

Structure	Atoms	Distance, Å	Overlap population	Bond index
$B_3H_7 \cdot NH_3$ (I)	B_1-B_2	1.93	0.36	0.51
	B_2-B_3	1.77	0.46	0.71
	B_2-H_4	1.40	0.38	0.47
	B_2-H_5	1.19	0.87	0.99
	B_1-H_9	1.20	0.83	0.92
	B_1-N_{11}	1.60	0.55	0.84
	N_{11}-H_{12}	1.03	0.67	0.94
$B_3H_7 \cdot NH_3$ (II)	B_1-B_2	1.89	0.36	0.54
	B_1-B_3	1.91	0.29	0.47
	B_2-B_3	1.71	0.55	0.72
	B_2-H_4	1.36	0.48	0.56
	B_3-H_4	1.46	0.27	0.38
	B_2-H_5	1.19	0.87	0.97
	B_1-H_8	1.20	0.84	0.96
	B_1-H_9	1.20	0.77	0.87
	B_3-H_9	2.13	0.03	0.08
	B_2-N_{11}	1.57	0.57	0.87
	N_{11}-H_{12}	1.03	0.67	0.94
$B_3H_7 \cdot NH_3$ (III)	B_1-B_2	1.76	0.47	0.63
	B_2-B_3	1.90	0.32	0.53
	B_2-H_4	1.19	0.87	0.98
	B_1-H_8	1.67	0.17	0.26
	B_2-H_8	1.29	0.57	0.66
	B_1-H_{10}	1.20	0.87	0.97
	B_1-N_{11}	1.58	0.58	0.86
	N_{11}-H_{12}	1.03	0.67	0.94
$B_3H_7 \cdot NH_3$ (IV)	B_1-B_2	1.82	0.40	0.53
	B_1-B_3	1.80	0.39	0.59
	B_2-B_3	1.82	0.43	0.63
	B_2-H_4	1.19	0.86	0.96
	B_1-H_7	1.70	0.10	0.21
	B_2-H_7	1.26	0.67	0.74
	B_1-H_8	1.64	0.20	0.28
	B_3-H_8	1.27	0.58	0.66
	B_1-H_9	1.19	0.87	0.99
	B_2-N_{11}	1.59	0.56	0.85
	N_{11}-H_{12}	1.03	0.67	0.94
$B_3H_7 \cdot NH_3$ (VI)	B_1-B_2	1.96	0.35	0.51
	B_1-B_3	1.99	0.26	0.40
	B_2-B_3	1.73	0.50	0.77
	B_2-H_4	1.36	0.43	0.52
	B_3-H_4	1.44	0.33	0.42
	B_2-H_5	1.19	0.87	0.98
	B_1-H_9	1.20	0.86	0.97
	B_1-N_{11}	1.62	0.53	0.83
	N_{11}-H_{12}	1.03	0.67	0.94
$B_3H_7 \cdot NH_3$ (exp[b])	B_1-B_2	1.80	0.36	0.52
	B_1-B_3	1.82	0.41	0.61
	B_2-B_3	1.74	0.40	0.63
	B_2-H_4	1.39	0.31	0.38
	B_3-H_4	1.23	0.50	0.57
	B_2-H_5	1.19[c]	0.88	0.98
	B_1-H_9	1.19[c]	0.76	0.81
	B_2-H_9	1.77	0.03	0.14
	B_1-H_{10}	1.19[c]	0.85	0.94
	B_1-N_{11}	1.58	0.57	0.85
	N_{11}-H_{12}	1.03[d]	0.68	0.94
$B_3H_7 \cdot OH_2$ (I)	B_1-B_2	1.91	0.35	0.51
	B_2-B_3	1.75	0.46	0.72
	B_2-H_4	1.39	0.39	0.47
	B_2-H_5	1.20	0.87	0.98
	B_1-H_9	1.20	0.82	0.92
	B_1-O_{11}	1.57	0.50	0.79
	O_{11}-H_{12}	0.98	0.56	0.92
$B_3H_7 \cdot OH_2$ (V)	B_1-B_2	1.96	0.25	0.46
	B_2-B_3	1.83	0.41	0.54
	B_2-H_4	1.19	0.86	0.98
	B_1-H_8	1.20	0.87	0.99
	B_1-H_9	1.20	0.81	0.91
	B_2-O_{11}	1.68	0.25	0.52
	O_{11}-H_{12}	0.99	0.55	0.90

[a] Reference 16. [b] Reference 1. [c] Fixed at 1.19 Å, see ref 21. [d] PRDDO optimized.

