components. Such estimates are consistent with assignment of the fraction as a mixture of $Me_3N{\cdot}BH_2N_3$ and $Me_3N{\cdot}BH(N_3)_2$ in a mole ratio of approximately 1:2. If the second component is indeed the diazidoborane, a suggestion compatible with the infrared spectrum of the fraction, it seems reasonable that this component be the kinetically more active one. First, there is a statistical factor favoring its reactivity due to the availability of two azide ligands for protonation. Further, if the activated complex for hydrolysis of substrate conjugate acid involves impending loss of HN_3 via cleavage of the boron–azido nitrogen linkage, a process presumably facilitated energetically by water, then the transition state may be stabilized through delocalization of positive charge of the incipient boronium ion into the remaining boron-bonded N_3 ligand. A comparable effect due to H^- would not be possible in the cationic complex originating from loss of HN_3 from the *mono*azidoborane. This interpretation remains highly spectulative in view of the uncertainty in the composition of the fraction. It is somewhat reminiscent of, but different from, the inductive substituent effects proposed to explain the *decrease* in kinetic activity observed on replacement of hydride by a second halide ion in the hydrolysis of the trimethylamine–haloboranes, $Me_3N{\cdot}BH_2I$ and $Me_3N{\cdot}BHI_2$.[10]

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Registry No. $Me_3N{\cdot}BH_2N_3$, 61652-29-7; D, 16873-17-9; $(Me_3N)_2BH_2I$, 64082-19-5; H^+, 12408-02-5; $Me_3N{\cdot}B(N_3)_3$, 64082-18-4.

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Contribution from the Laboratoire de Chimie de Coordination du CNRS, B. P. 4142, 31030 Toulouse, Cedex, France,
and Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

Microwave Spectrum and Structure of Trimethylamine–Boron Trifluoride. $Me_3N{\cdot}BX_3$ Adduct Stability and the Reorganization Energies of BF_3 and BH_3

PATRICK CASSOUX,[1a] ROBERT L. KUCZKOWSKI,*[1b] and ALAIN SERAFINI[1a]

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The microwave spectrum of deuterium and carbon-13 enriched samples of trimethylamine–boron trifluoride have been assigned. The structure of the complex has been determined as $d(BN) = 1.636 \pm 0.004$ Å, $d(BF) = 1.387 \pm 0.005$ Å, $d(CN) = 1.476 \pm 0.005$ Å, $d(CH) = 1.10 \pm 0.03$ Å, $\angle CNC = 108.6 \pm 0.2°$, $\angle FBF = 112.4 \pm 0.2°$, and $\angle HCH = 111 \pm 2°$. The reorganization energies of BF_3 and BH_3 upon complexation with trimethylamine have been calculated using an ab initio method (IBMOL6) as 27.9 and 15.1 kcal/mol, respectively. This work shows that the differences in the reorganization energies of the two acids parallel their Me_3N adduct stabilities and quantitatively account for a major contribution to their difference in stability.

Introduction

An accurate structure for the heavy atoms in $Me_3N{\cdot}BH_3$ was recently completed.[2,3] The B–N internuclear distance was 1.638 ± 0.010 Å which is virtually identical with the value 1.636 ± 0.004 Å in $Me_3N{\cdot}BF_3$.[4] It was therefore suggested[2] that the lesser stability of $Me_3N{\cdot}BF_3$ vs. $Me_3N{\cdot}BH_3$ might be rationalized by the assumption that the reorganization energy of BF_3 is greater than for BH_3. In order to test such a suggestion by estimating the reorganization energies of the two species, it would be extremely valuable to have precise values for the BF_3 geometry in the adduct.[5] Also, a comparison of the Me_3N geometry in both adducts is desirable as well as comparisons with other compounds such as $Me_3N{\cdot}BX_3$ (X = Cl, Br, I,[6] and $CH_3CN{\cdot}BF_3$[7]). For these reasons we have reinvestigated the microwave spectrum of $Me_3N{\cdot}BF_3$ with sufficient isotopic species to determine the heavy-atom

