(2) K. Niedenzu and J. W. Dawson in "The Chemistry of Boron and Its Compounds," E. Muetterties, Ed., Wiley, New York, N. Y., 1967, pp 377–442; G. W. Parshall, *ibid.*, pp 617–667.

(3) T. D. Coyle and F. G. A. Stone in "Progress in Boron Chemistry," Vol. I, H. Steinberg and A. L. McCluskey, Ed., Macmillan, New York, N. Y., 1964, pp 83–160.

(4) H. Hibbert, *Ber. Deut. Chem. Ges.*, **39**, 160 (1906).

(5) F. G. Mann, A. F. Wells, and O. Purdie, *J. Chem. Soc.*, 1828 (1937); F. G. Mann and A. F. Wells, *ibid.*, 708 (1938).

(6) L. H. Long and J. F. Sackman, *Res. Corresp.*, **8**, 523 (1955).

(7) M. Halmann, *Spectrochim. Acta*, **16**, 407 (1960).

(8) R. G. Kostyanovskii, I. I. Chervin, V. V. Yakshin, and A. U. Stepanyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1629 (1967); *Chem. Abstr.*, **68**, 75338 (1968).

(9) P. B. Ayscough and H. J. Emeleus, *J. Chem. Soc.*, 3381 (1954).

(10) H. Siebert, *Z. Anorg. Allg. Chem.*, **273**, 161 (1953).

(11) W. J. C. Dyke, W. C. Davies, and W. J. Jones, *J. Chem. Soc.*, 463 (1930).

(12) C. H. Bamford, D. L. Levi, and D. M. Newitt, *J. Chem. Soc.*, 468 (1946).

(13) F. Ostwald, *Z. Anal. Chem.*, **197**, 309 (1963).

(14) W. J. Lehmann, C. O. Wilson, and I. Sharpiro, *J. Chem. Phys.*, **28**, 777 (1958).

(15) A. Stock and F. Zelder, *Ber. Deut. Chem. Ges.*, **54**, 531 (1921).

(16) A. D. Norman and W. L. Jolly, *Inorg. Syn.*, **11**, 15 (1968).

(17) R. C. Taylor and A. R. Grimes, *Spectrochim. Acta*, **10**, 419 (1958).

(18) A. Stock and E. Kuss, *Ber. Deut. Chem. Ges.*, **47**, 3113 (1914).

(19) T. Wentink and V. H. Tiensuu, *J. Chem. Phys.*, **28**, 826 (1958).

(20) M. Green and G. A. Martin, *Trans. Faraday Soc.*, **48**, 416 (1952).

(21) D. A. Daws and G. Bottger, *J. Chem. Phys.*, **34**, 689 (1961).

(22) E. Pohland and H. Harlus, *Z. Anorg. Allg. Chem.*, **207**, 242 (1932).

(23) J. Vanderryn, *J. Chem. Phys.*, **30**, 331 (1959).

(24) (a) H. A. Skinner, Ed., "Experimental Thermochemistry," Vol. II, Interscience, New York, N. Y., 1962; (b) S. Sunner and I. Wadso, *Acta Chem. Scand.*, **13**, 97 (1959).

(25) D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

(26) J. L. Mills and L. C. Flukinger, *J. Chem. Educ.*, **50**, 636 (1973).

(27) G. W. Mappes, S. A. Fridmann, and T. P. Fehlner, *J. Phys. Chem.*, **74**, 3307 (1970). Over ten values for the dissociation of diborane into borane units have been reported. We have chosen what appears to be the most generally accepted recent value, although the use of other values would not appreciably change our results.

(28) F. G. A. Stone and A. B. Burg, *J. Amer. Chem. Soc.*, **76**, 286 (1954).

(29) H. C. Brown and M. Gerstein, *J. Amer. Chem. Soc.*, **72**, 2923 (1950); H. C. Brown, N. D. Taylor, and M. Gerstein, *ibid.*, **66**, 431 (1944).

(30) R. H. Harris, Ph.D. Thesis, Purdue University, Lafayette, Ind., 1952.

(31) F. Hewitt and A. K. Holliday, *J. Chem. Soc.*, 530 (1953).

(32) S. Sujishi, Ph.D. Thesis, Purdue University, Lafayette, Ind., 1949.

(33) R. S. Drago, G. C. Vogel, and T. E. Needham, *J. Amer. Chem. Soc.*, **93**, 6014 (1971).

(34) K. J. Alford, E. O. Bishop, P. R. Carey, and J. D. Smith, *J. Chem. Soc. A*, 2574 (1971).

(35) E. A. Fletcher, Ph.D. Thesis, Purdue University, Lafayette, Ind., 1952.