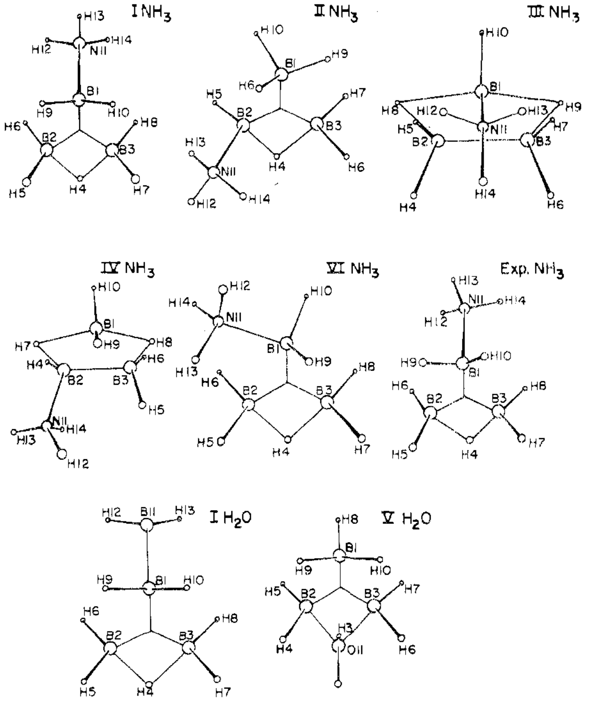


Figure 1. $B_3H_7 \cdot L$ structures.

Table II. $B_3H_7 \cdot L$ PRDDO Energies Relative to Structure I[a]

	Structure					ΔE_{PRDDO}
	II	III	IV	V	VI	$B_3H_7 + L \rightarrow B_3H_7 \cdot L$
NH_3	18.7	23.4	6.9	55.3	9.9	−85.6
H_2O	21.9	24.9	7.9	26.8	10.9	−74.6
$(CH_3)_2O$				21.9	9.6	−65.2
CO	27.4	37.4	8.6	45.9	8.1	−44.2

[a] In kcal/mol.

lowest in energy. Moreover, smooth synchronous transit paths can be constructed between I and II, I and IV, and II and III, which are entirely uphill in energy. Thus even though the geometries of structures II, III, and IV were refined by moving individual atoms and groups of atoms, we feel that an exhaustive geometry optimization would show that only structure I was in a local minimum on the PRDDO energy surface. Table II also shows the relative strengths of the four bases. The ΔE_{PRDDO} for the reaction $B_3H_7 + L = B_3H_7 \cdot L$ was determined after refining the geometries of B_3H_7 and each of the bases L. The calculation of the energy of reaction would require corrections for electron correlation, zero-point energies, and entropy effects. However, the correct order of base strengths is given by ΔE_{PRDDO} as witnessed by the ability of amines to displace ethers in B_3H_7 adducts[2] and the inability of CO to do so by simple displacement.[18] This same order of base strengths is found for both BH_3[19] and BF_3[20] adducts. Table II, therefore, illustrates the generalization that the weaker the base the stronger the preference for structure I. If H^- is considered as a very strong base, this generalization suggests that the preference for structure I in the octahydrotriborate ion would be weak, and perhaps the order of preference among the structures might be reversed, as seems to be the case from the crystal structure.[5]

The relatively small amount of energy required to distort structure I to IV for $B_3H_7 \cdot NH_3$ makes understandable the asymmetry in the crystal structure of ammonia–triborane.[1] The crystal structure of $B_3H_7 \cdot NH_3$ was found to lie above structure I in energy after corrections were made for the systematic shortening of B–H distances in x-ray determinations.[21] The experimental structure is easily refined to the C_s

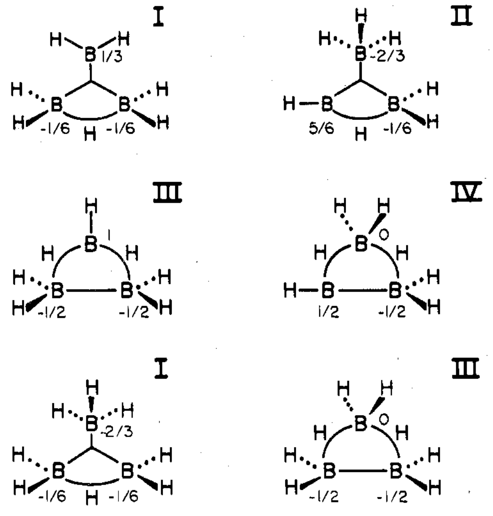


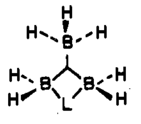
Figure 2. Formal charges in B_3H_7 and $B_3H_8^-$.

structure; however, distortions of up to 10° in the triangle of boron atoms from C_s symmetry require less than 0.2 kcal/mol. The strong preference for structure I for the CO adduct is reflected in the crystal structure of $B_3H_7{\cdot}CO$[3a] in which both molecular units in the unit cell have nearly C_s symmetry.

