π-Interactions in the Structures of 1- and 2-Methylpentaborane and 1- and 2-Silylpentaborane. An Electron Diffraction Study

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Abstract: The results of the present electron diffraction analyses of 1- and 2-methylpentaborane and 1- and 2-silylpentaborane are consistent with recent extended Hückel calculations regarding the relative stabilities of the four compounds. In the case of the silyl derivatives, where 1-$SiH_3B_5H_8$ is predicted to be significantly more stable than 2-$SiH_3B_5H_8$, the increased stability is reflected in the reported bond lengths: r_g (B–Si) = 1.981 ± 0.005 Å and 2.006 ± 0.004 Å for the 1- and 2-isomers, respectively. The difference, 0.025 ± 0.005 Å, can be rationalized in terms of increased π-interaction with the boron cage for the apically substituted isomer. For the methyl compounds, 2-$CH_3B_5H_8$ is predicted to be more stable than 1-$CH_3B_5H_8$ but the calculated difference is considerably less than in the case of the silyl pentaboranes. The experimental bond lengths are r_g(B–C) = 1.592 ± 0.005 Å for 2-$CH_3B_5H_8$ and 1.595 ± 0.005 Å for the 1-derivative. This difference, 0.003 ± 0.005 Å, is experimentally insignificant and supports the assumption that the degree of B–C π-interaction is small; however, this also seems to preclude the supposition that the difference in stability is due to increased σ-bonding. Other average structural parameters obtained include $r_g(B-H_t)$ = 1.223 ± 0.013, $r_g(B_1-B_2)$ = 1.707 ± 0.003, $r_g(B_2-B_3)$ = 1.813 ± 0.004, $r_g(B-H_b)$ = 1.389 ± 0.012, r_g(C–H) = 1.129 ± 0.011, and r_g(Si–H) = 1.514 ± 0.014 Å. Mean amplitudes of vibration calculated from transferred force constants were used in refining the experimental data. An estimate of the previously unreported B–Si stretching force constant (2.1 ± 0.4 mdyn/Å) was obtained from the average observed amplitude of vibration for this distance (l = 0.063 ± 0.005 Å). A comparison of the radial distribution curves for models assuming free rotation of the methyl and silyl groups with the curves generated for the static models led to the somewhat expected conclusion that the 12-fold barrier to internal rotation is extremely low.

Isomerization studies of pentaborane(9) derivatives have raised a number of interesting questions regarding the nature of the boron-substituent bond. In the case of fluorine substitution, Burg[2] has suggested that π-interaction with the boron cage could be the dominant factor stabilizing 2-FB_5H_8 relative to 1-FB_5H_8. A similar rationalization has been used to explain the isomerization of 1-$CH_3B_5H_8$ to 2-$CH_3B_5H_8$. Recent extended Hückel calculations on 1- and 2-RB_5H_8 (R = F, CH_3, and SiH_3)[3] predict the following relative stabilities: 2-FB_5H_8 > 1-FB_5H_8, 2-$CH_3B_5H_8$ > 1-$CH_3B_5H_8$, and 1-$SiH_3B_5H_8$ > 2-$SiH_3B_5H_8$. These theoretical considerations suggest that fluorine (2p) π-interactions and silicon (3p and 3d) π-interactions with the boron cage determine the relative stabilities of the isomers of FB_5H_8 and $SiH_3B_5H_8$. However, the extent of B–C π-bonding in methylpentaborane is small in comparison, and other factors are presumed to dominate.

Structurally there is little reported literature on the Si–B bond. This is due to the relative paucity (with the exception of the high-temperature boron silicides[4,5]) of compounds containing a B–Si bond. The Si–B bond length in perfluoroborodisilane[6] (r_g = 2.008 ± 0.017 Å) appears to be the only previous determination of this distance by gas phase electron diffraction.

In an attempt to obtain more insight into the nature of the boron-substituent bond, the structures of 1- and 2-$SiH_3B_5H_8$ and 1- and 2-$CH_3B_5H_8$ have been investigated by gas phase electron diffraction. What appears to be the first experimental evidence for a B–Si π-interaction has been obtained.

