makes an angle of approximately 11° to the square plane.

The Cl–Cu–O bond angle is 86.4°, which is close to the expected value of 90°. The distortion from 90° is a consequence of the repulsive interaction of the chlorine atom and the pyridine portion of the ligand which causes the Cl′–Cu–O angle to expand. The Cu–O–N angle also is expanded to 122.0° as a result of this interaction. The dihedral angle between the normal to the square-planar plane and the normal to the pyridine ring plane is 93.9° with the C_6 atom tilted toward the copper. This orientation of the ring minimizes intramolecular steric interactions of the ortho hydrogens with the chlorine atoms. The stability of several monomeric complexes with filled d orbitals has been rationalized in terms of back-π-bonding.[15,16] Back-π-bonding is not effective in this complex. The electron-donating nature of the 4-methyl substituent raises the energy of the π-antibonding orbital which would participate in back-π-bonding, and the steric effect would dominate.

The Cu–Cl vibration at 339 cm^{-1} is associated with a free terminal chlorine atom, and the frequency should serve as a reference for these vibrations. The green trans form is the thermodynamically stable isomer, and a minimum steric interaction is found. Intermolecular interactions are hindered along the axial direction of the square plane by the perpendicular orientation of the pyridine ring. A small solvent molecule can occupy these sites and adducts are formed readily.

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The Structure of Bis(trifluorophosphine)diborane(4), Determined by Electron Diffraction

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The gas-phase structure of bis(trifluorophosphine)diborane(4) has been determined by electron diffraction. The trifluorophosphine groups are trans about the boron–boron axis, with the phosphorus and boron atoms coplanar. The B–B distance is 1.800 ± 0.036 Å, B–P = 1.848 ± 0.028 Å, and P–F = 1.539 ± 0.003 Å. These are similar to the corresponding parameters found in trifluorophosphine–borane. The position of the hydrogen atoms could not be uniquely determined, but the data favor a structure with four terminal hydrogen atoms rather than a structure in which two of the hydrogen atoms form a bridge. The matrix-isolation infrared and gas-phase Raman spectra are consistent with a molecule which has a center of symmetry.

Introduction

Although diborane(4) has not been isolated, several of its bis adducts have been prepared.[1-4] Spectroscopic data suggest that the adducts do not contain bridging hydrogen atoms while their chemical properties indicate the presence of a boron–boron bond. However, no structural studies have been made on any member of this class of compounds. This is a report on a gas-phase electron diffraction determination of the molecular structure of bis(trifluorophosphine)diborane(4), $B_2H_4(PF_3)_2$; the conclusions are supported by infrared and Raman spectra.

Experimental Section

A sample of bis(trifluorophosphine)diborane(4) was prepared[2] and purified by glpc. The sample tube, fitted with a Teflon needle valve, was connected directly to the nozzle lead tube of the electron diffraction apparatus. The sample was held at −65° (vapor pressure 8 Torr) while the photographs were taken. The ambient pressure in the diffraction apparatus during sample injection was 2×10^{-5} Torr. Sectored electron diffraction photographs were taken (acceleration voltage 60.62 kV) for 35 sec using the long nozzle-to-plate position (25.6 cm) and for 60 sec using the short nozzle-to-plate position (12.4 cm). Procedures used in this laboratory for measuring plates and reducing the diffraction data have been described.[5-7]

The gas-phase Raman spectrum of the compound was recorded on a Spex-Ramalog spectrometer using a CRL 52MG laser as the excitation source.[8] The 488-nm argon line was multipassed through a cylindrical Pyrex cell (volume 23 cm^3) which held the sample (at a pressure of 10 cm and argon as a diluent at 20 cm). The cell was maintained at −196° until immediately prior to recording the spectrum, to minimize sample decomposition.

The matrix-isolation infrared spectrum was recorded with a Perkin-Elmer 521 spectrometer. The argon sample mixture (500:1) was deposited on a CsI window held near 5°K, at a rate of 10 mmol/hr.

Results

The reduced scattered intensity as a function of angle is shown in Figure 1 [$q = 8\text{–}127$ Å^{-1}, $q \equiv (40/\lambda) \sin(\theta/2)$]. The refined radial distribution curve,

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[8] Spectrum recorded by Dr. J. Allkins, Spex Industries, Metuchen, N. J.