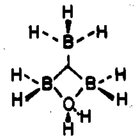
The order in energy of the structures, (more stable) I < IV < II < III (less stable), can be rationalized from the charge distribution in the corresponding B_3H_7 framework[22] (Figure 2). Structures which are more in accord with the electroneutrality principle are favored; the positive charge at the site of the vacant orbital in B_3H_7 increases in the order I < IV < II < III. Adducts of weaker bases are more strongly influenced by the unfavorable charge distribution in the corresponding B_3H_7 framework than are adducts of strong bases.

Bridge Bonded Bases

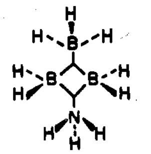
For each of the Lewis bases, NH_3, H_2O, $(CH_3)_2O$, and CO, structure V was also investigated. Structure V has C_s symmetry, and the base may be bonded via two two-center bonds as in Va or one three-center bond as in Vb. Primary attention was focused on $L = OH_2$ (as a model for ethers), as until recently it appeared that ligand migration or exchange in ether adducts of triborane(7) occurred at room temperature.[6d-f,23] The geometry of Va was refined with the constraint of C_s symmetry. For the other bases, the boron framework was taken from Va.



V



Va



Vb

Table II lists the results for each of the bases. The Vb structures are considerably higher in energy than the Va structures (cf. $B_3H_7F^-$ below). For CO the energy of Vb slightly exceeds the ΔE_{PRDDO} for adduct formation. The energy of Vb would be lowered somewhat by the refinement of the boron framework geometry, perhaps enough to show stability relative to dissociation.

Rotation of the BH_2L Group

The three-center bond in structure I suggests the possibility of relatively free rotation of the BH_2L group to structure VI, which also has C_s symmetry. For structures II and V and the octahydrotriboronate ion, the rotation of the BH_3 group would have local sixfold character and would be expected to be relatively free.[6f,24]

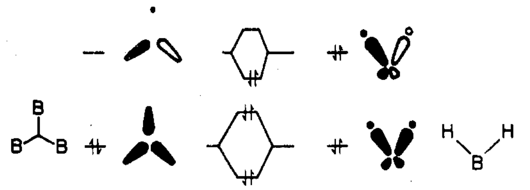
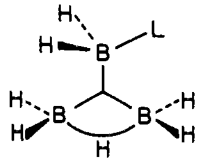


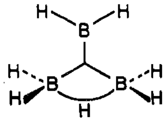
Figure 3. Interaction of the BBB orbitals and BH_2 orbitals in B_3H_7. The lower part of the figures shows an interaction between the central three-center bond and the symmetric combination of the BH_2 orbitals which to a first approximation is nonbonding. The upper part of the figure shows a favorable interaction which occurs between a virtual BBB orbital and the antisymmetric combination of the BH_2 orbitals when the BH_2 group is in the BBB plane.



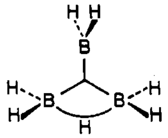
VI

For L = NH_3, H_2O, and CO the geometry of structure VI was refined extensively. For the methyl ether adduct the geometry of the boron framework was taken from the water adduct. For each base the rotation of the BH_2L group was found to have a periodicity of 180° with only structure I in a local energy minimum. Structure I is preferred over VI by about 10 kcal/mol as shown in Table II. This preference does not appear to vary markedly with the strength of the base. For structures II and V the height of the BH_3 rotational barrier was less than 1 kcal/mol. For both the water and methyl ether adduct in both structures I and VI the preferred rotamer about the O–B bond was found to have the oxygen lone pair trans to the BBB three-center bond. Based on preliminary calculations the rotational barrier about the O–B bond was approximately 5 kcal/mol for the water adduct and approximately 2 kcal/mol for the ether adduct.

The preference for structure I over structure VI again may be explained by reference to the corresponding B_3H_7 species. For B_3H_7 structure I is favored over VI by 11.0 kcal/mol (PRDDO value).



I



VI

As illustrated in Figure 3 the BH_2 orbitals in I interact favorably with the orbitals of the three-center bond. For a BH_2 group oriented as in VI no interaction occurs between the BBB orbitals and the BH_2 orbitals shown in Figure 3 because of symmetry. The result is a preference for structure I over structure VI in that the hydrogens on the unique boron can pick up some three-center bridging character in structure I, whereas in structure VI the geometry precludes this particular interaction.

The height of the triangle of boron atoms increases by 0.07 and 0.05 Å in B_3H_7 and $B_3H_7{\cdot}NH_3$, respectively, in the rotation from structure I to VI. The bond index[16] between the hydrogens on the unique boron and the closest of the remaining borons falls by 0.03 in the rotation from I to VI for both B_3H_7 and $B_3H_7{\cdot}NH_3$.