Experimental Section

Standard high-vacuum techniques were used for the manipulation and purification of the substituted pentaboranes studied in this experiment. 1-$CH_3B_5H_8$ was prepared using previously reported procedures.[7,8] 2-$CH_3B_5H_8$ was prepared by heating 1-$CH_3B_5H_8$ at 55° in the presence of hexamethylenetetramine, as was reported by Onak and coworkers.[9] Chlorosilane was prepared by the method of Stock and Somieski.[10] μ-$SiH_3B_5H_8$ was subsequently prepared and isomerized to 2-$SiH_3B_5H_8$.[3,11] 1-$SiH_3B_5H_8$ was prepared by gas phase isomerization of 2-$SiH_3B_5H_8$ at 120°.[3,12]

The samples of the above-mentioned pentaborane derivatives were then purified using repeated trap to trap distillations. Purity was monitored by 70.6-MHz ^{11}B nmr using a Varian Associates HR-220 spectrometer operating at 51.7 kG and equipped with a "home-built" pulse apparatus. The purity of the resultant samples was determined to be in excess of 99%.

The Indiana University electron diffraction unit, equipped with an r^3 sector, was used to record the data. The 0.3-μA beam, accelerated to 40 keV, gave exposure times of 2–3 min for the 12-cm camera distance and 1–1.5 min for the 29-cm distance. All four samples were run consecutively at ambient room temperature, without breaking the vacuum or altering the nozzle position. In this way it was hoped to keep between-sample systematic errors to a minimum. The background pressure was maintained at less than 4×10^{-5} Torr throughout the data collection by situating a liquid nitrogen cold trap opposite the nozzle. The nozzle-to-plate distance was measured using a cathetometer and the wavelength was determined with a precision voltage divider. The entire procedure is frequently calibrated with CO_2 (r_a(C–O) = 1.1646 Å).[13]

The Kodak electron image plates were developed according to the procedure originally reported by Foster.[14] Three high quality plates for each sample and camera length were selected for microphotometering on the Indiana University automated microdensitometer.[15] The data were corrected for emulsion saturation, plate flatness, and sector imperfections before being interpolated at integral $q(10s/\pi)$ intervals. The leveled intensities, as well as the correlation and error matrices from the least-squares analyses are available.[16]

Data Analysis

Figure 1 shows a generalized model for the molecules studied and the atomic numbering system used in defining the parameters. The following structural constraints were applied throughout the least-squares analysis of the data. (i) All terminal hydrogen–boron distances were constrained to be equivalent. Accurate neutron diffraction data[17] on decaborane lends credence to this assumption. (ii) The boron framework was constrained to have C_{4v} symmetry in both the 1- and 2-substituted derivatives. A crystallographic

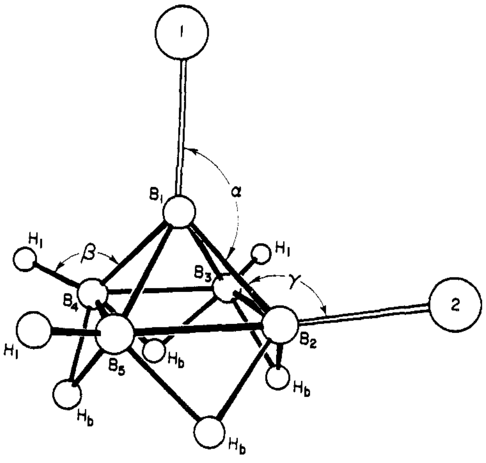

Figure 1. The numbering system used in defining the parameters for the generalized model of the four pentaborane(9) derivatives.