(36) G. M. Phillips, J. S. Hunter, and L. E. Sutton, *J. Chem. Soc.*, 146 (1945).

(37) M. L. Denniston and D. R. Martin, *J. Inorg. Nucl. Chem.*, in press.

(38) H. C. Brown and R. R. Holmes, *J. Amer. Chem. Soc.*, **78**, 2173 (1956).

(39) W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **3**, 164 (1956).

(40) W. A. G. Graham and F. G. A. Stone, *Chem. Ind. (London)*, 319 (1956).

(41) D. E. Young, G. E. McAchran, and S. G. Shore, *J. Amer. Chem. Soc.*, **88**, 4390 (1966).

(42) R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).

Contribution from the Department of Chemistry,
University of Michigan, Ann Arbor, Michigan 48104

Microwave Spectra of Trimethylamine–Borane. The Boron–Nitrogen Distance and Molecular Dipole Moment

PATRICK CASSOUX,[1] ROBERT L. KUCZKOWSKI,* PHILIP S. BRYAN, and ROBERT C. TAYLOR

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The $J = 2 \rightarrow 3$ and $J = 3 \rightarrow 4$ transitions for eight isotopic species of trimethylamine–borane were measured. The nitrogen coordinates in the principal axes systems of $Me_3{}^{14}N\cdot{}^{11}BH_3$ and $Me_3{}^{14}N\cdot{}^{11}BD_3$ were determined by the double-substitution method. In combination with previous studies this gave the following structural parameters: $d(BN) = 1.638 \pm 0.01$ Å, $d(CN) = 1.483 \pm 0.01$ Å, $\angle CNB = 109.9 \pm 1°$. The dative bond lengths and stabilities of $Me_3N\cdot BH_3$ and $Me_3N\cdot BF_3$ were discussed. A dipole moment of 4.84 ± 0.1 D was determined for $Me_3N\cdot BH_3$.

Introduction

The dative bond distance in compounds of the type $X_3A\cdot BY_3$ (A = group V, B = group III elements) is ordinarily expected to decrease as the stability to dissociation of the complex increases. A test of this assumption has been recently made for the series $(CH_3)_3P\cdot BH_3$,[2a] $CH_3PH_2\cdot BH_3$,[2a] $H_3P\cdot BH_3$,[2b] $F_3P\cdot BH_3$,[3] and $F_2PH\cdot BH_3$.[4] While the relationship seems to hold for the first three compounds, $F_3P\cdot BH_3$ is an exception. Although it is less stable than the methylated phosphine adducts, its P–B bond distance is about 0.07 Å shorter. Gas-phase structural data have heretofore not been precise enough to permit careful tests of the bond length–stability relationship for similar boron–nitrogen adducts. Three trimethylamine adducts have been studied in the gas phase. For $(CH_3)_3N\cdot B(CH_3)_3$, which is readily dissociated, the N–B distance appears to be long (>1.65 Å).[5] For $(CH_3)_3N\cdot BF_3$, which is undissociated at room temperature, a value of 1.636 ± 0.004 Å is reported.[6] For $(CH_3)_3N\cdot BH_3$, which is also undissociated but more stable than $(CH_3)_3N\cdot BF_3$ (see Discussion), there have been three gas-phase structure studies. An early electron diffraction report gave 1.62 ± 0.05 Å.[7] More recent investigations by microwave spectroscopy reported 1.65 ± 0.02 Å[8] and 1.609 Å, or 1.637 Å,[9] with preference expressed for the 1.609 Å value.

The purpose of our investigation was to determine a more accurate value for the B–N distance in $(CH_3)_3N\cdot BH_3$ in order to compare it with that in $(CH_3)_3N\cdot BF_3$ and to examine the bond length–stability relationship for the two adducts. The previous MW investigations differed in their estimates of this distance because (1) no spectra from nitrogen-15 species were observed,[10] (2) the nitrogen atom lies very near the center of mass, and (3) vibration–rotation interaction effects which occur upon isotopic substitution are apparently quite large for several of the deuterated species that were employed in the structure deductions. These factors make it difficult to locate the nitrogen atom accurately. We have obtained a more accurate B–N bond length by measuring the spectra of four ^{15}N-enriched species and by using the double-substitution procedure to analyze the data.[11] This procedure (previously applied to a small number of linear and asymmetric-top molecules) is prescribed to minimize isotopic vibration–rotation effects and to locate atoms near principal rotational axes accurately.