Analysis of Bonding

Table I shows overlap populations and bond indices.[16] In general the BN bond is shorter and stronger in the higher energy structures. Table III shows the results of the Boys

Table III. Localized Molecular Orbitals

Structure		Mulliken populations			% s character			
		BBB Bonds						
		B_1[b]	B_2	B_3	B_1	B_2	B_3	% d[a]
I	NH_3	0.72	0.66	0.66	19	24	24	15
II	NH_3	0.57	0.82	0.64	12	27	27	15
III	NH_3	0.68	0.67	0.67	41	15	15	17
IV	NH_3	0.51	0.81	0.71	33	20	15	16
VI	NH_3	0.67	0.74	0.61	21	23	24	14
Exptl	NH_3[c]	0.80	0.55	0.70	16	28	15	15
I	H_2O	0.72	0.66	0.66	20	23	23	15
V	H_2O	0.47	0.78	0.78	8	28	28	15
		BHB Bonds						
		H_4	B_2	B_3	B_2	B_3		
I	NH_3	0.91	0.55	0.55	18	18		12
II	NH_3	0.92	0.67	0.43	20	15		13
		H_8	B_2	B_1	B_2	B_1		
III	NH_3	0.92	0.74	0.36	19	14		14
		H_7	B_2	B_1	B_2	B_1		
IV	NH_3	0.93	0.87	0.23	22	8		13
		H_8	B_3	B_1	B_3	B_1		
		0.90	0.76	0.37	19	17		12
		H_4	B_2	B_3	B_2	B_3		
VI	NH_3	0.90	0.61	0.51	16	20		11
Exptl	NH_3[c]	0.93	0.45	0.64	16	17		12
I	H_2O	0.91	0.56	0.56	18	18		12
		BH Bonds						
		B	H		B			
I	NH_3 (av.)	1.05	0.97		35			11
II	NH_3 (av.)	1.04	0.96		33			11
II	NH_3 (B_1-H_9)	0.98	0.93		27			12
III	NH_3 (av.)	1.05	0.97		35			11
IV	NH_3 (av.)	1.05	0.97		35			11
VI	NH_3 (av.)	1.05	0.98		35			11
Exptl	NH_3 (av.)[c]	1.04	0.96		34			12
Exptl	NH_3 (B_1-H_9)[c]	0.95	0.93		24			15
I	H_2O (av.)	1.05	0.95		35			11
V	H_2O (av.)	1.03	0.98		34			11
		BL Bonds						
		N	B		N	B		
I	NH_3	1.51	0.56		34	36		15
II	NH_3	1.47	0.61		31	38		15
III	NH_3	1.47	0.60		33	38		16
IV	NH_3	1.49	0.58		34	37		15
VI	NH_3	1.50	0.56		34	32		15
Exptl	NH_3	1.49	0.58		33	38		15
		O	B		O	B		
I	H_2O	1.55	0.51		32	43		16
V	H_2O	1.73	0.33		30	34		14
I	$(CH_3)_2O$	1.56	0.48		36	44		17
		C	B		C	B		
I	CO	1.54	0.48		66	15		14
		LH Bonds						
		N	H		N			
I	NH_3 (av.)	1.29	0.76		30			12
II	NH_3 (av.)	1.31	0.73		31			11
III	NH_3 (av.)	1.31	0.74		30			11
IV	NH_3 (av.)	1.30	0.76		30			12
VI	NH_3 (av.)	1.30	0.75		30			12
Exptl	NH_3 (av.)	1.30	0.75		30			12
		O	H		O			
I	H_2O	1.31	0.73		27			12
V	H_2O	1.36	0.67		31			12

[a] % delocalization, ref 15d. [b] Atoms numbered as in Figure 1. [c] Reference 1; B–H distances adjusted; see ref 21.

localization for each of the ammonia–triborane structures and for the crystal structure[1] with a correction for the systematic error in the B–H distances.[21] Several features deserve special mention. Paralleling the results in Table I, the asymmetry of the BBB and BHB bonds, especially in structures II, III, IV, and the experimental structure, is quite noticeable. In structure II and the experimental structure, one BH bond is beginning to pick up three-center character, the Mulliken[25] population on the second boron being 0.09 and 0.14 e respectively for the two structures. Despite the asymmetry in the experimental structure, the LMO's in the experimental structure resemble those of structure I more than those of structure IV.