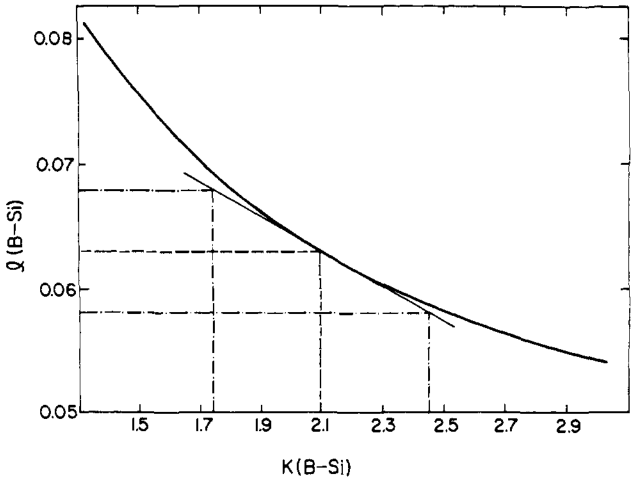

Figure 2. Dependence of B–Si amplitude of vibration on the corresponding stretching force constant.

Table I. Force Constants in the Calculation of Mean Amplitudes (K in mdyn/Å, H and τ in mdyn Å)

Force constant		Ref	Force constant		Ref
$K(B_1–B_2)$	2.054	20	$H(B_1B_2H_b)$	0.285	20
$K(B_2–B_3)$	1.631	20	$H(H_bB_2H_t)$	0.290	20
$K(B–C)$	3.600	22	$H(B_2H_bB_3)$	−0.037	20
$K(B–Si)$	2.100	a	$H(BCH)$	0.470	22
$K(B_2–H_t)$	3.669	20	$H(BSiH)$	0.490	a
$K(B_2–H_b)$	1.127	20	$H(HCH)$	0.440	22
$K(C–H)$	4.700	23	$H(HSiH)$	0.460	21
$K(Si–H)$	2.800	21	$H(CBB)$	0.240	22
$H(B_1B_2H_t)$	0.326	20	$H(SiBB)$	0.250	a
$H(H_bB_2H_b)$	0.758	20	$\tau(B_1B_2B_3H_b)$	0.479	20

[a] Estimated, see text.

study[18] of 2,3-dimethylpentaborane indicates only minor splittings in the boron–boron distances. Moreover, since the B–Si and B–C distances are separated by 0.17–0.30 Å and 0.11–0.22 Å from the B–B distances, it seems unlikely that this assumption would meaningfully alter the results of the analysis. (iii) All bridging hydrogen–boron distances were also contrained to be equal in the 2-substituted compounds. Although this is not generally the case in nonsymmetric boron hydrides,[17-19] it was felt that adopting this simplifying assumption would introduce no significant errors into the values obtained for the more interesting parameters. (iv) The methyl and silyl groups were constrained to local C_{3v} symmetry throughout.

For molecules of this size, it is advantageous to calculate all the amplitudes of vibration (and shrinkage corrections) and then vary only a small number of them in the analysis. This, however, requires a complete quadratic force field for the molecule. At the present time no such fields exist for the molecules included in this study. The somewhat less satisfactory alternative of transferring force constants from related molecules was therefore used. The valence force constants for the pentaborane skeleton were taken from Coriell,[20] while the force constants of Duncan[21] and Becher[22] were assumed for the methyl and silyl groups. In addition, the C–H stretching force constant of Schachtschneider and Snyder[23] was used and an initial estimate of K(B–Si) was obtained from the empirical equation of Herschbach and Laurie[24] since one could not be found in the literature. The amplitudes of vibration and shrinkage effects were calculated using a method described in detail elsewhere.[25]

The long and short camera distance data were leveled, spliced together, and analyzed by differential least squares. Power series polynomials were used to fit the correlation background at each stage of the analysis. This background was then refined using the criterion of Karle and Karle[26] for nonstructural regions of the resulting radial distribution curve. These calculations were performed on the Indiana University CDC-6600 computer using the elastic scattering factors and phase shifts of Schafer, Yates, and Bonham[27] and the inelastic scattering factors of Cromer.[28] The Morse anharmonicity parameters for C–H and Si–H were estimated to be a = 2.5 and 2.0 Å^{-1}. The values for the remaining bonded distances were approximated using the method of Herschbach and Laurie[24] to be a = 2.2 Å^{-1} for B_1–H_1, 1.9 for C–B, 1.8 for Si–B, and 1.7 for B_1–B_2 and B_2–B_3.

