g, 2.16 mmol) plus a mixture (0.090 g) of $(CF_3)_2P(S)SCH_3$ contaminated with unreacted $(CF_3)_2PS_2H$.

Acknowledgment. We thank the National Research Council of Canada for financial support of this work and for a scholarship to L. F. D. We also thank G. Bigam, T. Brisbane, and Dr. T. Nakashima for much assistance with the nmr spectroscopic studies. Preliminary discussions of the exchange mechanism with Dr. R. W. Rudolph (University of Michigan) proved helpful to our understanding of the process and we wish to express our thanks. We also thank Dr. R. E. D. McClung of this department for assistance with the line shape calculations.

Registry No. H_2S, 7783-06-4; SPF_2Cl, 2524-02-9; SPF_2SH, 20773-09-5; $(CF_3)_2PN(CH_3)_2$, 432-01-9; $(CF_3)_2PSP(S)F_2$, 52226-01-4; $(CF_3)_2PS_2H$, 18799-75-2; $PF_2N(CH_3)_2$, 814-97-1; $F_2PSP(S)(CF_3)_2$, 52226-02-5; $(CF_3)_2P(S)SP(CF_3)_2$, 23526-69-4; $F_2P(S)SPF_2$, 23526-68-3; HCl, 7647-01-0; $(CH_3)_2NH$, 124-40-3; CH_3SH, 74-93-1; Hg, 7439-97-6; CH_3OH, 67-56-1; Cl_2, 7782-50-5.

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Spectra and Structure of Phosphorus-Boron Compounds. VI.[1] Vibrational Spectra and Structure of Some Phosphine-Trihaloboranes

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The infrared (33–3000 cm^{-1}) and Raman (20–2700 cm^{-1}) spectra of $H_3P{\cdot}BX_3$ and $D_3P{\cdot}BX_3$ (X = F, Br, I) in the solid state at −196° have been recorded. The spectra have been interpreted on the basis of C_{3v} symmetry and 11 of the 12 fundamental vibrations have been assigned. A shift to higher frequency of the P–H stretching mode as compared to the corresponding mode in PH_3 is consistent with a shortening of this bond with coordination. A normal-coordinate calculation was carried out and the values obtained for the P–B force constants for this series of molecules are compared to the similar quantities of several other phosphorus-boron molecules. The observation of four lattice modes in solid $H_3P{\cdot}BF_3$ and $D_3P{\cdot}BF_3$ indicates that there are at least two molecules per primitive cell which give rise to in-phase and out-of-phase components of the P–B stretch.

Introduction

Investigations of phosphine-borane molecular adducts have demonstrated that the commonly accepted correlation between bond length and dissociative stability does not seem to hold for this class of compounds. For example, in trifluorophosphine-borane,[3] the P–B bond distance was found to be 1.836 ± 0.012 Å, whereas the distance for the same bond in trimethyl- and methylphosphine-borane[4] was found to be 1.901 ± 0.007 and 1.906 ± 0.006 Å, respectively. Therefore, one would expect in terms of bond length that the fluorophosphine-boranes would be more stable whereas, in fact, just the opposite has been observed; the $F_3P{\cdot}BH_3$ molecule is completely dissociated at 0°, while the methylphosphine-boranes are stable to much higher temperatures.

In order to provide additional information on the P–B bonding, the microwave spectrum of phosphine-borane[5] has been successfully studied, and a corresponding study of phosphine-trichloroborane was attempted but was unsuccessful because the compound was found to be completely dissociated in the gas phase.[6] However, phosphine-trichloroborane was studied by vibrational and nuclear magnetic resonance spectroscopy[6] and a normal-coordinate analysis has also been carried out. In order to complete our studies of the series of phosphine-trichloroboranes and to provide more data on P–B bonds, the infrared and Raman spectra of phosphine-trifluoro, -tribromo-, and -triiodoborane and the corresponding deuterated species were recorded. In addition, the ^1H and ^{11}B nmr spectra of phosphine-tribromoborane were obtained. The results of this investigation and a normal-coordinate analysis for these molecules are reported herein.

Experimental Section

With the exception of phosphine and phosphine-triiodoborane, all preparations and purifications were carried out in a standard high-vacuum system employing greaseless stopcocks.[7] Boron trifluoride was obtained commercially (Matheson) and purified by vacuum fractionation until it exhibited a vapor pressure of 301 mm[7] at −112° (carbon disulfide–liquid nitrogen slush). Boron tribromide was obtained commercially (Columbia Organic Chemicals) and purified by vacuum fractionation until it exhibited a vapor pressure of 19 mm[7] in a 0° bath. Boron triiodide was obtained commercially (Alfa Inorganics) and purified by vacuum sublimation until all traces of pink color (iodine) had been removed. Phosphine was prepared under a stream of gaseous nitrogen in a fume hood as described in the literature.[8] Phosphine-d_3 was prepared in a similar manner using D_2O and D_2SO_4. All phosphine species were purified by passing them through a −131° bath (n-C_5H_{12} slush) into a −196° bath. Purity was monitored by vapor pressure measurements[7] and infrared spectra.[9] Phosphine-trifluoroborane[10,11] and phosphine-tribromoborane[9,12] were prepared by condensing equimolar amounts of phosphine and the appropriate boron trihalide into an evacuated tube at liquid nitrogen temperatures. The tube was isolated from the vacuum system

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and allowed to warm slowly to approximately −30°. The resulting solid white adducts were then condensed from the tube to the appropriate window material for the vibrational studies.

Phosphine–triiodoborane was prepared by allowing phosphine to sublime onto the appropriate substrate which was maintained at −196°. Boron triiodide was then condensed on top of the phosphine. The system was allowed to warm to room temperature during which time the white solid phosphine–triiodoborane formed. After approximately 30 min at room temperature the sample cell was placed under dynamic vacuum to remove any unreacted phosphine and the sample was allowed to anneal for approximately 3 hr. The sample was then cooled to −196° and data were recorded. Considerable difficulty was encountered in getting mid-infrared data in that the source beam seemed to decompose the sample and the sample possibly reacted with the brass substrate holder during the annealing procedure.