In structures III and IV one boron atom is associated with five localized molecular orbitals, in contrast to the styx rules and despite the fact that boron has only four valence atomic orbitals (2s, 2p) in the PRDDO treatment. Centers associated with five or more valence LMO's have been termed fractional.[26] Fractional LMO's are indicative of an irremovable or inherent electronic delocalization.[27]

Table IV breaks down the SCF energy for each structure into its component parts. The relative instability of structures II, III, IV, and V is due to increases in nuclear repulsion, kinetic energy, and electron repulsion terms which are not offset by the more negative nuclear attraction term, while the instability of VI is due to more positive nuclear attraction and kinetic energy terms. Also shown in Table IV are dipole moments. The experimental dipole moment of $B_3H_7{\cdot}NH_3$ is 6.98 D.[28] Eigenvalues for each adduct are available in the Ph.D. thesis of L. D. Brown.

Table V shows PRDDO gross atomic charges[25] for eight structures. The charge distribution is more complicated than is suggesting by simple theory (Figure 2). Generally the boron attached to the base is the least negative. Charge is donated from the Lewis base to the boron framework somewhat more strongly in the higher energy structures as indicated in Tables III and V, suggesting that a resonance structure $B_3H_7{:}NH_3$ without charge donation is less stable in the higher energy structures.

PRDDO Minium Basis Set Error

Table VI shows the effect on the SCF energy of exponent refinement and basis-set expansion. The minimum basis set error for the energy of rotamer VI relative to I appears to be very small. The use of a minimum basis set considerably underestimates the energy of structure V relative to I. In constrast, the use of a minimum basis set overestimates the energies of structures II, III, and IV relative to I. Despite the quantitative failings of the minimum basis set treatment, the minimum basis set data (PRDDO and STO-3G) qualitatively show the correct order of energies among the alternative structures. The use of SCF optimized exponents for first row atoms and PRDDO refined H exponents provides a fairly good approximation to the STO-4-31G relative energies for all of the structures but V.

The error arising from using a minimum basis set and from neglecting electron correlation is likely to be constant if the bonding patterns in the structures are similar. However, structures I through VI exemplify several different types of bonding. Structures I, II, and VI have one BHB bond, structures III and IV have two, and V has none. Only in I is the BHB bond symmetrical. Structure V involves an unusual mode of attachment for the Lewis bases. Structures III and IV show fractional LMO's to boron. Thus greater confidence can be placed in the energies of structures II and VI relative to I and in the energy of III relative to IV than in other comparisons.

The effect of electron correlation might be roughly estimated from calculations on diborane.[29] The formation of B_2H_6 from

Table IV. PRDDO Energies[a] and Dipole Moments[b]

	NH_3					H_2O		$(CH_3)_2O$	CO
	I	II[c]	III[c]	IV[c]	VI[c]	I	V[c]	I	I
Nuclear repulsion energy	70 767.6	641.3	1244.9	870.4	−594.2	70 128.6	1957.3	149 510.8	84 117.2
Kinetic energy	83 702.6	42.6	44.9	31.0	14.8	96 304.9	38.7	144 720.1	119 059.9
Nuclear attraction energy	−335 389.9	−1201.1	−2341.2	−1742.3	1196.3	−364 645.8	−3628.1	−635 744.0	−445 343.5
Electron repulsion energy	96 788.2	536.0	1074.7	847.7	−606.9	101 734.2	1658.9	196 106.1	122 713.3
Total energy	−84 131.4	18.7	23.4	6.9	9.9	−96 477.9	26.8	−145 406.9	−119 453.0
Dipole moment	7.3	9.3	10.0	7.8	7.0	6.0	9.7	7.0	4.4

[a] In kcal/mol. [b] In D. [c] Energies relative to I.

Table V. PRDDO Gross Atomic Charges[a] and Valencies[b]

			B_1	B_2	B_3	H on B (av)	N	H on N (av)
I	NH_3	Charge	−0.27[c]	−0.33	−0.33	0.06	−0.37	0.29
		valency	3.75[c]	3.72	3.72	1.00	3.70	0.95
II	NH_3		−0.55	−0.12[c]	−0.29	0.06	−0.38	0.31
			3.86	3.72[c]	3.65	1.00	3.70	0.95
III	NH_3		0.00[c]	−0.49	−0.49	0.06	−0.39	0.31
			3.63[c]	3.85	3.85	1.00	3.70	0.95
IV	NH_3		−0.22	−0.24[c]	−0.53	0.07	−0.36	0.29
			3.60	3.77[c]	3.87	1.00	3.71	0.95
VI	NH_3		−0.21[c]	−0.43	−0.24	0.05	−0.36	0.29
			3.74[c]	3.79	3.61	1.00	3.71	0.95
Exptl	NH_3		−0.29[c]	−0.26	−0.44	0.07	−0.37	0.30
			3.78[c]	3.66	3.81	1.00	3.71	0.95
							O	H on O (av)
I	H_2O		−0.26[c]	−0.35	−0.35	0.07	−0.18	0.32
			3.69[c]	3.73	3.73	1.00	2.68	0.94
V	H_2O		−0.48	−0.19[c]	−0.19[c]	0.04	−0.17	0.37
			3.78	3.54[c]	3.54[c]	1.00	2.93	0.91

[a] Reference 25. [b] Reference 16. [c] Boron bonded to L.