Table I. Transition Frequencies and Moments of Inertia

Species	Transition $J \rightarrow J'$	ν/MHz	I_B/uÅ^2
$(^{13}CH_3)_3N\cdot{}^{11}BF_3$	5 → 6	20 473.31	296.2155
	6 → 7	23 885.48	296.2161
	8 → 9	30 709.74	296.2177
	9 → 10	34 121.80	296.2188
$(^{13}CH_3)_3N\cdot{}^{10}BF_3$	5 → 6	20 518.65	295.5609
	6 → 7	23 938.47	295.5604
	8 → 9	30 777.83	295.5623
	9 → 10	34 197.46	295.5634
$(CD_3)_3N\cdot{}^{11}BF_3$	9 → 10	30 935.79	326.7258
	10 → 11	34 029.23	326.7271
$(CD_3)_3N\cdot{}^{10}BF_3$	9 → 10	31 008.72	325.9573
	10 → 11	34 109.52	325.9560
$(CH_3)_3N\cdot{}^{11}BF_3$[a]	9 → 10	35 121.42	287.7879
$(CH_3)_3N\cdot{}^{10}BF_3$[a]	9 → 10	35 195.38	287.1831
$(CH_3)_3{}^{15}N\cdot{}^{11}BF_3$[a]	9 → 10	35 032.40	288.5192

[a] From ref 4.

Table II. Total Energies and Planar-Pyramidal Reorganization Energies (ΔH_R)[a] for BH_3 and BF_3

Species	Total energy/kcal mol^{-1}	ΔH_R/kcal mol^{-1}
BH_3, planar	−16 549.5	15.1
BH_3, pyramidal	−16 534.4	
BF_3, planar	−202 760.4	27.9
BF_3, pyramidal	−202 732.5	

[a] See ref 20.

Table III. Structural Parameters for $Me_3N\cdot BF_3$ (Distances, Å; Angles, deg)

$d(BN) = 1.636 \pm 0.004$

$d(BF) = 1.387 \pm 0.005$ $\angle FBF = 112.4 \pm 0.2$
$d(F\cdots F) = 2.305 \pm 0.01$ $\angle FBN = 106.3 \pm 0.2$

$d(CN) = 1.476 \pm 0.005$ $\angle CNC = 108.6 \pm 0.2$
$d(C\cdots C) = 2.400 \pm 0.01$ $\angle CNB = 110.4 \pm 0.3$

$d(CH) = 1.10 \pm 0.03$ $\angle HCH = 111 \pm 2$
$\angle HCN = 109 \pm 2$

structure with suitable precision.

Experimental Section

Samples. The samples of $(CD_3)_3N\cdot BF_3$ and $(^{13}CH_3)_3N\cdot BF_3$ were enriched ≥99% in D and ^{13}C, respectively. The deuterated sample was prepared by Dr. P. Clippard using standard techniques.[8] The ^{13}C sample was prepared by heating (3 h at 135 °C) 0.570 g of $(^{13}CH_2O)_3$ with 0.218 g of NH_4Cl. The mixture was frozen to −78 °C and 0.5 mL of H_2O was added. $(^{13}CH_3)_3N$ was liberated by addition of NaOH in excess and then reacted with BF_3 in the vacuum line. The $(^{13}CH_3)_3N\cdot BF_3$ sample was recrystallized in acetone.

Spectrometers. The spectrum of the $(CD_3)_3N\cdot BF_3$ species was measured using both oscilloscope and recorder display with a conventional spectrometer employing klystron sources.[9a] The spectrum of the ^{13}C species was recorded with a Hewlett-Packard Model 8460A spectrometer.[9b] The absorbtion cell was at room temperature and pressures between 0.005 and 0.020 mmHg were employed. The uncertainty in the frequency measurements was estimated to be ±0.1 MHz.