The ^1H nmr spectrum of a saturated solution of $H_3P{\cdot}BBr_3$ in C_6D_6 was obtained at ambient temperature on a Varian Associates A-60 spectrometer operating at 60 MHz. The spectrum consisted of a doublet with J_{PH} = 425 Hz and was 3.8 ppm deshielded from the proton resonance in an external TMS reference sample.

The ^{11}B nmr spectrum was obtained from the same sample under similar conditions on a Varian Associates XL-100-15[13] operating at 32.1 MHz. The spectrum consisted of a doublet with $J_{^{31}P-^{11}B}$ = 127 Hz and a chemical shift of +42.8 ppm with respect to the boron resonance in an external sample of $B(OCH_3)_3$.

Equimolar amounts of PH_3 and BF_3 were condensed into a 5-mm nmr tube attached to the vacuum system and allowed to warm to room temperature. Solvent (C_6D_6) and a trace of tetramethylsilane were then distilled onto the product at −196° and the tube was flame sealed from the system. Nmr spectra (^1H and ^{11}B) indicated that in C_6D_6 solution at room temperature no adduct was present. In a similar experiment BI_3 and an excess of PH_3 were condensed in a 5-mm nmr tube attached to the vacuum system. After allowing the contents to warm to approximately −30°, any excess phosphine was pumped from the tube. Solvent (C_6D_6) and a trace of TMS were then distilled onto the white solid at −196° and the nmr tube was flame sealed from the system. Attempts to obtain ^1H and ^{11}B nmr spectra were not successful, presumably because of the limited solubility of $H_3P{\cdot}BI_3$ in C_6D_6.

A Perkin-Elmer Model 621 infrared spectrophotometer purged with dry air was used for recording mid-infrared from 3000 to 200 cm^{-1}. The instruments were calibrated with standard gases[14] in the high-frequency region and with atmospheric water vapor[15] in the low-frequency region. A low-temperature cell equipped with a CsI window was employed to record the spectra of the solid samples. Conventional vacuum deposition techniques were used to obtain the solid film on the CsI substrate. The CsI substrate was held at −196° during deposition and then the solid films were annealed until there was no change in the spectrum. Typical spectra are shown in Figure 1 and the fundamental frequencies are listed in Table I.

Far-infrared spectra from 33 to 350 cm^{-1} were recorded with a Beckman Model IR-11 spectrophotometer. The atmospheric water vapor was removed from the instrument housing by flushing with dry air. The instrument was calibrated by using atmospheric water vapor.[15] Single-beam energy checks were made periodically to ensure the energy transmission was at least 10–15% at all times. A low-temperature cell similar to one described eariler[16] was employed to record the spectra of solid samples. Modifications have been made to allow the circulation of cold nitrogen liquid through a hollow brass cold finger. A wedged silicon window was used for the solid film support plate. Deposition and annealing of the samples were similar to methods used for mid-infrared studies. Typical spectra are shown in Figure 2.

The Raman spectra were recorded on a Cary Model 82 Raman spectrophotometer[17] equipped with an argon ion laser source with a frequency of 5145 Å for excitation. Raman spectra of the solids were obtained using a cold cell similar to that employed for the far-infrared instruments, except the sample holder consists of a solid brass plate at an angle of 75° from the normal. Deposition and annealing procedures are similar to those used for the mid-infrared studies. Typical spectra are shown in Figures 3 and 4.

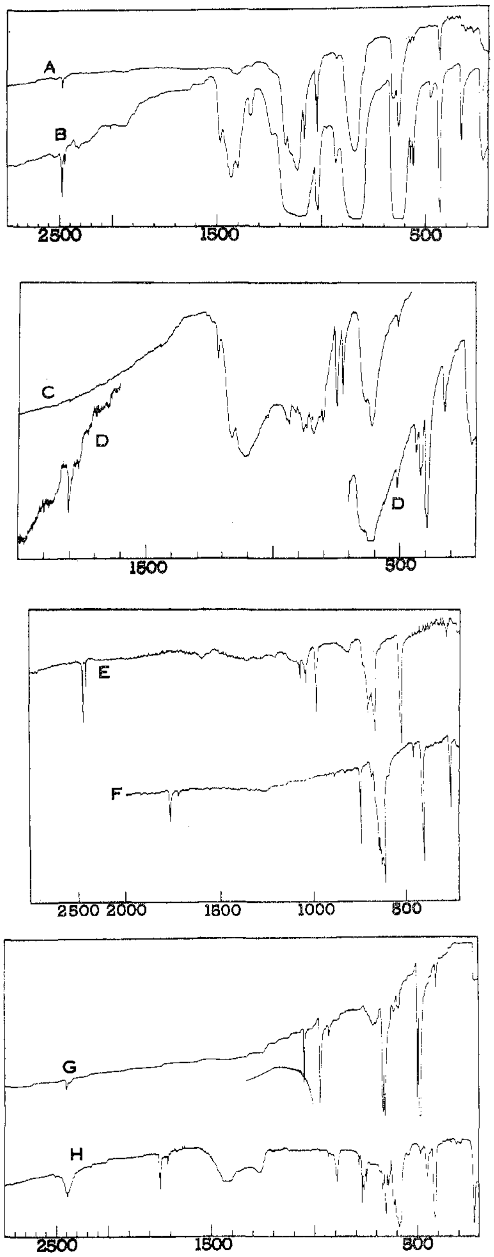

Figure 1. Infrared spectra: A and B, solid $H_3P{\cdot}BF_3$ where B > A; C and D, solid $D_3P{\cdot}BF_3$ where D > C; E, solid $H_3P{\cdot}BBr_3$; F, solid $D_3P{\cdot}BBr_3$; G, solid $H_3P{\cdot}BI_3$; H, solid $D_3P{\cdot}BI_3$.