Results

It became obvious in the early stages of the analysis that the approximated force constant for the B–Si stretching coordinate was too small. In general the calculated l_{ij}'s were all smaller than the experimental ones with the exception, that is, of the B–Si mean amplitude. To get a better estimate of K(B–Si), therefore, the amplitudes of vibration were calculated for a number of force fields differing only by the value of the force constant for the B–Si stretch. The results are shown in Figure 2. From the average experimental l(B–Si) = 0.063 ± 0.005 Å, it would appear that K(B–Si) = 2.1 ± 0.4 mdyn/Å is a more reasonable estimate than the value obtained from the approximate method of Herschbach and Laurie[24] (1.35 mdyn/Å). The final force constants used for the calculation of mean amplitudes and shrinkage effects are listed in Table I.

At the start of the refinement the methyl and silyl groups were constrained to a static position relative to the boron framework. When free rotation of these groups was introduced in the latter stages, a marginal improvement in the R factors was observed. Although the resulting radial distributions curves were not very sensitive to such modifications, we believe that the 12-fold barrier to internal rotation is indeed extremely low as has been suggested by the microwave work of Cohen and Beaudet[29] on $1\text{-}CH_3B_5H_8$.

The structural parameters obtained from the least-squares refinements are listed in the r_g representation in Table II. Also included in this table are the bonded amplitudes of vibration that were refined in the analyses along with the corresponding theoretical values obtained from the force field of Table I. The final radial distribution and intensity curves for all four molecules are reproduced in Figures 3 and 4, respectively.