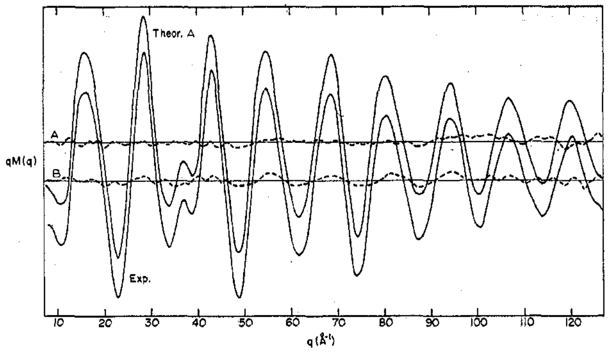

Figure 1.—Reduced scattered intensity curves for bis(trifluorophosphine)diborane(4). The experimental curve and the theoretical curve for model A are shown as solid lines. The difference curves for models A and B are shown as dotted lines.

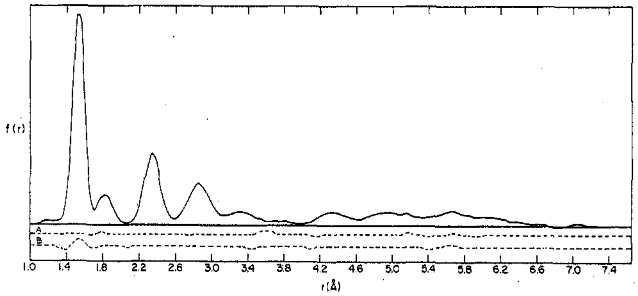

Figure 2.—The refined radial distribution curve for bis(trifluorophosphine)diborane(4) and the difference curve between the experimental and theoretical values for models A and B.

plotted in Figure 2, was calculated with a damping factor of 0.0015. The P–F bond distance is clearly resolved at 1.539 Å, and the terminal B–H distance is indicated by the small shoulder to the left of this peak, at 1.252 Å. The B–B and B–P distances together comprise the peak centered at 1.84 Å. The peak at 2.374 Å is predominantly due to neighboring fluorine–fluorine distances. The first acceptable model for the structure of bis(trifluorophosphine)diborane(4) is based on a trans planar configuration of boron and phosphorus atoms (see Figure 3). Three models were considered: cis trifluorophosphine groups with four terminal hydrogen atoms, trans trifluorophosphine groups with four terminal hydrogen atoms, and trans trifluorophosphine groups with two bridging hydrogen atoms and two terminal hydrogen atoms [diborane(6) analog]. The cis model was directly excluded since its maximum nonbonded distance is markedly less than that found in the experimental radial distribution curve. Also the spectroscopic data (presented below) are inconsistent with a cis configuration. The other two models were analyzed in detail.

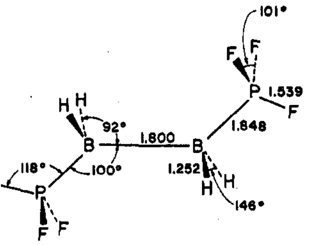

Figure 3.—Deduced structure of bis(trifluorphosphine)diborane(4).

Eleven geometrical parameters were assigned to specify the trans model (A) with the four terminal hydrogen atoms. These are four bonded distances: B–H, P–F, B–P, B–B; five angles: PBB, BBH, BPF, HBP, FPF; and two torsional angles: PBBP, BBPF. However, the torsional angle PBBP was set at 180°, since computational difficulties were encountered when both torsional angles were varied simultaneously. After the least-squares refinement on the $qM(q)$ function was completed, the calculated standard deviation was determined for models in which the value of the torsional angle PBBP was incrementally decreased in 5° steps from 180 to 160° while the torsional angle BBPF was allowed to vary. A smooth increase in the calculated standard deviation was observed, demonstrating that the boron–phosphorus atom group is planar. The calculated standard deviation for the refined structure is 0.022.