Spectra. The frequencies of the ground-state transitions measured for the ^{11}B and ^{10}B species of $(CD_3)_3N\cdot BF_3$ and $(^{13}CH_3)_3N\cdot BF_3$ are listed in Table I. Several excited vibrational satellites were also observed which were weaker (ω_{VIB} was estimated by microwave relative intensity measurements as about 150–200 cm^{-1} for the D_9 species) and resembled degenerate vibrations. They were not further investigated. A small centrifugal distortion contribution (D_J approximately 0.1–0.2 kHz) is apparent but difficult to measure accurately. To minimize this contribution, the I_B values used in the structure calculations were taken from the 9→10 transition for all isotopic species. They are listed in Table I including the values previously reported for the other available isotopic species.[4]

Computation. The reorganization energy of BH_3 and BF_3 was obtained by calculating the energy differences for free BH_3 and BF_3 and for a deformed geometry corresponding to complexation. All electron ab initio SCF–MO calculations were carried out by using the IBMOL6 computational scheme[10] with Gaussian type orbitals contracted in a double-ζ form (9/5 to 4/2) as described by Snyder and Basch.[11] An optimized BH bond length (1.186 Å) was employed for planar BH_3.[12] For pyramidal BH_3, $d(BH)$ and $\angle HBH$ were taken as in $Me_3N\cdot BH_3$.[2] In planar BF_3, the experimental BF bond length (1.313 Å)[13] was employed. For pyramidal BF_3, the BF_3 group geometry determined in the present work was used; i.e., $d(BF) = 1.387$ Å and $\angle FBF = 112.4°$. All these calculations were performed on the IBM 370-168 computer of the CNRS (CIRCE, Orsay, France). The results are listed in Table II.

Discussion

Structure Determination. If the methyl groups are assumed to have local C_{3v} symmetry about the CN bond, then seven structural parameters establish the geometry of the complex. The structural parameters can be determined by least-squares fitting[14] of the moments of inertia of the seven isotopic species. A variety of strategies were employed. For example, either the BN bond length was fixed to the value determined in ref 4 by Kraitchman's equations[15] and the remaining parameters were determined by least-squares fitting of the moments or $d(BN)$ was determined as a I_0 distance along with the remaining parameters. In other calculations $d(CH)$ was assumed a value between 1.08 and 1.11 Å and the remaining parameters were determined by fitting the moments. All of these types of calculations were also repeated with the moments of the D_9 species corrected for a shortening of 0.005 Å in the CH bond length upon deuteration. In addition, several calculations were made assuming that the CH_3 groups were tilted slightly toward the BN coordination bond, in order to test if this would affect the results derived for the heavy-atom parameters to any significant extent.

Table III summarizes the results. The heavy-atom parameters were quite reproducibly calculated regardless of the procedure employed. The variance in the heavy-atom parameters in Table III is sufficient to cover the deviations in the calculations and is typical for a calculation of this type.[14]

The CH_3 parameters were much more dependent upon the procedure chosen. The $d(CH)$ and $\angle HCH$ varied markedly and the two parameters were highly correlated. Consequently, the values listed in Table III are the mid-range values with uncertainties sufficient to cover the range of results. It is apparent that the methyl group parameters are not well determined.

The uncertainties in Table III are not only sufficient to cover the range of results obtained by the different methods of calculation but also to include experimental errors in the moments of inertia including the possible changes due to centrifugal distortion. From the type of analysis pursued, the structural parameters are called r_0 parameters.[16] The r_{av} parameters are probably close to the values in Table III;[17] doubling the uncertainties in Table III should encompass the r_{av} parameters.

Structure Analysis. The structure of the Me_3N group upon coordination to BF_3 is very similar to the structure observed in the BH_3 adduct ($d(CN) = 1.483 \pm 0.01$ Å and $\angle CNC = 109.0 \pm 1°$).[2] In both adducts, the $d(CN)$ has lengthened slightly and $\angle CNC$ has closed slightly compared to free Me_3N.[18] The values for $d(CN)$ are somewhat less than in the series $Me_3N\cdot BX_3$[6] (X = Cl, Br, I) while the $\angle CNC$ angle is a little larger in the BF_3 adduct. The BF_3 moiety is more markedly distorted upon coordination ($d(BF) = 1.313 \pm 0.004$ Å).[13] The BF_3 distortion is much greater than in $CH_3CN\cdot BF_3$ where $d(BF) = 1.334$–1.353 Å[7] although $\angle FBF$ is quite similar (112–113.5° in $CH_3CN\cdot BF_3$).