Vibrational Assignment

Regardless of whether phosphine–trihaloboranes are in an eclipsed or staggered conformation, they must belong to the point group C_{3v}. Since the normal vibrations for these molecules span the representations 5 A_1 + A_2 + 6 E_1, there should only be 12 fundamental vibrational frequencies. Vibrations of A_1 and E symmetry are active in both the infrared and Raman techniques, whereas the internal torsional (A_2) mode is inactive in both spectra for the isolated molecules. Frequently in the solid state, the site symmetry may be sufficiently low, C_s or C_1, to permit the observation of this A_2 mode.

The normal vibrations associated with the H_3P moiety can be readily assigned on the basis of isotopic shifts and the frequencies reported[18] for the "free" PH_3 molecule. The

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(13) This instrument was purchased with funds from the National Science Foundation through a Department Development Grant.

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(17) This instrument was purchased with funds from the National Science Foundation through Grant No. GP-28068.

Table I. Observed and Calculated Fundamental Frequencies (cm^{-1}) of Phosphine-Trihaloboranes[a]

	Observed	Calculated	Assignment and PED	Observed	Calculated	Assignment and PED
			H_3PBF_3			D_3PBF_3
				A$_1$ Species		
ν_1	2441	2452	r_{PH} (100)	1762	1754	r_{PD} (100)
ν_2	1021	1028	δ_{PH} (98), r_{PB} (2)	752	754	δ_{PD} (77), r_{BF} (23)
ν_3	797	800	r_{BF} (77), r_{PB} (14), δ_{BF} (9)	795	808	r_{BF} (63), r_{PB} (19), δ_{PH} (9), δ_{BF} (9)
ν_4	607	607	r_{PB} (59), δ_{BF} (41)	598	596	r_{PB} (56), δ_{BF} (44)
ν_5	331	312	δ_{BF} (73), r_{PB} (15), r_{BF} (12)	325	304	δ_{BF} (71), r_{PB} (17), r_{BF} (12)
				E Species		
ν_7	2468	2474	r_{PH} (100)	1799	1784	r_{PD} (100)
ν_8	1120	1124	r_{BF} (76), δ_{PH} (13), δ_{BF} (11)	1115	1115	r_{BF} (83), δ_{BF} (12), ρ_{BF} (5)
ν_9	1085	1078	δ_{PH} (79), r_{BF} (21)	776	774	δ_{PD} (94), ρ_{PD} (6)
ν_{10}	570	567	ρ_{PH} (88), δ_{PH} (8), r_{BF} (4)	417	401	ρ_{PD} (51), δ_{BF} (49)
ν_{11}	430	431	δ_{BF} (100)	435	459	δ_{BF} (56), ρ_{PD} (44)
ν_{12}	225	233	ρ_{BF} (90), δ_{BF} (5), r_{BF} (5)	222	225	ρ_{BF} (88), ρ_{PD} (4), δ_{BF} (4)
			H_3PBBr_3			D_3PBBr_3
				A$_1$ Species		
ν_1	2394	2408	r_{PH} (100)	1732	1725	r_{PD} (100)
ν_2	975	963	δ_{PH} (97), r_{PB} (3)	763	753	δ_{PD} (50), r_{PB} (50)
ν_3	699	697	r_{PB} (63), δ_{BBr} (23), r_{BBr} (14)	644	647	r_{PB} (40), δ_{PD} (40), δ_{BBr} (20)
ν_4	281	278	r_{BBr} (100)	277	277	r_{BBr} (100)
ν_5	160	152	δ_{BBr} (68), r_{BBr} (25), r_{PB} (7)	155	147	δ_{BBr} (67), r_{BBr} (25), r_{PB} (8)
				A$_2$ Species		
ν_6	174	178		133	126	τ (100)
				E Species		
ν_7	2430	2429	r_{PH} (100)	1777	1755	r_{PD} (100)
ν_8	1070	1064	δ_{PH} (90), ρ_{PH} (10)	763	759	δ_{PD} (88), ρ_{PD} (12)
ν_9	676	679	r_{BBr} (45), ρ_{PH} (31), δ_{BBr} (17), ρ_{BBr} (7)	638	640	r_{BBr} (57), δ_{BBr} (21), ρ_{PD} (10), ρ_{BBr} (8), δ_{PD} (4)
ν_{10}	528	509	ρ_{PH} (34), r_{BBr} (49), δ_{BBr} (16)	428	407	ρ_{PD} (69), r_{BBr} (31)
ν_{11}	186	189	δ_{BBr} (93), ρ_{BBr} (7)	185	186	δ_{BBr} (100)
ν_{12}	120	118	ρ_{BBr} (63), δ_{BBr} (22), r_{BBr} (15)	110	113	ρ_{BBr} (66), δ_{BBr} (20), r_{BBr} (14)
			H_3PBI_3			D_3PBI_3
				A$_1$ Species		
ν_1	2362	2379	r_{PH} (100)	1707	1701	r_{PD} (100)
ν_2	977	980	δ_{PH} (97), r_{PB} (3)	760	756	δ_{PD} (59), r_{PD} (41)
ν_3	679	679	r_{PB} (71), δ_{BI} (14), r_{BI} (13), δ_{PH} (2)	643	639	r_{PB} (46), δ_{PD} (31), r_{BI} (12), δ_{BI} (11)
ν_4	228	225	r_{BI} (97), r_{PB} (3)	221	220	r_{BI} (97), r_{PB} (3)
ν_5	91	95	δ_{BI} (76), r_{BI} (24)	90	92	δ_{BI} (80), r_{BI} (20)
				E Species		
ν_7	2396	2400	r_{PH} (100)	1750	1730	r_{PD} (100)
ν_8	1054	1038	δ_{PH} (90), ρ_{PH} (10)	760	741	δ_{PD} (83), ρ_{PD} (12), r_{BI} (5)
ν_9	657	671	r_{BI} (57), δ_{BI} (15), ρ_{PH} (28)	658	639	r_{BI} (68), δ_{BI} (18), ρ_{PD} (7), δ_{PD} (7)
ν_{10}	493	508	ρ_{PH} (44), r_{BI} (45), δ_{BI} (11)	413	400	ρ_{PD} (77), r_{BI} (23)
ν_{11}	138	137	δ_{BI} (100)	135	137	δ_{BI} (100)
ν_{12}	41	41	ρ_{BI} (100)	39	39	ρ_{BI} (100)