The magnitude of the torsional angle BBPF (68.5°) indicates an 8.5° rotation of the trifluorophosphine group about the boron–phosphorus bond from the position which specifies a structure with C_{2h} point group symmetry. Comparison of the fluorine–boron and fluorine–hydrogen nonbonded distances for the refined structure of model A and a corresponding model with C_{2h} symmetry shows no significant differences in the distances, suggesting that atom pair repulsion is probably not the cause of the displacement. Since the magnitude of the torsional angle PBBP was constrained during the least-squares analysis, and large amplitudes of vibration for the torsional motion about the boron–boron axis are expected, one may argue that the uncertainties in both torsional angles cumulated in the calculated value for the torsional angle BBPF, thus indicating a structure which deviates slightly from C_{2h} symmetry.

Eleven geometrical parameters were also employed in specifying the structure of the diborane(6) analog (model B). These include four bonded distances: B–P, P–F, B–H(terminal and bridging); four angles: BBP, BBH(terminal), BPF, FPF; two torsional angles: PBBP, FPBH(bridge); and one nonbonded distance: B–B. The bridging hydrogen atoms were constrained to the plane which contains the boron atoms and their location was allowed to vary along a line symmetrically bisecting the line which connects the boron atoms. The phosphorus, boron, and terminal hydrogen atoms were assumed to lie in a plane perpendicular to the plane containing the bridge hydrogen atoms. This configuration is analogous to that observed in diborane(6).[9] The trifluorophosphine group was allowed to rotate about the boron–phosphorus bond. The refined value, 69.3 ± 1.9°, reduces the molecular symmetry from D_{2h}, observed in diborane(6), to C_i. The standard deviation for the best least-squares structure is 0.034. The final values for both models are listed in Table I.

Attempts to vary the root-mean-square amplitudes of vibration in the least-squares analyses were only partially successful for both models (see Table I). The B–H bonded atom pair l_{ij} assumed unreasonably

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[9] W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.

TABLE I

GEOMETRICAL AND THERMAL PARAMETERS[a]

	Model A	Model B
	Bonded Distances, Å	
B–P	1.848 (0.009)	1.848 (0.012)
P–F	1.539 (0.001)	1.539 (0.001)
B–H(terminal)	1.252 (0.054)	1.228 (0.120)
B–H(bridge)		1.324 (0.120)
B–B	1.800 (0.012)	
	Angles, Deg	
BBP	100.2 (1.5)	100.2 (1.8)
BPF	118.1 (0.2)	118.1 (0.2)
BBH(terminal)	92.3 (6.0)	129.0 (12)
HBP	106.8 (4.8)	
	Torsional Angles, Deg	
BBPF	68.5 (1.5)	69.3 (1.9)
PBBP[b]	180.0	180.0
	Rotational Angles, Deg	
FPF	122.0 (0.6)	115.0 (9)
	l_{ij}, Å	
B1–B2	0.046	
B1–P1	0.064 (0.012)	0.057 (0.018)
P1–F1	0.037 (0.001)	0.036 (0.001)
P1–P2	0.145 (0.054)	0.127 (0.018)
B1–F1	0.090 (0.018)	0.071 (0.012)
F1–F2	0.053 (0.003)	0.065 (0.003)
B1–H1(terminal)	0.050	0.065
B1–H3(bridge)		0.100

[a] Calculated standard deviations are given in parentheses. l_{ij} values shown without accompanying standard deviations were estimated from the radial distribution curve. [b] Value constrained during least-squares analysis.

low values and had to be constrained. The longer nonbonded atom pair l_{ij}'s had standard deviations which were too large to be varied in a least-squares analysis; values for these atom pair l_{ij}'s were estimated from the radial distribution curve but constrained in the least-squares calculation.

Comparison of the matrix-isolation infrared and gas-phase Raman spectra shows no coincidence of any bands (see Table II, Figure 4). This is consistent with the assignment of C_{2h}, D_{2h}, or C_i point group symmetry to the molecule, since these groups do contain a center of symmetry. Note, however, that the presence of a center of symmetry requires that the boron–phosphorus group be planar.