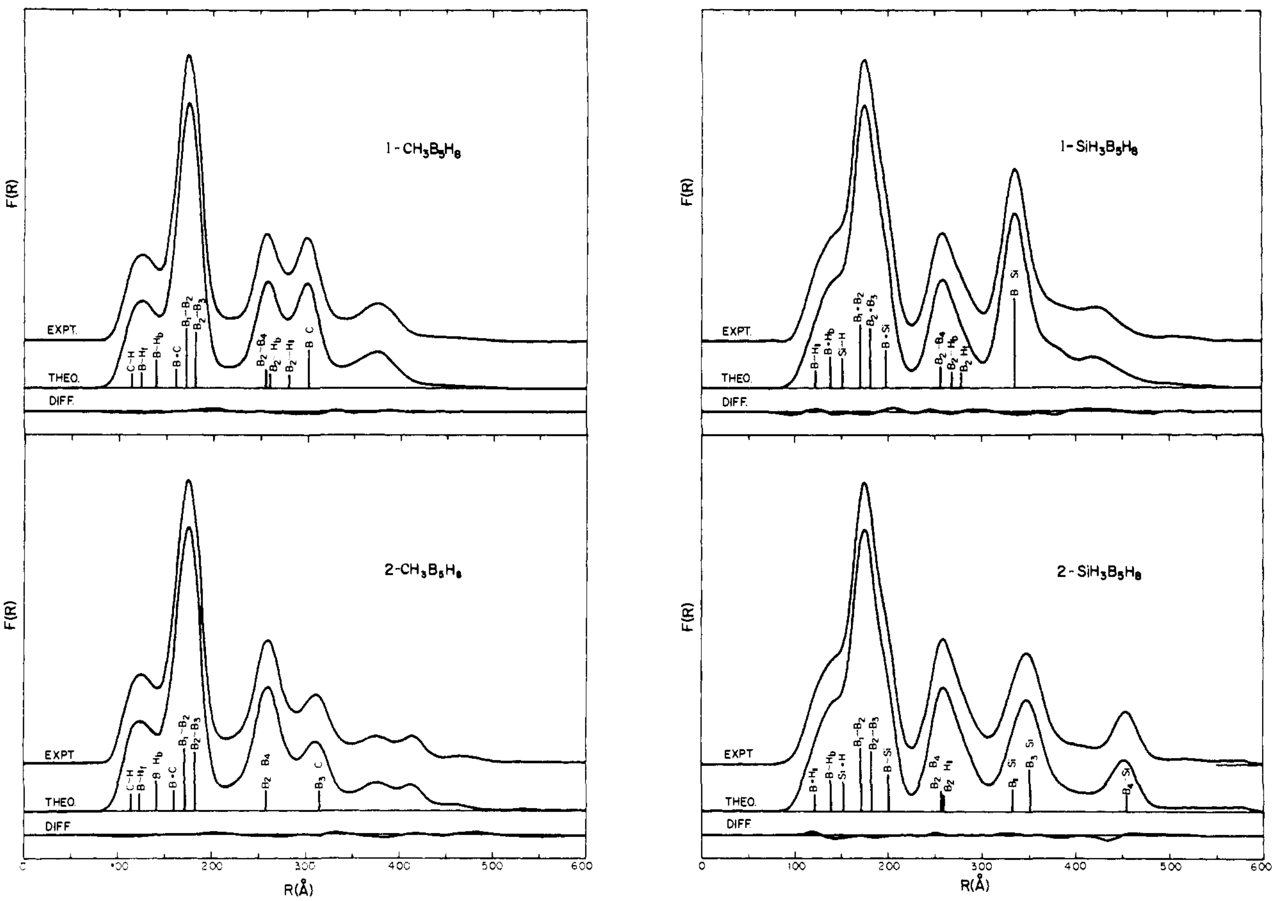

Figure 3. Radial distribution curves for 1- and 2-methylpentaborane and 1- and 2-silylpentaborane. The positions of the prominent distances are indicated by vertical bars.

Table II. Least-Squares Parameters Obtained for the Substituted Pentaboranes[a]

Parameter	Methylpentaborane			Silylpentaborane		
	1-Isomer	2-Isomer	Calcd	1-Isomer	2-Isomer	Calcd
r(B–X), Å	1.595 ± 0.005	1.592 ± 0.005		1.981 ± 0.005	2.006 ± 0.004	
$r(B_2–B_3)$, Å	1.805 ± 0.003	1.817 ± 0.003		1.811 ± 0.005	1.819 ± 0.004	
$r(B_1–B_2)$, Å	1.711 ± 0.002	1.703 ± 0.002		1.707 ± 0.003	1.709 ± 0.003	
$r(B_2–H_b)$, Å	1.389 ± 0.011	1.399 ± 0.010		1.382 ± 0.017	1.387 ± 0.010	
$r(B_2–H_t)$, Å	1.232 ± 0.011	1.221 ± 0.010		1.226 ± 0.019	1.221 ± 0.013	
r(X–H), Å	1.128 ± 0.012	1.131 ± 0.010		1.510 ± 0.014	1.518 ± 0.013	
α,[b] deg	131.8 ± 0.1	131.0 ± 0.1		131.4 ± 0.2	131.2 ± 0.2	
β,[b] deg	127.0 ± 3.2	134.3 ± 4.8		123.2 ± 2.4	142.1 ± 6.3	
<BXH, deg	104.8 ± 2.7	103.3 ± 2.1		116.2 ± 4.1	112.5 ± 3.8	
γ,[b] deg		132.7 ± 1.8			127.5 ± 1.5	
τ,[c] deg	194.3 ± 2.5	198.4 ± 2.0		185.5 ± 3.6	195.7 ± 1.9	
l(B–X), Å	0.059 ± 0.009	0.058 ± 0.007	0.053	0.062 ± 0.005	0.064 ± 0.004	0.063
$l(B_2–B_3)$, Å	0.072 ± 0.003	0.070 ± 0.004	0.063	0.076 ± 0.004	0.077 ± 0.004	0.063
$l(B_1–B_2)$, Å	0.066 ± 0.004	0.066 ± 0.004	0.060	0.072 ± 0.004	0.072 ± 0.005	0.060
$l(B_2–H_b)$, Å	0.117 ± 0.010	0.115 ± 0.009	0.116	0.130 ± 0.011	0.119 ± 0.010	0.116
$l(B_2–H_t)$, Å	0.100 ± 0.011	0.093 ± 0.010	0.084	0.120 ± 0.017	0.109 ± 0.014	0.084
l(X–H), Å	0.082 ± 0.010	0.081 ± 0.008	0.079	0.100 ± 0.011	0.101 ± 0.009	0.089
% R(Int)[d]	4.7	4.2		5.8	5.0	
% R(RD)[d]	1.6	1.5		2.3	2.0	