Adduct Stabilities. Coyle and Stone have discussed[19] stabilities of complexes in terms of three components, ΔH_G (heat of formation), ΔH_R (reorganization), and ΔH_T (dative

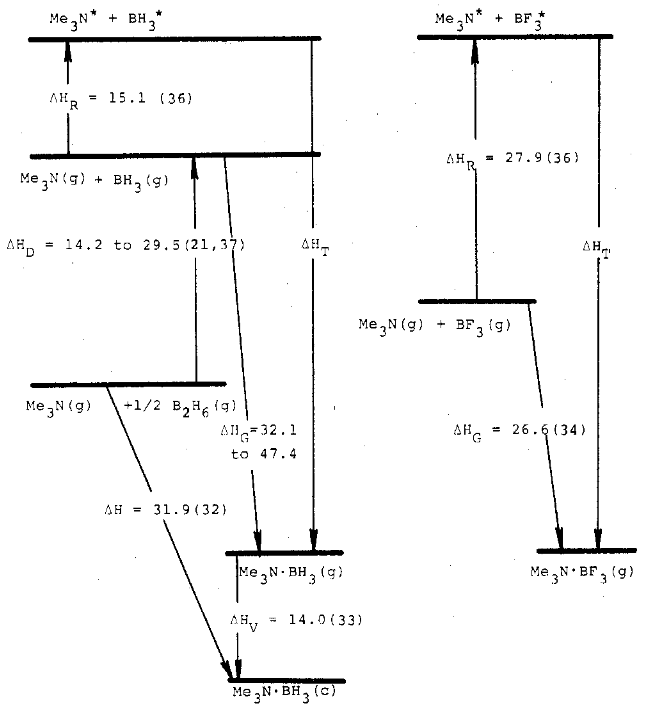

Figure 1. Thermodynamic cycles for $Me_3N \cdot BH_3$ and $Me_3N \cdot BF_3$ formation. ΔH_T was assumed equal for the two complexes. Heats are in kcal. Literature references are in parentheses.

bond formation). See Figure 1 for clarification of these terms for the $Me_3N \cdot BH_3$ and $Me_3N \cdot BF_3$ adducts. Since the geometry of the Me_3N moiety and the BN bond length are so similar in these two adducts, it is attractive to speculate that the major energy component determining a difference in stability (ΔH_G) for the two adducts arises from the difference in reorganization energies for BH_3 vs. BF_3. This assumption can be tested by comparing experimental values for ΔH_G with calculated values for ΔH_R (BX_3 group).[20]

It was previously estimated[2] that the BH_3 adduct is more stable by 5–21 kcal. This range is dependent on the value for the dissociation energy of diborane (28.4–59 kcal/mol of B_2H_6)[21] which enters in the estimation of ΔH_G for the BH_3 adduct.

Three previous comparative estimates of ΔH_R existed. An extrapolation based on force constants[22] led to an estimate for the difference in reorganization energy of BF_3 vs. BH_3 of 20 kcal/mol. Previous ab initio calculations have given values of 21[23a,b] and 16 kcal.[23c] It should be noted that these calculations were performed with assumed geometries for the deformed pyramidal BH_3 and BF_3 which do not correspond precisely to the values observed in the Me_3N adducts.

Our ab initio calculations of the difference in reorganization energies performed on extended basis sets with the experimental geometries for BH_3 and BF_3 yield a lower difference of 12.8 kcal (Table II). This is in the middle of the 5–21 kcal range for the difference in adduct stability. Therefore, it appears safe to conclude that the difference in reorganization energy parallels the adduct stabilities and quantitatively accounts for a major fraction of the difference in ΔH_G for the adducts.

