Phosphine–Borane Derivatives. Part VII.[1] The Vibrational Spectra of the Phosphine Adducts of Boron Trihalides

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The i.r. and Raman spectra of PH_3,BCl_3, PD_3,BCl_3, PH_3,BBr_3, PD_3,BBr_3, PH_3,BI_3, and PD_3,BI_3 are reported. A normal co-ordinate analysis, utilizing a modified Urey–Bradley force field, confirms the assignments. All the adducts give best fits for a HPH angle of *ca.* 105—106°.

A NUMBER of vibrational spectra studies have been reported concerning the boron trihalide adducts of various nitrogen donors.[2-5] However, at the initiation of this investigation, there were no reported vibrational analyses of 1 : 1 adducts of BX_3 with phosphine although the i.r. spectrum had been utilized to suggest that the adduct PH_3,BCl_3 was not entirely dissociated in the gas phase.[6] Studies concerned with the vibrational properties of the P–B bond have resulted in a wide range of assigned P–B stretching frequencies (*ca.* 500 cm^{-1} to *ca.* 900 cm^{-1}).[7-9] Moreover, studies have resulted in considerable differences in the assigned value of the PB stretching force constant.[10,11] Thus we undertook the study of an apparently simple system, the phosphine–boron trihalides, together with their deuteriated analogues, to investigate the area more thoroughly. At the time that this manuscript was in preparation a paper appeared which included a vibrational analysis of phosphine–boron trichloride.[12] Our more general coverage of the area and additional data leads us to suggest some alternative assignments.

EXPERIMENTAL

Starting Material.—Phosphine (Matheson) was distilled through a trap at −126 °C and its i.r. spectrum corresponded with that of the pure material.[13] [$^2H_3$]Phosphine was prepared by reduction of PCl_3 with $LiAlD_4$ (Alpha Inorganics) in a slurry of sodium-dried diethyl ether.[14] The volatile materials were passed through a trap at −126 °C and pure PD_3 was collected in a trap at −196 °C. Its i.r. spectrum corresponded with that given in the literature[15] with 5% ^1H impurity as estimated from 10 cm gas-phase spectra. Boron trichloride (Matheson) and boron tribromide (Alpha Inorganics) were distilled through traps at −65 and −45 °C respectively; their vapour pressures and i.r. spectra were in agreement with literature values. Boron tri-iodide (Alpha Inorganics) was purified as needed by agitation of a benzene solution with elemental mercury in a closed vessel under moisture-free conditions.

Formation of the Adducts.—All reactions were carried out on a conventional Pyrex-glass vacuum system. Equimolar quantities (usually, *ca.* 0·5 mmol) of phosphine and boron trichloride or boron tribromide were distilled into a small-diameter (4 mm. o.d.) thin-walled glass tube with a constriction *ca.* 5 cm from the bottom. As the contents were allowed to slowly warm from −196 °C to room temperature the formation of the white adducts became evident. After 30 min at ambient temperature the reaction tube was momentarily opened to the pump to remove excess of one or the other reactant. The tube was then sealed with the product held in the bottom portion at −196 °C.

For the phosphine adduct of BI_3, the purified benzene solution was transferred to the reaction vessel in a dry-box before attachment to the vacuum line. The tube and contents were then placed at −196 °C and evacuated. Phosphine was introduced in slight estimated excess. Upon warming and gentle agitation a white precipitate formed which gradually settled. After 30 min at ambient temperature the system was placed at −78 °C and opened to the manometer. A slight positive pressure indicated an excess of phosphine and completeness of reaction. The

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[2] R. I. Amster and R. C. Taylor, *Spectrochim. Acta*, 1964, **20**, 1487 and references therein.

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[4] P. D. H. Clippard, Ph.D. Thesis, University of Michigan, 1969.

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[6] P. A. Tierney, D. W. Lewis, and D. Berg, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1163.

[7] M. A. Frish, H. G. Heal, H. Mackle, and I. O. Madden, *J. Chem. Soc.*, 1965, 899 and references therein.

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[9] J. Davis and J. E. Drake, *J. Chem. Soc.* (*A*), 1971, 2094.

[10] W. Sawodny and J. Goubeau, *Z. anorg. Chem.*, 1968, **356**, 289.

[11] G. W. Chantry, A. Finch, P. N. Gates, and D. Steele, *J. Chem. Soc.* (*A*), 1966, 896.

[12] J. D. Odom, S. Riethmiller, J. D. With, and J. R. Durig, *Inorg. Chem.*, 1973, **12**, 1123.