$2BH_3$ converts two terminal hydrogens into bridge hydrogens. The CI correction for this process was estimated to be about 15.9 or 8.0 kcal/mol for each BHB bridge.[29a] The minimum basis set error was almost as large, 12.6 kcal/mol for the minimum basis set as compared with near-Hartree–Fock results, or 6.3 kcal/mol for each bridge.[29b]

Comparison to the Triborate Ion

The crystal structure[5] of $B_3H_8^-$ reveals a 2013 bonding pattern. The equivalence of all hydrogens and borons on the NMR time scale[6,30] suggests that the difference in energy between the 1104 and 2013 structures is 8 kcal/mol or less.[30] A NEMO study of $B_3H_8^-$ indicated that the 1104 structure was actually preferred by 4.4 kcal/mol over a 2013-like structure.[24] PRDDO results[31] reduce that figure to 2.5 kcal/mol, while SCF-CI and STO-4-31G results[31a] show that the 2013 structure is preferred, though by less than 1 kcal/mol.

The synthesis of $B_3H_7Br^-$ and $B_3H_7Cl^-$ was recently reported.[32] The structure of the ion was deduced as structure III by ir spectroscopy. For $B_3H_7F^-$ at the PRDDO level structures I, II, IV, and VI are less stable than III[33] by 9.7, 2.9, 11.6, and 9.6 kcal/mol, respectively. Thus the triborate ions, in constrast to the triborane adducts, prefer structure III over I, generally reversing the order of preference among structures I through IV. The preference for structure III as opposed to I appears to be stronger in $B_3H_7F^-$ than in $B_3H_8^-$. We feel that this stronger preference may be ascribed largely to B–F π bonding. The B–F bond index[16] is greater than one in structures I–IV. Furthermore, one of the fluorine lone pairs in each of these structures has significant two-center character (Table VII). The geometry of the boron framework in these ions was taken from the corresponding ammonia–triborane structure. The minimum basis set error is expected to be larger for F^- than for NH_3, and the error arising from a limited geometry refinement might also be more significant here than in Table II. Therefore, these results should be regarded as preliminary. Structure V is more stable than III by 40.1 kcal/mol at the PRDDO level using the boron geometry from the water–triborane adduct. Because the minimum basis set error was expected to be significant (cf. structure V for $B_3H_7{\cdot}OH_2$, Table VI), STO-4-31G calculations were carried out on structures III and V for $B_3H_7F^-$. Structure V was then found to be less stable than III by 24.3 kcal/mol, a striking reversal in the order of stability.[34] These preliminary figures suggest the possibility that flourine migration in $B_3H_7F^-$ might be observable on the NMR time scale. Table VII shows that the fluorine atom is beginning to pick up bridging character in structure VI. The PRDDO method seems to favor such an arrangement. At the STO-4-31G level, with the PRDDO geometry, structure VI is 19.4 kcal/mol less stable than structure III.

Fluxional Processes and NMR

The ^{11}B NMR and ^1H NMR spectra of several triborane(7) adducts have been reviewed.[6e,f] The spectra show two types of boron in these compounds. Ether adducts were previously thought to show only one type of boron, implying rapid ligand migration or exchange. However, high-resolution ^{11}B NMR of THF and dimethyl ether adducts of triborane(7) show two distinct types of boron.[23]

Structure I has been proposed to explain this feature of the spectra.[6f] Rapid rotation of the BH_2L group with either a 180° rotation or a torsional movement which interconverted the crystal structure of ammonia–triborane with its mirror image was also proposed.[6f] Also consistent with two kinds of boron would be structures III and V.

This study confirms the explanation that structure I is the preferred geometry. While rotation of the BH_2L group

Table VI. Exponent Refinement and Basis Set Improvement[a]

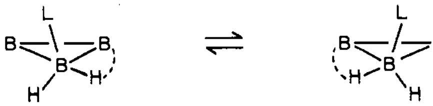
Method	Exponents	$B_3H_7{\cdot}NH_3$					$B_3H_7{\cdot}OH_2$	
		I	II[b]	III[b]	IV[b]	VI[b]	I	V[b]
PRDDO	Slater	−84 131.4	18.7	23.4	6.9	9.9	−96 477.9	26.8
PRDDO	Pople's standard molecular[c]	−84 136.1	20.3	26.4	7.1	9.7	−96 482.4	31.1
PRDDO	SCF optimized[d]	−84 156.5	17.6	27.9	9.4	8.1	−96 499.0	26.1
PRDDO	PRDDO refined[e]	−84 170.6	14.7	19.1	5.9	7.4	−96 511.9	25.4
STO-3G	Pople's standard molecular[c]	−83 230.9	21.8	27.5	8.4	11.5	−95 468.8	36.9
STO-4-31G	Pople's standard molecular[c]	−84 137.7	15.4	18.7	6.7	11.5	−96 547.8	40.8