[a] Distances are reported as $r_g(0)$ values while angles are assigned the values in an r_α structure. Uncertainties are 3σ but do not include an estimate of systematic error. [b] See Figure 1. [c] Derived external dihedral angle defined by the planes $B_1B_2B_3$ and $B_2B_3H_b$. [d] Generalized R factors for the intensity and radial distribution curves.

Conclusions

Previously reported extended Hückel calculations[3] predict 1-silylpentaborane to be favored over 2-silylpentaborane by approximately 0.40 eV. Both Si(3d) and Si(3p) π-interactions with the boron cage are suggested to contribute to this increased stability. The B–Si bond lengths obtained in the present study, 1.981 ± 0.005 Å for 1-$SiH_3B_5H_8$ vs. 2.006 ± 0.004 Å for 2-$SiH_3B_5H_8$, show a shortening of 0.025 ± 0.005 Å for the more stable apically substituted derivative. Hence the structural data are consistent with the postulate of stronger B–Si π-bonding in the 1-silyl compound.

In the case of the methylpentaboranes, the correct stabil-

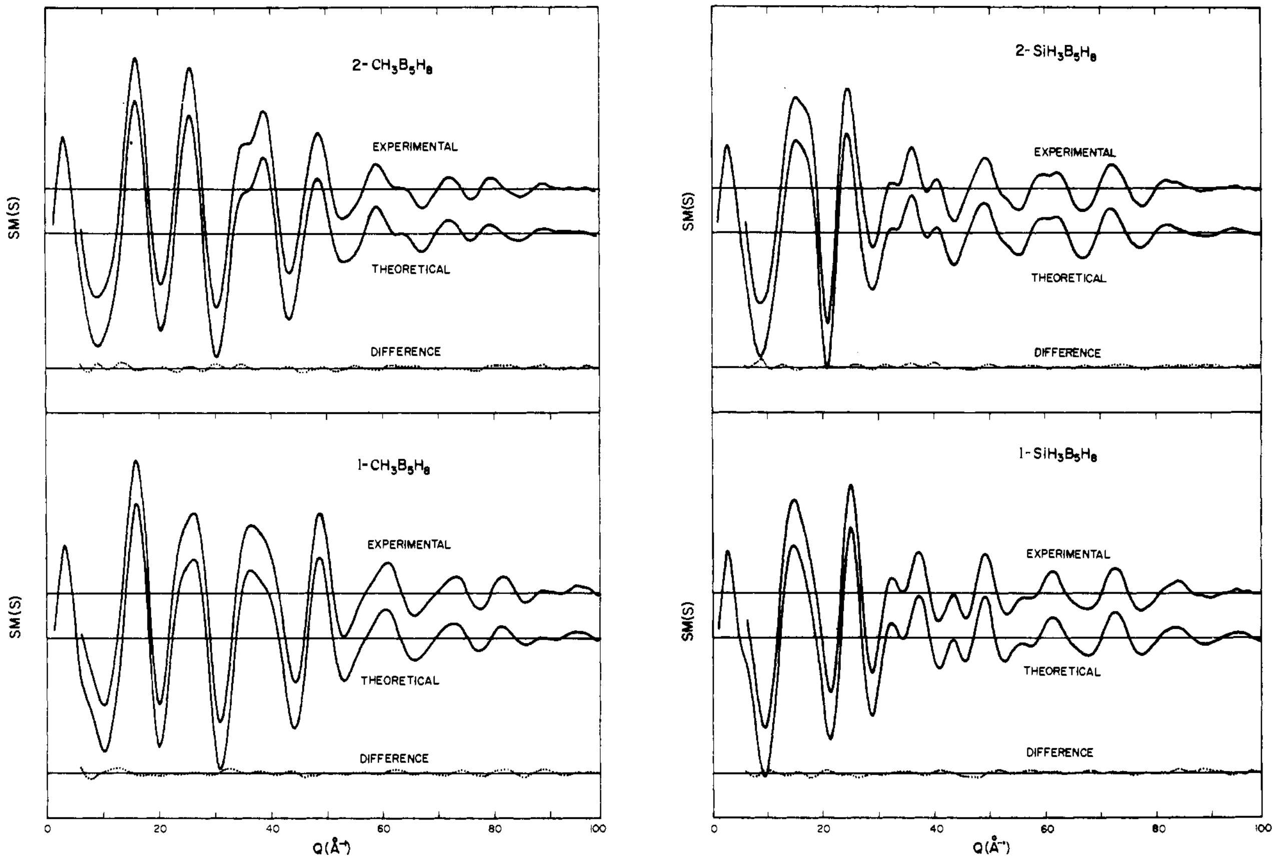

Figure 4. The experimental and theoretical molecular intensity curves for 1- and 2-methylpentaborane and 1- and 2-silylpentaborane. $q \equiv (40/\lambda) \sin(\theta/2)$.

ity trend (2 > 1) is also predicted by the theoretical considerations.[3] These calculations, however, indicate that the difference (0.19 eV) is almost entirely a result of boron cage-methyl proton interactions, and the effect of B-C π-interaction is minimal. The B-C bond lengths reported in this electron diffraction investigation for 1- and 2-$CH_3B_5H_8$, 1.595 ± 0.005 and 1.592 ± 0.005 Å, respectively, are equal within the experimental uncertainties. Thus B-C π-interactions most likely do not contribute greatly to the increased stability of the basal substituted derivative. In addition, these distances are inconsistent with the alternative explanation of increased σ-bonding and factors such as steric effects and methyl proton-cage interactions may indeed be of greater importance.