Experimental Section

Samples. The samples were prepared by using standard vacuum-line procedures.[12] The $J = 3 \rightarrow 4$ transition of $Me_3{}^{14}N\cdot{}^{11}BH_3$ and the transitions of $Me_3{}^{14}N\cdot{}^{10}BH_3$ were measured from a sample containing 93% ^{10}B–7% ^{11}B. The $J = 2 \rightarrow 3$ transition of $Me_3{}^{14}N\cdot{}^{11}BH_3$ was obtained from a sample containing a mixture of BH_3, BD_3, etc., but the normally occurring abundances of boron-10 and -11. The $Me_3{}^{15}N\cdot BH_3$ transitions were measured with a sample containing about 99% ^{15}N and 90% ^{10}B–10% ^{11}B. A sample containing the same enrichments for nitrogen and boron but >95% deuterium was employed for $Me_3{}^{15}N\cdot BD_3$. The transitions for $Me_3{}^{14}N\cdot BD_3$ were measured with a sample containing >95% deuterium and the normal 81:19 ratio of boron-10:boron 11.

Table I. Transition Frequencies Measured for the Isotopic Species of $Me_3N{\cdot}BH_3$

No.	Species	Transition $J \rightarrow J'$	Freq, MHz	I_B,[a] μ Å^2
1	$Me_3{}^{14}N{\cdot}{}^{11}BH_3$	2 → 3	27,097.94	111.8999
		3 → 4	36,130.51	111.9001
2	$Me_3{}^{15}N{\cdot}{}^{11}BH_3$	2 → 3	27,100.54	111.8891
		3 → 4	36,133.84	111.8897
3	$Me_3{}^{14}N{\cdot}{}^{10}BH_3$	2 → 3	27,766.79	109.2044
		3 → 4	37,022.38	109.2044
4	$Me_3{}^{15}N{\cdot}{}^{10}BH_3$	2 → 3	27,769.44	109.1940
		3 → 4	37,025.72	109.1946
5	$Me_3{}^{14}N{\cdot}{}^{11}BD_3$	2 → 3	24,257.56	125.0025
		3 → 4	32,343.26	125.0031
6	$Me_3{}^{15}N{\cdot}{}^{11}BD_3$	2 → 3	24,258.33	124.9985
		3 → 4	32,344.30	124.9991
7	$Me_3{}^{14}N{\cdot}{}^{10}BD_3$	2 → 3	24,740.16	122.5641
		3 → 4	32,986.74	122.5646
8	$Me_3{}^{15}N{\cdot}{}^{10}BD_3$	2 → 3	24,741.60	122.5570
		3 → 4	32,988.61	122.5577

[a] Calculated from $\nu = 2B(J + 1)$; $I_B B = 5.05376 \times 10^5$ MHz μ Å^2.

Spectra. The frequencies of the $J = 2 \rightarrow 3$ and $J = 3 \rightarrow 4$ transitions of the eight isotopic species studied are listed in Table I. The transitions were measured at low pressures with the absorption cell cooled slightly below room temperature. Klystron sources and oscilloscope display were used with a standard Stark spectrometer. Line widths could not be reduced below about 0.5-1.0 MHz, probably due to unresolved quadrupole coupling. Nevertheless, typically about 10 measurements on a transition were made at different pressures and Stark voltages and a standard deviation of about ±0.05 MHz was obtained. Stark voltages sufficient to modulate the $K = 0$ components were employed. To avoid any systematic errors arising from measurements in different laboratories, we also remeasured the eight transitions for the nitrogen-14 species that we utilized in our calculations. The agreement with Schirdewahn's measurements[8] was between ±0.01 and ±0.08 MHz. The measurements of the other workers[9] were less precise and the agreement was typically ±0.1–0.3 MHz.[13]

The dipole moment measurements were made using a precision dc power supply[14] (Fluke, Model 412B). The dipole moment of OCS[15] was used to calibrate the Stark septum.

Analysis and Discussion

Boron–Nitrogen Distance. Ordinarily, the boron–nitrogen distance would be calculated from measurements on three isotopic species—a parent isotopic species and two species in which the boron atom and the nitrogen atom, respectively, were substituted. For example, a set of suitable species would be $Me_3{}^{14}N{\cdot}{}^{11}BH_3$ (parent), $Me_3{}^{15}N{\cdot}{}^{11}BH_3$, and $Me_3{}^{14}N{\cdot}{}^{10}BH_3$. The coordinates of the boron and nitrogen atoms would be calculated from Kraitchman's equations[16] which have the form