[a] Energies in kcal/mol. [b] Energies relative to I. [c] Reference 8. [d] From B_2H_6, NH_3, and H_2O, ref 9 and 10. [e] B, N, and O exponents from B_2H_6, NH_3, and H_2O, ref 9 and 10. H exponents refined in PRDDO framework.

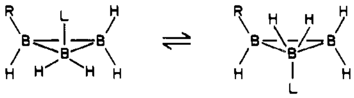
Table VII. BF Bonds in $B_3H_7F^-$

Structure	Atoms	Distance, Å	Overlap population	Bond index[a]	Most delocalized F lone pair Mulliken population		%d[b]
					F	B	
I	B_1-F_{11}	1.46	0.48	1.06	1.96	0.04	10
II	B_2-F_{11}	1.41	0.54	1.15	1.89	0.11	13
III	B_1-F_{11}	1.40	0.55	1.18	1.84	0.17	14
IV	B_2-F_{11}	1.50	0.45	1.05	1.98	0.02	10
V	$B_{2,3}$-F_{11}	1.47	0.37	0.76	2.00	0.00	10
VI	B_1-F_{11}	1.49	0.38	0.93	1.82	0.20[c]	15
	B_2-F_{11}	1.92	0.10	0.22			

[a] Reference 16. [b] % delocalization, ref 15d. [c] On B_2.

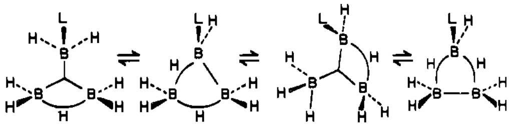


probably does occur on the NMR time scale, this is not observed since only structure I is in an energy minimum. If triborane was suitably substituted it might be possible to observe the BH_2L rotation via NMR.[35]



The high energy for the I–V–I process (41 kcal/mol by STO-4-31G) confirms that ligand migration for ether adducts is slow on the NMR time scale.[35] For NH_3 and CO adducts, the process would be even more difficult, though it appears to be easier for $B_3H_7F^-$. The mobility of the hydrogens as observed by NMR for amine and ether adducts[6b–g,36] is more difficult to reconcile with the data in Table II. For L = $(C_6H_5CH_2)_2CH_3N$ the upper limit for the potential barrier to intramolecular hydrogen scrambling is assigned to be about 6 kcal/mol.[36]

The scheme shown below shows a plausible path for hydrogen scrambling in B_3H_7·L suggested by work on $B_3H_8^-$.[6,24]

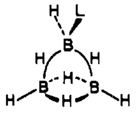


Progress along the reaction coordinate to IV would cost only about 7 kcal/mol in energy (STO-4-31G result, Table VI). However, movement beyond IV to II or III is required for hydrogen scrambling. Structure II is about 15 kcal/mol less stable than I, and scrambling of hydrogens in II is facilitated by the low barrier to rotation of the BH_3 group in II. Structure III is close to II in energy (18.7 kcal less stable than I) and provides for complete hydrogen scrambling. Smooth synchronous transit paths also have been found which interconvert structures I and II and structures I and III directly.

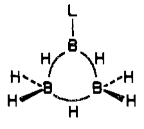
If the instability of III relative to I is taken as the barrier to hydrogen scrambling in B_3H_7·L, then the STO-4-31G result of 18.7 kcal/mol is 12.7 kcal/mol too high compared with experiment.[36]

Several explanations may be offered for this discrepancy. The Lewis basicity of amines varies with substitution with both steric and electronic factors being important.[37] If $(C_5H_6CH_2)_2CH_3N$ is a stronger base than NH_3 with respect to B_3H_7 then a lower barrier to hydrogen scrambling would be expected for $B_3H_7{\cdot}NCH_3(C_6H_5CH_2)_2$ than for $B_3H_7{\cdot}NH_3$ and vice versa. The STO-4-31G basis set is a distinct improvement over the minimum basis set results (Table VI). The addition of polarization functions might bring further improvement, particularly since structures I and III show distinctly different bonding patterns. The neglect of electron correlation is also important. The results for diborane (see above) suggest that basis set expansion and electron correlation could each account for several kilocalories per mole in relative energy. The results for $B_3H_8^-$ suggest the same, though the figures are more modest.[31] Solvent effects cannot be ruled out but do not appear to be critical. The NMR experiments have been carried out in a variety of solvents,[38] some of which are not expected to interact strongly with boron hydrides. Moreover, B_3H_7 adducts (and $B_3H_8^-$) are rather crowded molecules, suggesting that solvent approach may be difficult as far as the boron atoms are concerned. Exhaustive geometry optimization (with the constraint of C_s symmetry for structure III) might narrow the gap in energy between structures I and III.