Although the primary interest of this comparative study was the effect of π-interactions on the B-C and B-Si bond lengths, the results are consistent with previously reported electron diffraction and microwave substitution values for related systems. In order to compare the results obtained here with the microwave r_s structures, it is first of all necessary to estimate the r_e parameter by

$$r_e \cong r_g - \tfrac{3}{2} a l_{ij}^2 - \delta_{\text{cent}}$$

where a is the Morse anharmonicity parameter and δ_{cent} is the centrifugal distortion. The average values obtained for the B_1-B_2 distance, $r_g = 1.707 \pm 0.003$ Å ($r_e = 1.695$ Å) agree well with the electron diffraction result of Hedberg[30] on pentaborane, $r_g = 1.700 \pm 0.017$ Å, and the microwave bond lengths reported by Hrostowski[31] and Beaudet,[29] $r_s = 1.687 \pm 0.005$ Å, for pentaborane and 1-methylpentaborane. The average B_2-B_3 distance, $r_g = 1.813 \pm 0.004$ Å ($r_e = 1.800$ Å), shows similar agreement with Hedberg,[30] $r_g = 1.805 \pm 0.014$ Å, and the substitution parameter,[29,31] $r_s = 1.800 \pm 0.005$ Å. Also, the mean value for the B-C bond length, $r_g = 1.593 \pm 0.005$ Å, agrees well with the r_g(B-C) = 1.590 ± 0.003 Å distance reported by Bartell[32] for the "electron-deficient" tetramethyldiborane. However, the value arrived at for this parameter by Beaudet[29] through several simplifying assumptions, $r_s = 1.62 \pm 0.01$ Å, is in rather poor agreement with the present work, $r_e = 1.583 \pm 0.003$ Å. Finally, the B-Si bond length of 2.008 ± 0.017 Å determined by Bauer and coworkers,[6] compares very well with the value obtained for 2-$SiH_3B_5H_8$ of 2.006 ± 0.004 Å, where very little bond shortening is expected due to π-interactions.

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Supplementary Material Available. A tabulation of the experimental data, correlation matrices, and error matrices will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JACS-75-1074.