$$I_s - I_p = \mu Z_s^2 \qquad (1)$$

where I_s and I_p are moments of inertia of the substituted and parent isotopic species, μ is a reduced mass calculated from the known masses,[17] and Z_s is the coordinate of the substituted atom in the principal-axis system of the parent isotopic species. Equation 1 can be reliably used to locate an atom on the symmetry axis when it is far from the center of mass. When the substituted atom has a small coordinate (<0.15 Å), then the consequent small difference in moments of inertia can be the same order of magnitude as vibration–rotation interaction effects which are not the same for the two isotopic species. The value calculated from eq 1 is often then not reliable; in fact examples are occasionally observed where the heavier isotopic species has the smaller moment of inertia and application of eq 1 leads to an imaginary value for Z_s.[11,18-20] $Me_3N{\cdot}BH_3$ falls into this latter category. Although the boron atom can be reliably located, the nitrogen atom is too close to the center of mass for reliable calculation; in fact the ^{15}N species have smaller moments of inertia than their ^{14}N counterparts.

Table II. Nitrogen and Boron Coordinates and the Nitrogen–Boron Bond Distance

Species[a]	$J \rightarrow J'$	Z_N,[b] Å	Z_B,[b] Å		d(B–N), Å
1, 2, 3, 4	2 → 3	−0.0042	1.6335		1.6377
1, 2, 3, 4	3 → 4	−0.0009	1.6336		1.6345
5, 6, 7, 8	2 → 3	−0.0883	1.5541		1.6424
5, 6, 7, 8	3 → 4	−0.0825	1.5541		1.6366
				Av	1.638 ± 0.01

[a] Species identified in Table I. [b] Coordinates in principal axis system of $Me_3{}^{14}N{\cdot}{}^{11}BH_3$ for first two rows and $Me_3{}^{14}N{\cdot}{}^{11}BD_3$ for last two rows. Masses taken from W. Gordy and R. L. Cook, "Microwave Molecular Spectra," Interscience, New York, N. Y., 1970.

Pierce[11] has proposed a procedure to locate the nitrogen atom more accurately. It is called the double-substitution procedure and requires measurements on four isotopic species. Labeling the moments of inertia for $Me_3{}^{14}N{\cdot}{}^{11}BH_3$, $Me_3{}^{15}N{\cdot}{}^{11}BH_3$, $Me_3{}^{14}N{\cdot}{}^{10}BH_3$, and $Me_3{}^{15}N{\cdot}{}^{10}BH_3$ as I_1, I_2, I_3, and I_4, respectively, the following relationships can be derived from eq 1 and a center of mass relationship[11]

$$\Delta II = (I_4 - I_3) - (I_2 - I_1) \qquad (2)$$

$$\frac{\Delta II}{\mu'} = \left(1 - \frac{\mu}{\mu'}\right) Z_N^2 - \left(\frac{2\Delta M}{M + \Delta M}\right) Z_B Z_N + \left(\frac{\Delta M}{M + \Delta M}\right)^2 Z_B^2 \qquad (3)$$

If Z_B (boron coordinate) is known from eq 1 for a suitable parent species, then application of eq 3 will give Z_N, that is, the nitrogen coordinate in the same axis system. The relative signs of Z_B and Z_N will also be determined. The quantities μ, μ', ΔM, and M can be calculated from the known masses.[21]

Evidence indicates that if eq 3 is applied, the vibrational effects due to isotopic substitution are sufficiently reduced to allow calculation of a more reliable coordinate. The theoretical justification was presented by Pierce, who showed that these zero-point vibrational effects are removed to a higher order by this procedure. In cases where this procedure has been tested, such as N_2O,[11] CH_3SiH_2F,[18] CH_3SiHF_2,[18] and HNO_3,[19] more consistent results were indeed obtained by this procedure than with the normal single-substitution calculation. The drawbacks in using eq 3 are that very accurate moments of inertia are required and a greater amount of isotopic data is needed.

For $Me_3N{\cdot}BH_3$, the B–N distance was calculated using eq 1 and 3 to determine the boron and nitrogen coordinates, respectively. This distance was calculated using four sets of data. The results of the calculation are listed in Table II. Two calculations were made using the $Me_3N{\cdot}BH_3$ species in Table II by employing separately the moments obtained from the $J = 2 \rightarrow 3$ transitions and the $J = 3 \rightarrow 4$ transitions. The procedure was repeated for the four $Me_3N{\cdot}BD_3$ species. A small effect from centrifugal distortion is evident from the effective moments listed in Table II. However, it can be shown that this should not affect the precision of the calculation if I's determined from the same J states are taken or if the average I from the two J states is used. It seemed more suitable to treat the $J = 2 \rightarrow 3$ and $J = 3 \rightarrow 4$ transitions separately since they provide independent evaluations of the bond length and test the precision of the frequency measurements. Since measurements are available on a BH_3 and BD_3 adduct, an independent check on the reliability of the double-substitution procedure can also be made.