TABLE II

INFRARED AND RAMAN SPECTRA (CM^{-1}) OF BIS(TRIFLUOROPHOSPHINE)DIBORANE(4)

Raman spectrum[a]		Infrared spectrum[b]	
230 s	990 w	375 m	965 w
280 w	1050 w	408 m	970 w, sh
360 m	1065 m	445 w	1020 vvw
385 w	1270 w	455 m	1055 vvw
535 m	1300 vs	522 vw	1108 w
570 w	1335 w	608 w	1165 vvw
590 m	1375 w	638 m	1415 vvw
655 w, b	1665 w	830 s	1500 vvw
745 m	2380 w, b	910 w	2368 w, b
840 vvw	2420 w, b	935 s, sh	2415 w, b
945 vvw, b		950 vs	2590 vw, b
		955 s	

[a] Uncertainty ±5 cm^{-1}. [b] Uncertainty ± 2 cm^{-1}.

Discussion

The deduced trans structure of bis(trifluorophosphine)diborane(4) is consistent with either model A or B and although the diffraction pattern is better fitted by A than by B (standard deviation 0.022 *vs.* 0.034) the latter is almost acceptable as a fit to the diffraction data. However, consideration of all the physical and chemical evidence strongly suggests that model A is the better representation of the structure. The infrared spectrum of the compound contains no band in the region 1600–1800 cm^{-1} which is associated with absorption due to boron-bridging hydrogen-stretching motion.[10] Since this is the most intense band in the spectrum of diborane(6),[11] the absence of any absorption in that region argues against model B. Hydrolysis of bis(trifluorophosphine)diborane(4) produces 5 mol of hydrogen per mole of compound.[2] Model A would be expected to produce 5 mol of hydrogen (four boron–hydrogen bonds and one boron–boron bond) but model B would be expected to produce only 4 mol (four boron–hydrogen bonds). Finally, a rather unusual formulation for bonding must be invoked if the compound has the structure of model B. There are two possibilities. First, the boron atoms could have sp^3 hybridization, as is the case for the boron hydrides and their adducts. This requires that an unpaired electron be associated with each boron atom. Second, the bonding coordination number of the boron atoms could be increased to 5 by the formation of a boron–boron bond, but in this case use of a high-energy orbital is required.

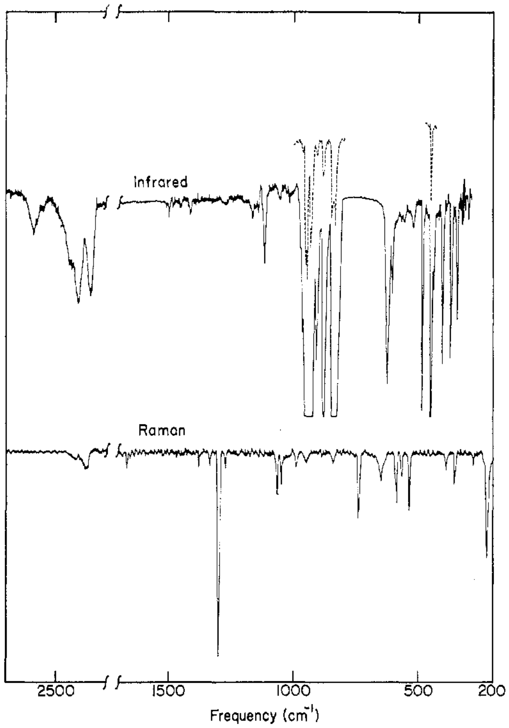

Figure 4.—The matrix-isolation infrared absorption spectrum and the gas-phase Raman spectrum of bis(trifluorophosphine)diborane(4).

The boron–boron distance of 1.80 Å, while somewhat long for a nonbridged bond, is within the range of values observed in other boron hydrides. Consequently the boron–boron distance cannot be used as evidence in favor of model B. The B–B separation is somewhat longer than that reported for diboron tetra-

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(10) R. M. Adams, Ed., "Boron, Metallo-Boron Compounds and Boranes," Interscience, New York, N. Y., 1964, p 527.

(11) Reference 10, p 556.

chloride (1.75 Å)[12] and markedly longer than in diboron tetrafluoride (1.67 Å).[13] The B–P and P–F bond distances are very similar to those observed in trifluorophosphine–borane ($F_3P \cdot BH_3$),[14] while the P–F distances are equal and the B–P distance is only slightly shorter in the borane adduct (0.012 Å). However, the trifluorophosphine group in the borane adduct has C_{3v} symmetry but not in the refined structure of model A. A planar projection of the trifluorophosphine group shows two FPF angles of 122 ± 0.6°, which reduces the symmetry to C_{2v}. The deviation from C_{3v} symmetry is such as to increase the nearest fluorine–hydrogen nonbonded distance.