[a] Abbreviations used: r, bond stretching; δ, deformation; ρ, rock; τ, torsion.

symmetric P-H stretching mode, ν_1, is observed at 2441, 2394, and 2362 cm^{-1} in the infrared and Raman spectra for $H_3P{\cdot}BF_3$, $H_3P{\cdot}BBr_3$, and $H_3P{\cdot}BI_3$, respectively, with the resulting Raman bands being the most intense lines in these spectra, whereas the corresponding infrared bands are quite weak. The antisymmetric P-H stretch, ν_7, comes at 2471, 2430, and 2397 cm^{-1} for $H_3P{\cdot}BF_3$, $H_3P{\cdot}BBr_3$, and $H_3P{\cdot}BI_3$, respectively, with the infrared bands being much stronger than those for the symmetric motion, whereas the opposite is true in the Raman effect. Upon deuteration, ν_1 shifts to 1762, 1732, and 1707 cm^{-1} and ν_7 shifts to 1799, 1777, and 1750 cm^{-1} for $D_3P{\cdot}BF_3$, $D_3P{\cdot}BBr_3$, and $D_3P{\cdot}BI_3$, respectively.

The PH_3 symmetric deformation is observed at 1021, 975, and 977 cm^{-1} with the antisymmetric motion falling at 1085, 1070, and 1054 cm^{-1} for the $H_3P{\cdot}BF_3$, $H_3P{\cdot}BBr_3$ and $H_3P{\cdot}BI_3$ molecules, respectively. In the Raman spectrum of solid $H_3P{\cdot}BF_3$, there are clearly two bands which could be the H_3P antisymmetric deformation and they are the bands of medium intensity at 1098 and 1085 cm^{-1}. Only the band at 1085 cm^{-1} has an infrared counterpart at 1083 cm^{-1} and is, therefore, assigned as the H_3P antisymmetric deformation. These two vibrations shift to 752, 763, and 760 cm^{-1} and 776, 763, and 760 cm^{-1}, respectively, whereas for the latter two molecules the antisymmetric and symmetric deformations are assumed to be accidently degenerate. The resulting shift factors are consistent with nearly pure hydrogen motion. In an earlier study[6] of phosphine-trichloroborane, we assigned the 1052-cm^{-1} band to the symmetric PH_3 deformation with the lower band at 977 cm^{-1} to the antisymmetric motion mainly on the basis of their relative intensities. However, in a recent investigation of $H_3P{\cdot}BH_3$, Odom, *et al.*,[18] found that the higher frequency line at 1101 cm^{-1} was depolarized whereas the lower frequency line was polarized. On this basis we have reversed the assignments of these two PH_3 deformations in these halides.

The PH_3 rocking mode gives rise to a line of medium intensity in both the Raman and infrared spectra at 576, 528, and

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(18) J. D. Odom, V. F. Kalasinsky, and J. R. Durig, *J. Mol. Struct.*, in press.

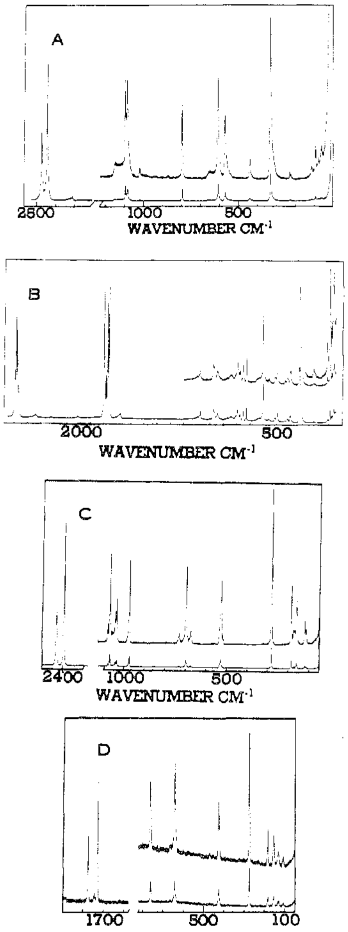

Figure 2. Raman spectra: A, solid $H_3P{\cdot}BF_3$; B, solid $D_3P{\cdot}BF_3$; C, solid $H_3P{\cdot}BBr_3$; D, solid $D_3P{\cdot}BBr_3$.

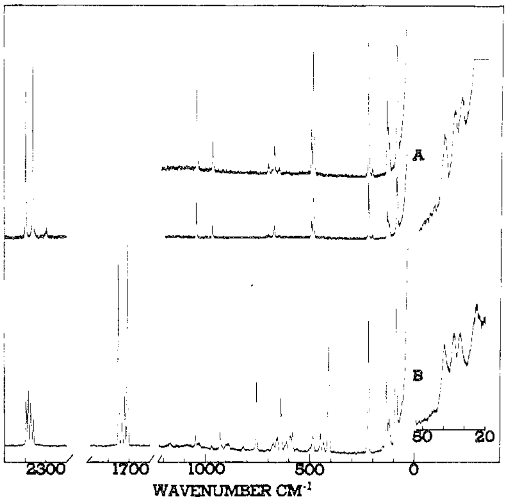

Figure 3. Raman spectra: A, solid $H_3P{\cdot}BI_3$; B, solid $D_3P{\cdot}BI_3$.