The four B–N distances that were calculated are pleasingly close. The average of the values gives r(B–N) = 1.638 ± 0.010 Å. The error is assigned based on the uncertainties in the frequency measurements. An errors treatment indicates that any single r(B–N) in Table II would have an uncertainty of ±0.01 Å based on the standard deviations in the frequency

Table III. Stark Coefficients (10^6 MHz cm^2/V^2) and Dipole Moments (D) for $(CH_3)_3N \cdot BH_3$

Transition	Stark coeff		μ
$J = 2$–3, $K = 0$, $\lvert M \rvert = 1$	-4.57 ± 0.07		4.77 ± 0.07
$J = 3$–4, $K = 0$, $\lvert M \rvert = 1$	-3.74 ± 0.02		4.87 ± 0.03
$\lvert M \rvert = 2$	$+3.47 \pm 0.04$		4.88 ± 0.05
		Av	4.84 ± 0.10

measurements. Although the values for *r*(B–N) in Table II might justify a smaller uncertainty range, we prefer the more conservative estimate of ±0.01 Å. This narrows down the B–N distance to a small enough range to make useful comparisons with other compounds.

Some additional calculations were made to clarify the origin of the vibration–rotation effect that produces smaller moments of inertia for the heavier nitrogen-15 species. This effect could arise from a shortening of the average B–N bond length by about 0.00015-0.0002 Å upon substitution of nitrogen-14 by nitrogen-15. Bond shortenings of this magnitude were sufficient to reproduce the change in moments of inertia for the four ^{15}N, ^{14}N pairs of species in Table I when structural parameters consistent with the experimental data were assumed. This magnitude for a "shrinkage effect" is also similar to previous estimates.[19]

Carbon–Nitrogen Distance and ∠CNB. More precise values for these parameters can be calculated combining the nitrogen atom data here with substitution coordinates for carbon from the previous study.[9] The substitution parameters are *d*(CN) = 1.483 ± 0.01 Å and ∠CNB = 109.9 ± 1°.[22] The other substitution parameters reported earlier are unchanged.[9] Thus, *d*(BH) = 1.211 ± 0.003 Å, and ∠NBH = 105.32 ± 0.16°. The only parameters not readily determined by the substitution procedure are methyl group parameters. It does not appear possible to extract very reliable values easily for these parameters without making assumptions about the methyl group symmetry and/or the magnitude of the large vibrational effects upon substitution. The methyl group parameters appear to be close to those in $(CH_3)_3N$.[9,23]

Our results for *d*(CN) and ∠CNB confirm the earlier conclusions[9] that *d*(CN) is significantly longer than in $(CH_3)_3N$ (*d*(CN) = 1.451 ± 0.003 Å)[23] but that the bond angles have not changed much (increased about 1.2°) upon coordination. It would be desirable to study this effect in several other nitrogen-containing adducts before further speculating on its significance. It is interesting to note the contrast with $(CH_3)_3P$ where *d*(PC) is shortened by about 0.023 Å upon coordination to BH_3 and ∠CPC opens up about 6°.[2a,4]

Dipole Moment. The Stark shifts were measured for three transitions in $Me_3{}^{14}N \cdot {}^{11}BH_3$. The Stark coefficients and calculated dipole moments are listed in Table III. The value determined was 4.84 ± 0.10 D. This can be compared with previous values 4.92 ± 0.03 D[8,24] and 4.59 ± 0.16 D[9,13] in the gas phase and 4.45 ± 0.05 D[25] and 4.62 ± 0.01 D[26] in benzene solution.

Adduct Stability. It is interesting to note that the nitrogen–boron bond lengths are nearly identical for gaseous $Me_3N \cdot BH_3$ (1.638 ± 0.01 Å) and $Me_3N \cdot BF_3$ (1.636 ± 0.004 Å).[1] These N–B distances also appear to be shorter than in gaseous $Me_3N \cdot BMe_3$ (1.65–1.80 Å)[5] although this has not been unambiguously established. A longer bond length in $Me_3N \cdot BMe_3$ is quite plausible however since it is extensively dissociated at room temperature in contrast to the other two adducts which are undissociated.

It is also interesting to consider if the similar coordination bond lengths in $Me_3N \cdot BH_3$ and $Me_3N \cdot BF_3$ are also reflected in similar stabilities to dissociation. At first consideration, this would not seem to be the case since BF_3 has been observed to displace BH_3 from $Me_3N \cdot BH_3$.[27-29] However, in displacement reactions involving BH_3, the additional dimerization energy of BH_3 (14.2–29.5 kcal/mol of BH_3, *cf.* below) would make the displacement reaction proceed even though the stability of $Me_3N \cdot BH_3$ would be equal to or somewhat greater than $Me_3N \cdot BF_3$.