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Kinetics of Thallium(I)–Triiodide Complexation in Aqueous Perchloric Acid

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Abstract: The specific rate constant for the formation of the 1:1 thallium(I)–triiodide complex in aqueous perchloric acid (10^{-2} *M*) has been measured over the temperature range 5–45° using the stopped-flow technique. The reaction is first order in both ions when Tl^+ is kept in large excess over the I_3^- ion concentration, at least 200:1. Formation of higher complexes complicates the kinetic interpretation when the ion concentration ratio is reversed. Consequently, rate studies were made under pseudo-first-order experimental conditions. The resultant second-order rate constant k_3 is $(1.75 \pm 0.03) \times 10^4\ M^{-1}\ sec^{-1}$ at 25° which is comparatively low for substitution rates into univalent ions and may indicate ligand dependence in the rate-determining step. Activation parameters for the reaction are $\Delta H^\ddagger = 7.24$ kcal mol^{-1} and $\Delta S^\ddagger = -14.8$ cal deg^{-1} mol^{-1} which are large for univalent ion interactions and may indicate drastic solvent reorganization around Tl(I) in forming the activated complex.

The equilibrium reaction in which iodide ion and the iodine molecule associate to form the triiodide complex ion has been the subject of numerous investigations in a variety of solvents.[2] Anomalies observed when the data were treated in terms of only the one to one association, have, for the most part, been rationalized in terms of higher associations,[3,4] *e.g.*, to I_5^- and I_6^{2-}. From recent laser resonance Raman spectroscopy,[5] equilibrium,[6] and calorimetric[7] investigations, there is evidence in favor of a cation–triiodide association reaction which could be offered as an alternative reaction to polyiodide formations. The evidence is especially convincing when Tl(I) is the counterion. We report here what we believe to be the first kinetic study of the complexation of Tl(I), although the two-electron transfer process Tl(I) ⇌ Tl(III) has been the subject of extensive study and much controversy for many years.[8]

Experimental Section

Solutions were prepared using redistilled, deionized water and analytical grade thallium nitrate (Matheson Coleman and Bell Co., Inc.), potassium iodide (Matheson Coleman, and Bell Co., Inc.), and resublimed iodine (Allied Chemical Co.). To supress the hydrolysis of iodine, all solutions contained 10^{-2} *M* perchloric acid. All other solute concentrations were 10^{-3} *M* or less so the studies were made at essentially constant ionic strength. Potassium iodide was kept at least five times in excess of iodine, solutions being prepared immediately prior to the kinetic studies.

Kinetic experiments were done on a Durrum-Gibson stopped-flow instrument at 5, 15, 25, 35, and 45°, all temperatures being maintained to within ±0.2°. In the presence of thallium(I) ion the spectrum of triiodide solutions shows a new absorption band[7] with a maximum optical density at 395 nm. The kinetics of the reaction were followed at two wavelengths, at 395 and at 360 nm, the wavelength of maximum absorption of triiodide. Both analyses gave the same kinetic result and as such demonstrated the one to one correspondence between the loss of triiodide and the production of the TlI_3 complex.

Results

The compound with the stoichiometric formula TlI_3 is known to be thallium(I) triiodide, and not thallium(III) iodide, because of an internal oxidation–reduction reaction. At pH 2, no complications from the hydrolysis of Tl(I) arise, and the hydrolysis of iodine is suppressed. The equilibrium reactions which exist in solution are therefore

$$I_2 + I^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} I_3^- \tag{1}$$

and the complexation of thallium(I).

$$Tl^+ + I_3^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} TlI_3 \tag{2}$$

Other possible complexes[9] such as $TlNO_3$ and $TlI_x^{(x-1)-}$ have been shown to be unimportant provided the metal ion was kept in large excess.[6] A kinetic study of reaction 1 was reported by Sutin, *et al.*,[10] using the laser-Raman temperature jump technique, and the reaction is too rapid to be that observed in the stopped-flow experiments: $k_1 = 6.2 \times 10^9\ M^{-1}\ sec^{-1}$, $k_2 = 8.5 \times 10^6\ sec^{-1}$. A steady state kinetic analysis of the successive reactions 1 and 2 shows that the observed rate constant, k_{obsd}, is equal to k_3. Equilibrium