Model A does show one unusual structural feature. The HBH angle of 146 ± 12° is much larger than that reported for diborane(6) and tetraborane(10), 122°;[9] in trifluorophosphine–borane and carbonyl–borane, these are 115 and 113°,[15] respectively. The small BBH angle of 92.3° is associated with a short nonbonded boron–hydrogen distance of 2.23 Å. In contrast, the hydrogen positions in model B are not significantly different from those reported for diborane(6).

Acknowledgments.—We gratefully acknowledge financial support from the Advanced Research Projects Agency (Material Science Center, Cornell University) and the Army Research Office—Durham.

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[13] L. Trefonas and W. N. Lipscomb, *ibid.*, **28**, 54 (1958).

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[15] Reference 10, 546.

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The Crystal Structure of Tetraethylammonium Hexabromoantimonate(V), $(C_2H_5)_4NSbBr_6$[1]

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Tetraethylammonium hexabromoantimonate(V) has been prepared and its crystal structure determined by three-dimensional X-ray analysis. The dark red-brown compound crystallizes in the tetragonal space group *I*4$_1$*md* with four molecules in a unit cell of dimensions $a = b = 8.7008$ (7) and $c = 24.797$ (3) Å. Data were collected with an automated diffractometer using the θ–2θ step scan technique and Mo Kα radiation (λ 0.7107 Å). The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques to a discrepancy index $R = 0.042$ for the 276 independent reflections used in the analysis. The structure consists of slightly distorted octahedral $Sb^{V}Br_6^-$ anions and $(C_2H_5)_4N^+$ cations which are twofold disordered about intersecting mirror planes. The average Sb–Br distances corrected for thermal motion assuming a riding model are 2.561 (5), 2.564 (5), and 2.570 (4) Å. The only close Br–Br van der Waals contact is along the a axis at 3.584 Å. The similar sizes of the tetraethylammonium and the more spherical hexabromoantimonate(V) ions permit efficient packing which contributes to the stability of this compound.

Introduction

The crystal structure investigation of tetraethylammonium hexabromoantimonate(V) was undertaken as part of a series of investigations of halo-coordinated antimony compounds being performed in this laboratory.[4–11] A series of intervalence antimony bromide complexes of varying stoichiometries has been investigated to relate, if possible, their crystal structures and charge transfer properties and to evaluate the effects of cation size, type, and stereochemistry on the antimony bromide anion and on the resulting solid-state structure. The structure of the tetraethylammonium salt was undertaken as a result of preliminary investigations[8] on the physical and chemical properties of this material and other intensely colored $R_xSb_yBr_z$ complexes. The tetraethylammonium complex was shown to be unusually stable in comparison to the other antimony bromide complexes studied, being stable in air and more slowly hydrolyzed in water. Although the tetraethylammonium complex is also deeply colored,[12] appearing a dark red-brown, the preliminary X-ray results indicated the stoichiometry was $RSb^{V}Br_6$ with only four formula units per unit cell. Intervalence charge transfer could not occur if indeed all the $SbBr_6$ species present were equivalent. Also, the saturated cation would not be expected to participate in any other possible type of charge-transfer path.

Experimental Section

Tetraethylammonium hexabromoantimonate(V), $(C_2H_5)_4NSbBr_6$, mol wt 479.5, crystallizes in the tetragonal space group *I*4$_1$*md*, with $F(000) = 1344$ e, $Z = 4$, $a = b = 8.7008$ (7) Å, $c = 24.797$ (3) Å, temperature ~24°, $V = 1877.3$ Å^3, $d_m = 2.62$ g/cm^3, $d_c = 2.59$ g/cm^3, Mo Kα (λ 0.7107 Å), and $\mu = 150.7$ cm^{-1}.

The $(C_2H_5)_4NSbBr_6$ salt was prepared by the method of Law-

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[1] Work was performed at the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2784.

[2] To whom correspondence should be addressed.

[3] Ames Laboratory undergraduate summer student trainee, 1968.

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