A more useful stability criterion[30] should be comparison of the heat of reaction (ΔH_G) for $Me_3N \cdot BY_3(g) \rightarrow Me_3N(g) + BY_3(g)$. For the BF_3 adduct a value of 26.6 kcal is reported.[31] For $Me_3N(g) + {}^1/_2B_2H_6(g) \rightarrow Me_3N \cdot BH_3(c)$, values of 31.3 kcal[31] and 32.3 kcal[32] are reported. The heat of sublimation of $Me_3N \cdot BH_3$ is 14 kcal[12] and values for the dissociation energy of $B_2H_6 \rightarrow 2BH_3$ have been reported between 28.4 and 59.0 kcal/mol of B_2H_6.[33] This yields a range of values between 31.5 and 47.8 kcal/mol for the dissociation reaction $Me_3N \cdot BH_3(g) \rightarrow Me_3N(g) + BH_3(g)$. The conclusion is that the BH_3 adduct is 5–21 kcal more stable than the BF_3 adduct. The $Me_3N \cdot BH_3$ adduct also is more stable in nitrobenzene by 3.7–19.0 kcal;[30] this range is likewise dependent on the value for the dissociation energy of diborane. In a similar case, the heats of dissociation of the pyridine adducts in nitrobenzene also favor the BH_3 adduct by 3.8–19.1 kcal.[34,35] It appears safe to conclude therefore that there is a difference in stability for the two adducts, although possibly a small one, while there is little or no difference in the coordination bond lengths; the exact extent of this discrepancy, of course, depends on the value chosen for the dissociation energy of diborane.[36-39]

This conclusion does not seem very informative; it would indeed be valuable to have a more precise value for the dissociation energy of diborane. Nevertheless, even with this rather large range estimated for ΔH_G, an interesting argument presents itself. The heat of reaction of a donor and acceptor in the gas phase (ΔH_G) can be interpreted as arising from two terms, a reorganization energy (ΔH_R) and a dative bond energy (ΔH_T).[30] If the assumption is made that the similar bond lengths in the two adducts indicate similar dative bond energies, then the difference in ΔH_G estimated above indicates a higher reorganization energy for BF_3 *vs.* BH_3 by about 5–21 kcal/mol. It is quite plausible that the reorganization energy should be greater for BF_3. First, the p_π–p_π stabilization mechanism present in planar BF_3[40] is absent in BH_3; second, the structural changes in BF_3 after coordination to Me_3N (and to other nitrogen adducts)[41-44] appear to be much larger than those for the BH_3 moiety in $Me_3N \cdot BH_3$. In fact, one suspects that the difference in the two reorganization energies should be closer to the high end of the range suggested above.[45] The only estimate that we know of comparing these two reorganization energies is an extrapolation based on force constants: values for BF_3 of 30 kcal and for BH_3 of 10 kcal were obtained.[46,47] If indeed the reorganization energies differ by about 20 kcal, then this would in turn support the recent mass spectrometrically determined values for the dissociation energy of diborane. Those values (*ca.* 55–59 kcal/mol of B_2H_6) are much higher than the values estimated from kinetic measurements as discussed recently.[33,48]

The above conclusion regarding the dissociation energy of B_2H_6 must be considered speculative. The argument does suggest that careful theoretical estimates of the reorganization energies of BH_3 *vs.* BF_3 and investigations that can strengthen the correlation between bond length and dative bond energy assumed above[49] could contribute to establishing, albeit indirectly, the dissociation energy of B_2H_6 to BH_3.

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53011-62-4; $(CH_3)_3N\cdot BH_3$, 75-22-9.

References and Notes

(1) NSF-CNRS, U. S.-France Exchange Scholar, 1973-1974.

(2) (a) P. S. Bryan and R. L. Kuczkowski, *Inorg. Chem.*, **11**, 553 (1972); (b) J. R. Durig, Y. S. Li, L. A. Carreira, and J. D. Odom, *J. Amer. Chem. Soc.*, **95**, 2491 (1973).

(3) R. L. Kuczkowski and D. R. Lide, Jr., *J. Chem. Phys.*, **46**, 357 (1967).

(4) J. P. Pasinski and R. L. Kuczkowski, *J. Chem. Phys.*, **54**, 1903 (1971).

(5) D. R. Lide, Jr., R. W. Taft, Jr., and P. Love, *J. Chem. Phys.*, **31**, 561 (1959); S. Geller, *ibid.*, **32**, 1569 (1960); D. R. Lide, Jr., *ibid.*, **32**, 1570 (1960).