[13] V. M. McConaghie and H. H. Neilsen, *J. Chem. Phys.*, 1953, **21**, 1836.

[14] A. E. Finholt, A. C. Bond, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 1947, **69**, 1199.

[15] K. K. Lee and C. K. Wu, *Trans. Faraday Soc.*, 1939, **35**, 1366.

phosphine was then removed and the benzene gently distilled from the reaction vessel. The adduct was then opened to the pump for 3 h after which the tube was sealed.

Table 1

Approximate description of the fundamental vibrational modes for PH_3,Bx_3 ($H = {}^1H, {}^2H$; $X = Cl, Br, I$)

ν_1	PH_3 sym stretch	ν_7	PH_3 asym stretch
ν_2	PH_3 sym deformation	ν_8	PH_3 asym deformation
ν_3	PB stretch	ν_9	BX_3 asym stretch
ν_4	BX_3 sym stretch	ν_{10}	PH_3 rock
ν_5	BX_3 sym deformation	ν_{11}	BX_3 asym deformation
		ν_{12}	BX_3 rock

A_2

ν_6 H_3P,BX_3 torsion.

When solutions of the adducts (MeI and CH_2Cl_2) were required, the sample tubes were broken open under moisture-free conditions, the appropriate solvent added, and the contents agitated. A syringe was used to extract clear solutions for spectroscopic analysis.

Table 2

Observed i.r. and Raman frequencies/cm^{-1} ± 3 cm^{-1} of solid phosphine–boron trichloride, with Raman polarization data taken from MeI and CH_2Cl_2 solutions

	PH_3,BCl_3			PD_3,BCl_3		
	Ir (CsI)	Raman (s)	(Sol)	Ir (CsI)	Raman (s)	(Sol)
ν_7	2445m	2447s	2445m, dp	1790w	1787s	1789s, dp
ν_1	2415w	2412vs	2415vs, p	1745vw	1743vs	1744vs, p
$2\nu_2$		1952w			1560w	
$2\nu_9$		1455vw			*ca.* 1440vw	
$2\nu_3$		1382w			*ca.* 1250vw	
$2\nu_{10}$	1120vw	1118w	1120vw, dp	880w	880vw	
ν_8	1058s	1061s	1060m, dp	775m *	774ms	775m, dp?
ν_2	988s	981m	988w, p	785sh *	(*ca.* 780)	780sh, p
$\nu_9(^{10}B)$	750sh			*ca.* 750sh		
$\nu_9(^{11}B)$	725s	730m		720s	718w	725w, dp?
$\nu_{10} + \nu_{12}$		(*ca.* 700)			585vw	
$\nu_3(^{10}B)$		700sh		658m	647m	650sh, p?
$\nu_3(^{11}B)$	675m	693m	675m, p	635m	632ms	633sh, p?
$\nu_4 + \nu_5$	640sh	640m			(*ca.* 645)	
ν_{10}	553m	560m	556w, dp	440w	441s	440m, dp
ν_4	395m	399vs	399vs, p	398vw	395vs	397vs, p
ν_5	252s	254s	250m, p	249vw	247s	244m, p
ν_{11}	240sh	244s	240m, dp	238w	241s	235m, dp
ν_{12}		148w	147w, dp		144w	143vw, dp

Lattice modes not listed; only combinations coincident in both system can be assigned.

* Taken from solution.

Spectroscopic Techniques.—Raman spectra were recorded on solid samples in thin-walled glass tubes on a Spectra-Physics Model 700 spectrometer in conjunction with a Model 164 Argon-ion laser and Model 265 Exciter Unit. Typical power output was varied between 100 and 300 mW; the 20 492 cm^{-1} frequency was employed as the exciting line. Before use the instrument was corrected to zero wavenumbers and checked against the spectrum of CCl_4 for precision and polarization efficiency. Polarization data were secured by use of MeI and CH_2Cl_2 solutions of the adducts in capped solution cells. These solvents are far from ideal but were the only ones that gave significant, though low, solubility for solution spectra. The low solubility of the adducts required high instrument gain and laser output between 300 and 700 mW. Two different solvents were used so that any adduct peaks masked by the spectrum of one solvent would be observed in the spectrum of the other solution.

I.r. spectra were recorded on a Beckman IR 12 spectrometer with CsI pellets and Nujol mulls between CsI plates for solid samples and typical KBr solution cells for the various solution spectra. The spectrometer calibration was periodically checked against the polystyrene spectrum.