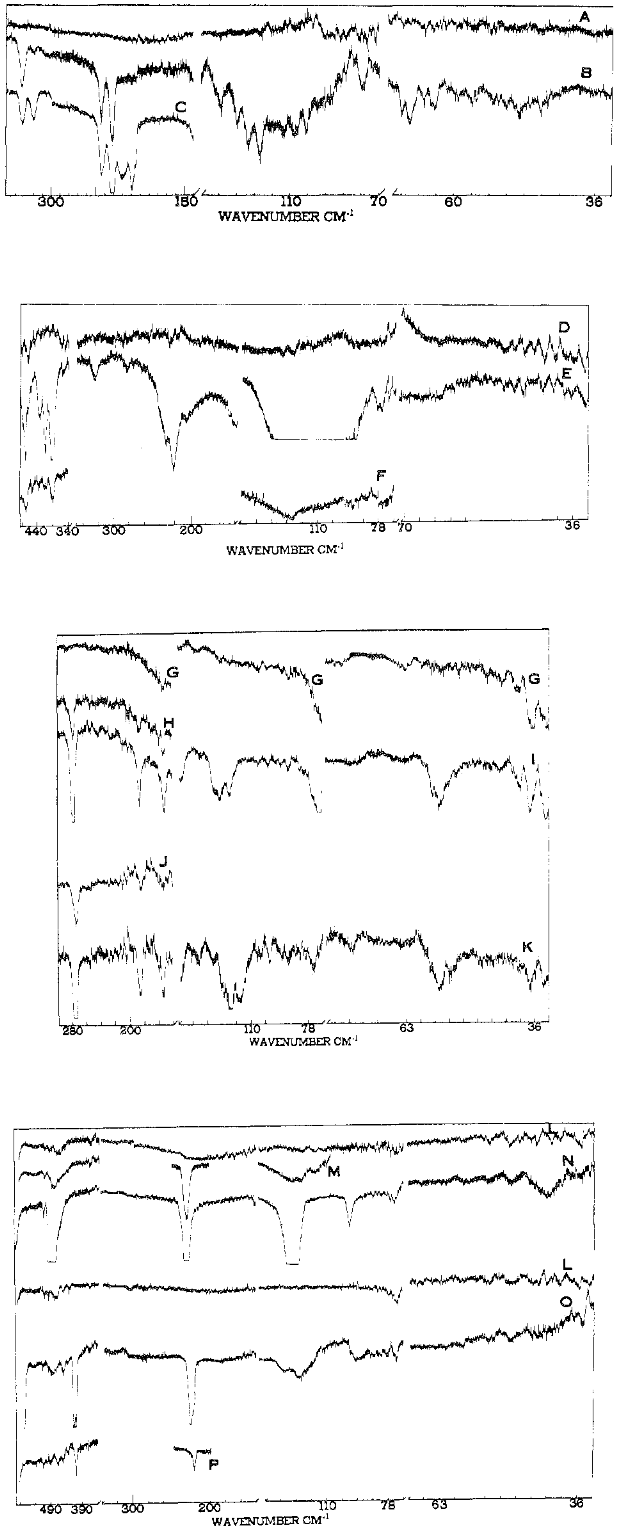

Figure 4. Far-infrared spectra A, cell background; B, annealed solid $H_3P{\cdot}BF_3$; C, nonannealed solid $H_3P{\cdot}BF_3$; D, cell background; E and F, solid $D_3P{\cdot}BF_3$ where F > E; G, cell background; H and I, solid $H_3P{\cdot}BBr_3$ where I > H; J and K, solid $D_3P{\cdot}BBr_3$ where K > J; L, cell background; M and N, solid $H_3P{\cdot}BI_3$ where N > M; O and P, solid $D_3P{\cdot}BI_3$ where O > P.

493 cm^{-1} and in the deuterated species at 417, 428, and 413 cm^{-1} for the fluoro, bromo, and iodo adducts, respectively. The P–B stretching mode turns out to be rather weak in the Raman effect and relatively strong in the infrared spectra. In the bromo and iodo compounds, this frequency occurs at 699 and 679 cm^{-1}. In the fluoride, there appear to be two frequencies in the infrared: a broad band of strong intensity at 631 cm^{-1} and a broad band of medium intensity at 663 cm^{-1}. The Raman frequencies in this region give poor correlation to the infrared modes and they appear at 607 cm^{-1} (medium intensity) and as a very weak broad band at 643 cm^{-1}. It appears that the P–B stretch for this molecule is at 607 cm^{-1} in the Raman effect and at 631 cm^{-1} in the infrared spectrum. This pair of frequencies may be attributed to in-phase and out-of-phase P–B stretching modes due to the presence of two molecules per primitive cell. Upon deuteration, the P–B stretching frequencies shift to

598, 638, and 643 cm^{-1} for the Raman effect and 610, 632 and 640 cm^{-1} in the infrared spectra for the fluoro, bromo, and iodo adducts, respectively.

The remaining fundamentals are all associated with the BX_3 (X = F, Br, I) moiety, except for the internal torsion, ν_6, and their assignment follows fairly straightforwardly from the frequencies previously determined for the uncomplexed BX_3 molecules.[19,20] All of the BX_3 fundamental vibrations are found to shift very little upon deuteration, as one would expect, and this aids in the assignment of some questionable bands. Since all work was done on solid samples, there were no depolarization data available to enable us to decide on any doubtful assignments with such information.

The antisymmetric B-X stretching mode gives rise to weak Raman lines at 1120, 676, and 657 cm^{-1} and strong infrared counterparts at 1120, 664, and 660 cm^{-1} for the BF_3, BBr_3, and BI_3 adducts, respectively, with the corresponding symmetric motions at 797, 281, and 228 cm^{-1} in the Raman spectra. The antisymmetric and symmetric deformations for these adducts are assigned to infrared bands at 430, 186, and 128 cm^{-1} and 333, 153, and 98 cm^{-1}, respectively. The final BX_3 fundamental is the rocking motion of E symmetry and is found to be split in the spectra of these solids, probably due to lower site symmetry in these crystals. For the BF_3 and BBr_3 adducts, these vibrations occur at 242 and 231 cm^{-1} and at 118 and 113 cm^{-1}. Since the rocking mode in the BI_3 species is expected to be less than the 90-cm^{-1} band found for the BI_3 symmetric deformation, it is rather arbitrarily assigned to the next lowest frequency band, which occurs at 40 cm^{-1}. Actually, one cannot differentiate between it and the low-frequency lattice modes for this molecule.