(6) P. S. Bryan and R. L. Kuczkowski, *Inorg. Chem.*, **10**, 200 (1971).

(7) S. H. Bauer, *J. Amer. Chem. Soc.*, **59**, 1804 (1937).

(8) H. G. Schirdewahn, Doctoral Thesis, University of Freiburg, 1965.

(9) J. R. Durig, Y. S. Li, and J. D. Odom, *J. Mol. Struct.*, **16**, 443 (1973).

(10) Both ref 8 and 9 report spectra for the ^{10}B and ^{11}B isotopes of the $(CH_3)_3N\cdot BH_3$, $(CH_3)_3N\cdot BD_3$, $(CD_3)_3N\cdot BH_3$, and $(CD_3)_3N\cdot BD_3$ species. Reference 9 also reports on the $(CH_3)_3N\cdot{}^{11}BD_2H$ and $(^{13}CH_3)(^{12}CH_3)_2N\cdot{}^{11}BH_3$ species.

(11) L. Pierce, *J. Mol. Spectrosc.*, **3**, 575 (1969).

(12) A. B. Burg and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **59**, 780 (1937).

(13) Two measurements (for transitions 1 and 9 in Table I) differed by +0.64 and -0.76 MHz. Fortunately, however, this does not seem to affect markedly the calculations in ref 9, except possibly the dipole moment evaluation.

(14) W. H. Kirchhoff, *J. Amer. Chem. Soc.*, **89**, 1312 (1967).

(15) J. S. Muenter, *J. Chem. Phys.*, **48**, 4544 (1968).

(16) J. Kraitchman, *Amer. J. Phys.*, **21**, 17 (1953).

(17) $\mu = M\Delta M/(M + \Delta M)$ where ΔM is the change in mass upon substitution and M is the mass of the parent species.

(18) L. C. Krisher and L. Pierce, *J. Chem. Phys.*, **32**, 1619 (1960).

(19) A. P. Cox and J. M. Riveros, *J. Chem. Phys.*, **42**, 3106 (1966).

(20) L. C. Krisher and L. Pierce, *J. Chem. Phys.*, **31**, 875 (1959).

(21) M is the mass of the parent species; $\Delta M = {}^{15}N$ mass $- {}^{14}N$ mass; $\mu = M\Delta M/(M + \Delta M)$; $\mu' = M' \Delta M/(M' + \Delta M)$, where M' is the mass of the substituted species used in eq 1.

(22) Previously:[9] $d(CN) = 1.495$ Å; $\angle CNB = 110.9°$.

(23) J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.*, **51**, 1580 (1969).

(24) The value of 4.90 D in ref 8 was corrected for the newer dipole moment value of OCS in ref 15.

(25) N. Noth and H. Beyer, *Chem. Ber.*, **93**, 939 (1960).

(26) C. H. Bax, A. R. Katritzky, and L. E. Sutton, *J. Chem. Soc.*, 1258 (1958).

(27) This conclusion seems warranted based on the reports in ref 28 and 29, assuming that irreversible decomposition of the $Me_3N\cdot BH_3$ adduct at the temperatures employed can be neglected.

(28) J. M. Miller and M. Onyszchuk, *Can. J. Chem.*, **41**, 2898 (1963).

(29) W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **3**, 164 (1956).

(30) T. D. Coyle and F. G. A. Stone, *Progr. Boron Chem.*, **1**, 83 (1964).

(31) R. E. McCoy and S. H. Bauer, *J. Amer. Chem. Soc.*, **78**, 2061 (1956).

(32) S. R. Gunn, *J. Phys. Chem.*, **69**, 1010 (1965).

(33) For original literature references, see H. D. Johnson, II, and S. G. Shore, *Fortschr. Chem. Forsch.*, **15**, 94 (1970).

(34) H. C. Brown and R. R. Holmes, *J. Amer. Chem. Soc.*, **78**, 2173 (1956).

(35) H. C. Brown and L. Domash, *J. Amer. Chem. Soc.*, **78**, 5384 (1956).

(36) The interpretation that BH_3 is a better acid than BF_3 toward Me_3N has also been drawn from studies on their nmr spectra,[37,38] mass spectra,[39] and dipole moments.[26] However, these studies are measuring effects more related to the intrinsic properties of the complexes after formation and do not necessarily indicate which adduct is more stable to dissociation as evaluated by ΔH_G.

(37) J. M. Miller and M. Onyszchuk, *Can. J. Chem.*, **42**, 1518 (1964).