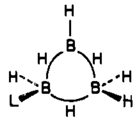
It is possible that additional paths to hydrogen scrambling are available. Several possibilities were explored, and none were found to be superior to a path through structure III. Breaking a bridge bond in the rotation of a BH_2H_μ or $BHLH_\mu$ fragment is quite energetically expensive. More exotic transition state candidates, VII, VIII, and IX, were found to be much higher in energy than III.



VII



VIII



IX

One way of elucidating pathways to rearrangement in triborane adducts would be to use crystal packing to trap low-energy structures. For instance, the ammonia–triborane structure appears to be trapped along the I–IV path. Analysis of the LMO's and internuclear distances reveals that the progress toward IV is slight but nonetheless noticeable.

The results in Table II suggest that $B_3H_7{\cdot}CO$ is more likely to show a frozen NMR spectrum than are ether or amine adducts, and this is indeed the case. In constrast to the mobility of the hydrogens in amine and ether adducts,[6b–g,36] the ^{11}B NMR spectrum for B_3H_7CO reveals a static system with structure I over a temperature range of −40 to 30 °C.[18] Likewise, triborane(7) adducts with PF_2X where X = F, Cl, or Br show a frozen structure I over the same temperature range.[18] PF_3 might be expected to have a base strength toward B_3H_7 comparable to that of CO.[39] PF_2X adducts where X = H or $N(CH_3)_2$ show a frozen structure III[40] in constrast to all other known neutral B_3H_7·L compounds[41] and the results of this study. Interestingly, a second isomer was observed[40] for these adducts, but was not fully characterized. Structure I would be a likely candidate and is consistent with the ^{11}B NMR spectrum reported for the second isomer.[40]

In general, triborane adducts with strong bases (amines and ethers) show fluxional behavior on the NMR time scale, while adducts with weak bases (CO and PF_3) show nonfluxional structure. Thus with the exception just noted[40] it appears that the preference for structure I as opposed to III is stronger with weaker bases.

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Registry No. $B_3H_7{\cdot}NH_3$, 12447-20-0; $B_3H_7{\cdot}H_2O$, 60718-92-5; $B_3H_7{\cdot}(CH_3)_2O$, 12347-17-0; $B_3H_7{\cdot}CO$, 11126-92-4; $B_3H_7F^-$, 60745-58-6.

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Stereochemistry of Some Aminoboranes Containing *N*-Trimethylsilyl, -germyl, or -stannyl Substituents[1]

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Rotational barriers ($\Delta G_c^‡$) about the B–NMe_2 bond in the compounds $RR'NB(Ph)NMe_2$ were determined from variable-temperature proton NMR data. The $\Delta G_c^‡$ values vary from approximately 9 to 20 kcal/mol depending on the nature of the RR′N substituent. Compounds containing bis(trimethylsilyl)amino or *tert*-butyltrimethylsilylamino groups were found to have the highest B–NMe_2 barriers while significantly lower $\Delta G_c^‡$ values were obtained for those compounds with other alkyltrimethylsilylamino, Me_3SiNR (R = H, Me, Et, *i*-Pr), *N*-trimethylgermyl, Me_3GeNR (R = Me_3Ge, *t*-Bu), or *N*-trimethylstannyl, Me_3SnNR (R = Me_3Sn, Me), substituents. The results, which are discussed primarily in terms of the steric interactions between the RR′N and Me_2N amino groups, lead to the main conclusion that in compounds such as $(Me_3Si)_2NB(Ph)NMe_2$ the bulky bis(trimethylsilyl)amino substituent is rotated out of the plane of the B–NMe_2 moiety and thus is not an effective π donor to boron.

Introduction

The existence of $(p-p)\pi$ bonding in aminoboranes and the resultant possibility of cis–trans isomerization was first postulated in 1948 by Wiberg.[2] The concept was formulated primarily on the basis of the isoelectronic nature of the $>B{=}N<$ and $>C{=}C<$ linkages. A large number of studies have since been conducted in an effort to better define the extent of π interaction in the boron–nitrogen bond. Molecular orbital calculations[3] and detailed vibrational spectra analysis[4] both indicate a boron–nitrogen π-bond order of at least 0.4 in simple aminoboranes. In a report of the electron diffraction study of dichloro(dimethylamino)borane Clippard and Bartell[5]