The internal torsional vibration, ν_6, is inactive in both the infrared and Raman spectra for the "free" molecules. In the solid state, however, the selection rules may be sufficiently relaxed (low site symmetry) to permit its observation. In fact, this has been found to be true in a sufficient number of cases so that the observation of torsional modes in the solid has been found to be the rule rather than the exception for many molecules of C_{3v} symmetry.[21-23] A careful check of both the low-frequency Raman and infrared spectra showed no band with a shift factor near 1.4 and all of the observed bands which had not been assigned as intramolecular fundamentals would be assigned to lattice modes for the fluoro and iodo adducts. For the $H_3P{\cdot}BBr_3$ adduct, one can clearly see in the Raman spectrum a weak line at 172 cm^{-1} which lies between the two BBr_3 deformations at 186 and 160 cm^{-1}, respectively. Upon deuteration, this line is evidently missing and a new line of smaller intensity appears at 133 cm^{-1}. The BBr_3 deformations and rocking modes remain approximately at the same frequencies. There is a very broad and weak corresponding band at about 135 cm^{-1} in the far-infrared spectrum of $D_3P{\cdot}BBr_3$, but the 172-cm^{-1} band in the far-infrared spectrum of the "light" molecule is not observable, possibly because of its close proximity to the BBr_3 symmetric deformation. The shift factor for the 172- and 133-cm^{-1} bands is 1.31 and a periodic barrier calculation gave the values of 2.92 and 3.28 kcal/mol for the $H_3P{\cdot}BBr_3$ and $D_3P{\cdot}BBr_3$ molecules, respectively. Since the shift factor for this proposed assignment is very low compared to a theoretical value of 1.41 which has usually been found for methyl torsions,[24] these two bands could be the result of a combination of the BBr_3 rocking mode and two different low-frequency lattice modes for the two isotopic molecules. This would explain the 174-cm^{-1} band in the "light" molecule as a combination band arising from the lattice band at 56 cm^{-1} and the BBr_3 rocking mode at 118 cm^{-1}. The 133-cm^{-1} line in the Raman spectrum of the deuterium compound could be assigned as a combination of the BBr_3 rock with a zone edge acoustical mode.

The vibrational assignments are supported by the Teller-Redlich product rule calculations. For the $H_3(D_3)P{\cdot}BF_3$, $\text{-}{\cdot}BBr_3$, and $\text{-}{\cdot}BI_3$ adducts, respectively, the calculated τ values for the A_1 symmetry species are 1.97, 1.99, and 1.99, respectively; the observed τ values are 1.96, 1.99, and 1.96 for these three molecules. Similarly, for the E symmetry species, we have calculated τ values for these adducts of 2.72, 2.80, and 2.81 with observed values of 2.66, 2.76, and 2.59. The calculated and observed τ values for the A_1 and E symmetry species compare favorably, and the high error for the E symmetry species of $H_3P{\cdot}BI_3$ can be accounted for by the ±2-cm^{-1} uncertainty of the low-frequency motions.

Normal-Coordinate Analysis

No calculations have been reported for the force constants or normal coordinates of H_3PBX_3 where X = F, Br, I. Since there have been no structural data reported on these compounds, we assumed the following parameters: P-H distance, 1.40 Å; P-B distances of 1.96, 1.90, and 1.87 Å for the $H_3P{\cdot}BF_3$, $H_3P{\cdot}BBr_3$, and $H_3P{\cdot}BI_3$ adducts, respectively; B-F distance, 1.38 Å; B-Br distance, 1.87 Å; B-I distance, 2.00 Å; HPH angle, 101°; X-B-X angle, 114°. The 20 internal coordinates which form a basis for the equations of motion were the same as those previously defined[25] for the H_3CGeI_3 molecule. Similarly, the same symmetry coordinates were defined and 11 valence force field constants were chosen which included seven principal and four interaction constants. Schachtschneider's perturbation program[26] was used to adjust the force constants for a best fit to the observed frequencies and to test the constants for significance. Because of the importance of the matrix $\mathbf{J}^t\mathbf{W}\mathbf{J}$ in the least-squares equation, the determinant of the matrix was tested after each iteration for singularity by comparing the product of the diagonal elements[27] to the determinant and these two quantities were found to be of similar magnitude. The final constants which were found reproduced the observed frequencies to an average error of 8, 6, and 6 cm^{-1} (1.8, 1.5, and 1.4%) for the fluoride, bromide, and iodide, respectively. The final force field is given in Table II from which the frequencies listed in Table I were calculated. The potential energy distribution which is also given in Table I shows appreciable mixing of the P-B stretch with the BX_3 stretch and deformation and also some mixing of the PH_3 rock and BX_3 antisymmetric stretch. Most of the other vibrations are reasonably "pure" motions. In addition to the

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Table II. Internal Force Constants for H_3PBX_3 and D_3PBX_3 (X = F, Br, I)

		Value,[b] mdyn/A		
Force constant[a]	Group X = F, Br, I	F	Br	I
K_R	P–B str	2.04 ± 0.04	2.00 ± 0.03	2.07 ± 0.03
K_Q	B–X str	4.86 ± 0.03	2.42 ± 0.03	2.48 ± 0.04
K_r	P–H str	3.50 ± 0.02	3.38 ± 0.01	3.29 ± 0.01
H_α	X–B–X bend	0.901 ± 0.019	1.15 ± 0.05	0.987 ± 0.040
H_β	X–B–P bend	0.651 ± 0.024	0.552 ± 0.055	0.064 ± 0.011
H_γ	H–P–H bend	0.562 ± 0.005	0.532 ± 0.004	0.506 ± 0.005
H_δ	B–P–H bend	0.367 ± 0.009	0.350 ± 0.01	0.361 ± 0.009
H_τ	Torsion	*c*	0.0097 ± 0.0004	*c*
$F_{R\alpha}$	P–B str/X–B–X bend	−0.384 ± 0.022	0.0	0.0
F_{QQ}	B–X str/B–X str	0.582 ± 0.027	0.530 ± 0.035	0.465 ± 0.023
$F_{Q\alpha}$	B–X str/X–B–X bend	0.693 ± 0.018	0.848 ± 0.049	0.676 ± 0.051
$F_{\delta\delta}$	B–P–H bend/B–P–H bend	−0.050 ± 0.005	−0.090 ± 0.004	−0.057 ± 0.005

[a] Valence force field constants. [b] All bending coordinates weighted by 1 A. [c] Not calculated; fundamental not observed.