(38) T. D. Coyle and F. G. A. Stone, *J. Amer. Chem. Soc.*, **83**, 4138 (1961).

(39) G. F. Lantier and J. M. Miller, *J. Chem. Soc. A*, 346 (1971).

(40) F. A. Cotton and J. R. Leto, *J. Chem. Phys.*, **30**, 993 (1959).

(41) B. Swanson, D. F. Shriver, and J. A. Ibers, *Inorg. Chem.*, **8**, 2182 (1969).

(42) S. Geller and J. L. Hoard, *Acta Crystallogr.*, **3**, 121 (1950); **4**, 399 (1951).

(43) J. L. Hoard, S. Geller, and T. B. Owen, *Acta Crystallogr.*, **4**, 408 (1951).

(44) Z. V. Zvonkova, *Kristollografiya*, **1**, 73 (1960); *Sov. Phys.—Crystallogr.*, **2**, 403 (1957).

(45) A similar viewpoint was stated recently by R. W. Rudolph and R. W. Parry, *J. Amer. Chem. Soc.*, **89**, 1621 (1967).

(46) E. R. Alton, Ph.D. Thesis, University of Michigan, 1960.

(47) An MO estimate of the deformation energy of BF_3 gave 48 kcal.[40] However, no estimate for BH_3 was given.

(48) P. S. Ganguli and H. A. McGee, Jr., *J. Chem. Phys.*, **50**, 4658 (1969).

(49) For example, the nmr experiments[39,40] which show small differences for the two adducts lend support for this assumption. On the other hand, some unpublished data in this laboratory seem to indicate that the B-N force constants may be different. This would not be readily reconciled with the assumption although it is possible that the force constants do not reflect similar bond energies. This point deserves further investigation.

Contribution from the Materials Science Laboratory, Department of Chemical Engineering,
University of Texas at Austin, Austin, Texas 78712

Structural Chemistry of the Polysulfides Ba_2S_3 and BaS_3

S. YAMAOKA, J. T. LEMLEY, J. M. JENKS, and H. STEINFINK*

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The crystal structures of Ba_2S_3 and BaS_3 were determined from three-dimensional single-crystal X-ray diffraction data. Ba_2S_3 is tetragonal, $I4_1md$, $a = b = 6.112$ (1) Å, $c = 15.950$ (2) Å, $Z = 4$, and BaS_3 is tetragonal, $P\bar{4}2_1m$, $a = b = 6.871$ (2) Å, $c = 4.1681$ (4) Å, $Z = 2$. Least-squares refinement gave final R's of 0.0623 for 174 observed reflections and 0.028 for 151 observed reflections, respectively. Ba_2S_3 contains a sulfide ion and a $S_2{}^{2-}$ polysulfide ion. The S-S distance in the polysulfide ion is 2.32 (9) Å. One barium ion is in the center of a distorted trigonal prism whose corners are occupied by the S_2 ions. The distances between Ba^{2+} and the nearest sulfur of the dumbbell-shaped ions are 3.11 and 3.91 Å with three additional S^{2-} capping the rectangular faces at 3.15 and 3.24 Å. The second barium ion has an irregular polyhedron of nine sulfur atoms around it. Three of the vertices are occupied by S^{2-} at 3.14 and 3.72 Å and six vertices are occupied by S_2 ions. The nearest sulfur atoms of the polysulfide ion are at 3.21 and 3.42 Å from barium. In BaS_3 the polysulfide anion is $S_3{}^{2-}$ with S-S = 2.074 Å and the S-S-S angle is 114.8°. Barium is in 12-fold coordination with Ba-S distances varying from 3.204 to 3.541 Å.

Introduction

During high-pressure investigations of the systems Ba-Ge-S and Ba-Mn-S we frequently observed lemon yellow crystals in the reaction products. They were birefringent and X-ray diffraction powder patterns could not be matched with known patterns. Single-crystal X-ray structural investigations were carried out to determine the stoichiometries of these phases and they proved to be Ba_2S_3 and BaS_3. The existence of BaS_3 had been reported by Miller and King[1] and the powder pattern due to this phase was probably not identified in our experiments because BaS_3 was a minor constituent in a multiphase reaction product. These authors deduced an incorrect unit cell and space group from their X-ray powder diffraction data but their proposed structure is remarkably accurate. The phase Ba_2S_3 is new and its structure was determined in this investigation.

Experimental Section

A single crystal of what proved to be Ba_2S_3 was selected from the product resulting from a high-pressure experiment carried out in a tetrahedral press at about 50 kbars and 800° on a mixture of 3BaS + Ge + 2S. The crystal had a lemon yellow color and was ap-