This correlation is noncontrovertible (given reliable numbers). It could, however, be less noteworthy if arising from a fortuitous cancellation of ΔH_T and ΔH_R (Me_3N) for both adducts. The evidence that the correlation is significant (i.e., $\Delta[\Delta H_T]$ and $\Delta[\Delta H_R(Me_3N)]$ are nearly zero) includes the similarity in d(BN) and Me_3N geometries in both adducts, the similar force constants for the Me_3N group,[24,25] and the plausible value for the dissociation energy of B_2H_6 obtained if $\Delta[\Delta H_T]$ and $\Delta[\Delta H_R(Me_3N)]$ are set at zero (confer below).

A possibility that the dative bond energies may not be nearly identical is raised by the reports that the BN force constant is larger in the BF_3 adduct by about 1 mdyn Å^{-1}.[24-26] Employing a typical correlation between force constant and dissociation energy[27] implies a B–N bond strength as much as 15 kcal greater for the BF_3 adduct. If $\Delta[\Delta H_T]$ reflects this, it would indicate that $\Delta H_R(Me_3N)$ is also 7–23 kcal greater for the BF_3 adduct. In other words, the larger reorganization energies for both acid and base in the BF_3 adduct cancel the relative gain in stability from a stronger acid–base interaction.

A choice between these two alternatives is somewhat discretionary; for either case, reorganization energies play the major role in determining the relative stability.[28] This can be contrasted with the $H_3CCN \cdot BX_3$ (X = F, Cl, Br) series where reorganization energy differences were considered less important in determining the relative stabilities.[29]

It is also interesting to note that a value of about 43 kcal/mol of B_2H_6 can be estimated for the dimerization energy of BH_3, if ΔH_T and $\Delta H_R(Me_3N)$ are assumed equal for the two adducts.[30] It is very difficult to attach reliable uncertainty limits to this estimate. It is nevertheless gratifying to find reasonable agreement with previous estimates since this provides an indirect check on the plausibility of the values and assumptions used in the thermocycle arguments. The previous experimental estimates for $B_2H_6 \rightarrow 2BH_3$ range from 28 to 59 kcal; two recent ab initio theoretical estimates including corrections for the correlation energy gave values of 36[31] and 38 kcal.[12b,c]

Summary

Analysis of adduct stabilities is inherently a speculative enterprise due to the tentative assumptions which must be advanced to obtain inferences. The comparison of $Me_3N \cdot BH_3$ and $Me_3N \cdot BF_3$ seems especially propitious. The convergence of available thermodynamic data, vibrational frequencies, force constants, similar values for d(BN) and amine geometries, the parallel trend (and good quantitative agreement) between the differences measured for ΔH_G and calculated for $\Delta H_R(BX_3)$, and the reasonable value inferred for $\Delta H_D(B_2H_6)$ provide support for the hypothesis that the reorganization energies of the acids play a major role in the difference in stability for the adducts.

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Registry No. $(^{13}CH_3)_3N \cdot {}^{11}BF_3$, 64091-98-1; $(^{13}CH_3)_3N \cdot {}^{10}BF_3$, 64091-97-0; $(CD_3)_3N \cdot {}^{11}BF_3$, 64091-95-8; $(CD_3)_3N \cdot {}^{10}BF_3$, 64091-94-7; BH_3, 13283-31-3; BF_3, 7637-07-2; $Me_3N \cdot BF_3$, 420-20-2.

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(36) This is the ΔH_R for the BX_3 moiety, calculated in Table II.

(37) The range 14.2–29.5 is taken from experimental and theoretical estimates in the literature.[12b,c,21,31] If $\Delta H_R(Me_3N)$ and ΔH_T are the same for both cycles then $\Delta H_D = 21.5$ kcal/mol of BH_3.