Table III. Comparison of Force Constants and Bond Distances of Some Phosphine–Boranes

Molecule	P–B distance, A	P–B str freq, cm^{-1}	P–B force constant, mdyn/A	Ref
$F_3P{\cdot}BH_3$	1.836	607	2.46	3
$H_3P{\cdot}BH_3$	1.937	563	2.04 and 1.97	5, 18, 38, 39, 40
$(CH_3)_3P{\cdot}BH_3$	1.901	571	2.37	4, 32
$H_3P{\cdot}BCl_3$		699	1.96	6
$H_3P{\cdot}BF_3$		607	2.04	
$H_3P{\cdot}BBr_3$		699	2.00	
$H_3P{\cdot}BI_3$		679	2.07	

11 force constants listed in Table II the interaction constants $F_{RQ}, F_{R\alpha}, F_{R\beta}, F_{Rr}, F_{R\delta}, F_{Q\beta}, F_{rr}, F_{\alpha\beta}, F_{\beta\beta}, F_{\beta\gamma}, F_{\beta\delta}$, $F_{\gamma\gamma}, F_{\gamma r}$, and $F_{\gamma\delta}$ were also calculated but their values were all less than 0.02 mdyn/Å and the frequency fit was not appreciably improved with the additional force constants. Therefore, these additional interaction constants were not retained in the final force field.

The force constants show some interesting trends. The P–H force constant values are all higher than the 3.24 mdyn/Å reported for PH_3 itself.[19] This increase is consistent with a shorter P–H bond upon adduct formation. The P–B force constant remains relatively unchanged (Table III) for fluoride, bromide, and iodide, and the much lower P–B stretching frequency in the fluoride is attributed to the extensive mixing of that motion with the low-frequency BF_3 symmetric deformation. The change in the nature of the bonding in the BX_3 moiety in the free Lewis acid (sp^2) *vs.* the bonding in the adduct ($\sim sp^3$) is reflected in the decrease of the vibrational fundamentals and force constants associated with this group.

Discussion

In all of the adducts studied, the P–H stretching motions are shifted to higher frequencies than those found for the corresponding motion in the PH_3 molecule. This is consistent with a shortening of the P–H distance and an increase in the HPH angle upon coordination. Coordination decreases lone pair–bond pair interaction in PH_3 and allows this change in P–H distance and ∠HPH to occur. It is very interesting to note that in the series $H_3P{\cdot}BX_3$ (X = F, Cl, Br, I) the PH_3 stretching motions and associated force constants decrease in a regular manner. The PH_3 antisymmetric and symmetric stretches fall at 2468 and 2441 cm^{-1} for $H_3P{\cdot}BF_3$, 2450 and 2416 cm^{-1} for $H_3P{\cdot}BCl_3$,[6] 2430 and 2934 cm^{-1} for $H_3P{\cdot}BBr_3$, and finally 2396 and 2362 cm^{-1} for $H_3P{\cdot}BI_3$. Since these stretches are essentially "pure motions" and show no mixing, their force constants show a regular decrease also. The P–H stretching force constant is 3.50 mdyn/Å for $H_3P{\cdot}BF_3$, 3.43 mdyn/Å for $H_3P{\cdot}BCl_3$,[6] 3.37 mdyn/Å for $H_3P{\cdot}BBr_3$, and 3.29 mdyn/Å for $H_3P{\cdot}BI_3$. This decrease in frequency and force constant reflects a longer P–H bond and smaller ∠HPH as one goes down the series of adducts from BF_3 to BI_3. This means that the changes in "PH_3" hybridization are greatest in $H_3P{\cdot}BF_3$ and smallest in $H_3P{\cdot}BI_3$ so that in $H_3P{\cdot}BI_3$ the bonding is more nearly p^3 for the H_3P moiety and sp^2 for the BI_3. This is also confirmed in the frequencies and force constants for the stretching motions of the BX_3 moiety. Going from $H_3P{\cdot}BF_3$ to $H_3P{\cdot}BBr_3$ the antisymmetric and symmetric stretches for the BX_3 moiety decrease from those of the free BX_3 molecules, and the corresponding force constants[19] of 8.83, 4.63, and 3.66 mdyn/Å for the free Lewis acids decrease to 4.86, 2.20, and 2.42 mdyn/Å in the fluoro, chloro, and bromo adducts, respectively. However, for $H_3P{\cdot}BI_3$, the decrease is much less pronounced, and even though the antisymmetric stretch is less than that of free BI_3 (660 cm^{-1} in the adduct and 737 cm^{-1} in BI_3),[23] the symmetric stretch actually goes up in frequency in the adduct compared to BI_3 (228 cm^{-1} in the adduct and 190 cm^{-1} in BI_3).[23] This is reflected in the normal-coordinate calculation in that the BBr and BI stretching force constants are of very similar magnitude.

One of the parameters of interest in these molecules is the P–B force constant since we are interested in whether or not this reflects the stability of the complex. Unfortunately, no trend is observed in this series of compounds since the P–B force constant is essentially the same (within the stated error limits) in all these compounds as well as in the $H_3P{\cdot}BCl_3$ adduct.[6] Thus no correlation between dissociative stability and the donor–acceptor force constant is observed although the very close similarity in this parameter for all complexes may simply be a result of the extensive mixing of the P–B stretch with other modes in the molecule. Solution nmr studies as well as our experience with the dissociation of the pure compounds indicate that the stability toward disproportionation to the free acid and base is of the order $BF_3 < BCl_3 < BBr_3 \simeq BI_3$. In the absence of thermodynamic data, the most reliable information which may be used to infer relative band energies are, as pointed out by Shriver,[28] bond distances and force constants. However, it is clear that bond distances are not a good indicator for these particular adducts. It does appear that the order of stability of these complexes is not that expected from electronegativities (*i.e.*, $BF_3 > BCl_3 > BBr_3$)[29] and is in agreement with the findings of Shriver and coworkers in boron trihalide–acetonitrile complexes.[28,30]

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Earlier studies[10] of $H_3P{\cdot}BF_3$ reported that not only was there a 1:1 adduct produced, *i.e.*, $H_3P{\cdot}BF_3$ but that the species $H_3P{\cdot}2BF_3$ was also produced. Our annealed spectral data did not confirm this in that all of the data are interpretable on the basis of a 1:1 adduct of C_{3v} symmetry. However, in the far-infrared spectrum of nonannealed $H_3P{\cdot}BF_3$ one can clearly see pairs of bands for the BF_3 symmetric deformation (A_1) and the BF_3 rock (E). Upon annealing it is evident that there is only one band for the BF_3 symmetric deformation and two bands for the BF_3 rocking motions. Since the BF_3 rocking is of E symmetry, it is split in the solid as were many of the other E modes of this series of adducts. Thus, it is concluded that this splitting is due to a lower site symmetry in the crystal compared to the molecular symmetry or due to two molecules per primitive cell in the crystal. Therefore, there was no evidence for a species such as $H_3P{\cdot}2BF_3$.

The nuclear magnetic resonance spectra of these phosphine-trihaloborane adducts serve to confirm results obtained by previous investigators.[31,32] The most extensive nmr study of these complexes is that of Rapp and Drake.[32] The failure of PH_3 and BF_3 to form an adduct in solution has been previously noted in a study in which CD_3I was used as a solvent. This failure of $H_3P{\cdot}BF_3$ to form a stable adduct is not surprising in view of the behavior[6,31] of $H_3P{\cdot}BCl_3$ in both C_6D_6 and CD_3I in which a rapid equilibrium exists which results in an averaging of the nmr signals of the adduct and the free species. In contrast to this behavior, $H_3P{\cdot}BBr_3$ appears to be completely stable in C_6D_6 solution with a relatively large phosphorus-boron coupling constant ($J_{PB} = 127$ Hz) in comparison with other phosphine-borane complexes.[33,34] However, it should be noted that the $Me_3P{\cdot}BX_3$ series (where X = F, Cl, Br) also exhibits[35,36] large J_{PB} values relative to BH_3 complexes. Our values for J_{PH}, J_{PB}, δ_{PH}, and δ_B in $H_3P{\cdot}BBr_3$ agree well with those[31,32] previously reported. The failure to observe experimental nmr parameters for the $H_3P{\cdot}BI_3$ adduct is thought to be simply a consequence of very low solubility in C_6D_6. Nmr parameters have been reported[31,32] for this molecule in CD_3I. The failure to observe a boron-phosphorus coupling constant in $H_3P{\cdot}BF_3$ and $H_3P{\cdot}BCl_3$ unfortunately prevents a meaningful correlation between J_{BP} and the boron-phosphorus stretching force constant in the $H_3P{\cdot}BX_3$ series. Earlier studies have indicated[37] that the B-P force constant is a measure of the stability of the adduct and a comparison of these values to J_{BP} values would be interesting. From the limited data available it appears that the invariance of the B-P stretching force constant is mirrored in the J_{BP} values for $H_3P{\cdot}BBr_3$ and $H_3P{\cdot}BI_3$[32] which are within experimental error of one another.

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Registry No. $H_3P{\cdot}BF_3$, 41593-56-0; $D_3P{\cdot}BF_3$, 52002-92-3; $H_3P{\cdot}BBr_3$, 38822-66-1; $D_3P{\cdot}BBr_3$, 52002-94-5; $H_3P{\cdot}BI_3$, 38822-60-5; $D_3P{\cdot}BI_3$, 52002-93-4.

Supplementary Material Available. Tables IV-IX, showing observed frequencies and calculated fundamentals for $H_3P{\cdot}BX_3$ and $D_3P{\cdot}BX_3$ (X = F, Br, I), 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 \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-2729.

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Chemical Studies of the $B_9H_{14}^-$ and $B_9H_{12}S^-$ Ions

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Chemical procedures are outlined for the *in situ* formation of the reactive anions $B_9H_{13}^{2-}$, $B_9H_{11}S^{2-}$, and $B_9H_9S^{2-}$. These compounds are used to produce the new derivatives 6-$PhB_{10}H_{13}$, $(B_9H_{11}S)_2M^{2-}$ (M = Ni, Pd), and $(B_9H_9S)Pd(ligand)_x^n$ [ligand = PPh_3 ($x = 2, n = 0$), phen ($x = 1, n = 0$), and $C_2S_2(CN)_2$ ($x = 1, n = 2-$)]. The syntheses of new $B_9H_{11}S{\cdot}$ligand (where the ligand is OH^-, tetrahydrofuran, and PPh_3) compounds are described. The chemical and spectral properties of these compounds are discussed.

Introduction

It has been previously reported that the $B_9H_{14}^-$ anion exchanges some terminal hydrogens with D_2O under basic conditions.[2] During an nmr study of the $B_9H_{12}S^-$ anion, it was found that D_2O under basic conditions causes H-D exchange involving the two bridge hydrogens and one of the hydrogens on the BH_2 group at the B(9) position.[3] These observations suggested that, if sufficiently strong bases were used, the anions $B_9H_{13}^{2-}$ and $B_9H_{11}S^{2-}$ might be obtained

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