Contribution from the Department of Chemistry,
The University of Michigan, Ann Arbor, Michigan 48109

Directive Effects in the Electrophilic Substitution of Deltahedral Boranes and Heteroboranes. Deuteration and Halogenation of 1-SB_9H_9 and $SB_{11}H_{11}$

WAYNE L. SMITH,[1] B. J. MENEGHELLI, D. A. THOMPSON, P. KLYMKO, N. McCLURE, M. BOWER, and R. W. RUDOLPH*

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Because of a moderate reaction rate, it is possible to determine the course of the sequential electrophilic halogenation of 1-SB_9H_9. The directive effect of the sulfur heteroatom does not correlate with the ground-state charge distribution of 1-SB_9H_9. It appears that initial attack is at the 6 position instead of the anticipated 10 position. In the case of monobromination and monoiodination there is a significant degree of rearrangement to also give the thermodynamically more stable 10 isomer in the reaction mixture ($\Delta H_{\text{isomerization}} = 6.8$ kcal/mol). Only the 6 isomer results from monochlorination. Rearrangement is also a significant factor as halogenation becomes more extensive. The initial halogenation of $SB_{11}H_{11}$ is analogous to that of 1-SB_9H_9. The site of initial deuteration was not established clearly, but under forceful conditions deuteration was not complete and 6,7,8,9,10-D_5-1-SB_9H_4 and 7,8,9,10,11,12-D_6-1-$SB_{11}H_5$ were obtained.

Introduction

For closo (deltahedral) heteroboranes like 1,2- and 1,7-$C_2B_{10}H_{12}$ and 2,4-$C_2B_5H_7$, ground-state charge distributions correlate nicely with the results of electrophilic halogenation.[2,3] In the case of the deltahedral borane anions $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$ electrophilic halogenation[4] does not appear to correlate well with predictions for sequential substitution.[5] However, interpretation of the results was complicated somewhat by the ease of halogenation and the difficulty of isomer separation. No evidence for the rearrangement of these deltahedral dicarbaboranes or borane anions during the course of halogenation has been presented. We expand here our previous communication[6] on the halogenation of 1-SB_9H_9 and $SB_{11}H_{11}$ which can be followed sequentially and thus provides a good probe for the theory of directive effects in substitution reactions in deltahedral boranes. The results suggest that intramolecular rearrangement plays a role in the ultimate stereochemistry of the products. Exhaustive deuteration appears to proceed in a manner similar to that which we found for the Friedel–Crafts alkylation of 1-SB_9H_9.[7]

Experimental Section

Apparatus and Techniques. Gases and volatile materials were handled using standard vacuum line techniques.[8] Bromine and chlorine samples were measured by expansion of the vapors into a weighing bulb fitted with an all-Teflon valve.[9] The mercury manometer in this section was coated with Kel-F oil.

Solids were handled on the bench top, but all reaction tubes and handling tubes were evacuated and back-filled with dry nitrogen to minimize exposure to air and moisture. Samples were weighed in 6-mm o.d. tubes previously flushed with dry nitrogen.

All reactions were performed in sealed tubes. Iodination tubes were fitted with an extension to be opened with a modified "key" breaker; tubes for chlorination or bromination had a greaseless (Fischer-Porter) valve. After reaction, tubes were opened on the vacuum line. Noncondensable gases were collected via a Toepler pump. Condensable gases were fractionated through appropriate slush baths and identified by vapor pressure, IR, and gas density measurements. Volatile solids were purified by vacuum sublimination and gas chromatography. Product identification was by means of IR, mass, and ^{11}B NMR spectra. Yields are reported in terms of the initial amount of SB_9H_9. Melting points were determined in sealed capillaries and are uncorrected.

Infrared spectra were obtained using a Perkin-Elmer 457 grating spectrophotometer. Gases were investigated in a 10-cm cell fitted with KBr windows. Solid spectra were obtained from KBr pellets. The ^{11}B NMR spectra were obtained in $CDCl_3$ on a JEOL JNM-PS-100 operating at 32.1 MHz using pulsed Fourier transform methods. Chemical shifts are reported relative to external $(C_2H_5)_2O \cdot BF_3$ with positive values downfield.[10] Mass spectra were determined on an Associated Electronics Industries MS-902. GC separations were obtained on a Varian Aerograph Series 2700 with