DISCUSSION

The molecules PH_3,BX_3 and PD_3,BX_3 are assumed to possess C_{3v} symmetry in staggered conformation leading to five a_1 fundamental modes, six doubly-degenerate e modes, and one a_2 mode. All fundamentals, with the exception of the a_2 mode, are expected to be both Raman- and i.r.-active. The a_1 modes should be polarized and the e modes depolarized in the Raman effect. The conventional description of these fundamentals is given in Table 1.

All of the frequency values (Tables 2—4) are initially obtained from the Raman spectra of the solid samples since these in general provide the more intense set of bands as well as some overtone and combination bands. The general agreement between solid and solution phase Raman and i.r. spectra suggest only minimal solvation effects though in a few instances there are appreciable differences in one or two modes in the solution spectra. Several intense bands at low frequency in the Raman spectra of the solids, which are absent from the solution spectra, are assumed to be lattice modes and are not listed. Overtones are only listed where the particular combination occurs for more than one species.

Relative band intensities as well as peak broadness [16]

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[16] G. Herzberg, ' Molecular Spectra and Molecular Structure,' vol. II, Van Nostrand, Princeton, 1968, p. 491.

are of some assistance in determining symmetry type, but polarization data from the Raman spectra of the solutions are used whenever possible in assigning symmetry species. Unfortunately, the extremely low solubility of these adducts [17] required the use of solvents not particularly suited to Raman work, thereby hampering these studies to some extent. I.r. band intensities are used to corroborate assignments based on the Raman data. The Raman spectra of the solid adducts gives no clear evidence of free BX_3. The solution spectra contain low-intensity bands, attributable to the presence of some free boron trihalide in PH_3,BCl_3 and, to a lesser extent, in PH_3,BBr_3. This is not surprising in view of the relatively high dissociation pressure associated with the adducts [6] and our experience in studying their n.m.r. spectra.[1,17] The Raman spectrum of solid PH_3,BBr_3 (Figure 1) and its i.r. spectrum in MeI (Figure 2) are provided as representative examples of the various spectra listed in Tables 2—4 of PH_3,BCl_3 and PD_3,BCl_3, PH_3,BBr_3 and PD_3,BBr_3, and PH_3,BI_3 and PD_3,BI_3 respectively.

TABLE 3

Observed i.r. and Raman frequencies/cm^{-1} ± 3 cm^{-1} of solid phosphine–boron tribromide, with Raman polarization data taken from MeI and CH_2Cl_2solutions

	PH_3,BBr_3			PD_3,BBr_3		
	Ir (CsI)	Raman (s)	(Sol)	Ir (CsI)	Raman (s)	(Sol)
ν_7	2430m	2428s	2426s, dp	1768m	1773s	1772s, dp
ν_1	2390w	2390vs	2390vs, p	1730w	1726vs	1727vs, p
$2\nu_2$		1947w			*ca.* 1516vw	
$2\nu_9$		*ca.* 1384vw				
$2\nu_3$		*ca.* 1353vw				
$\nu_2 + \nu_4$		*ca.* 1250				
$\nu_8 + \nu_{11}$		*ca.* 1200				
$2\nu_{10}$	1070vw *	1071m	1070m, dp			
ν_8	1052w *	1048m	1050m, dp	760m	760m	765m
ν_2	982m	977m	976m, p			
$\nu_9(^{10}B)$	722m,sh				678w	
		722w				*ca.* 665
$\nu_9(^{11}B)$	*ca.* 700m,sh				633w	
$\nu_3(^{10}B)$	*ca.* 695m,sh			650m		
		690m	685mbr, p?		640	*ca.* 640
$\nu_3(^{11}B)$	682m			634m		
ν_{10}	529m	530m	531m, dp	431m	428m	430m, dp
ν_4	281w	282m	282s, p	278m	278s	280s, p
ν_5		183w	181vw, p		182m	181m, p
ν_{11}		160w	160vw, dp		150m	150w, dp
ν_{12}		*ca.* 116br,w	*ca.* 112w, dp		112w	112w, dp

* Taken from solution.

TABLE 4

Observed i.r. and Raman frequencies/cm^{-1} ± 3 cm^{-1} of solid phosphine–boron tri-iodide, with Raman polarization data taken from MeI and CH_2Cl_2 solutions

	PH_3,BI_3			PD_3,BI_3		
	Ir (CsI)	Raman (s)	(Sol)	Ir (CsI)	Raman (s)	(Sol)
ν_7	2398w	2397s	2402s, dp	1750vw	1752s	1755s, dp
ν_1	*ca.* 2365w	2362vs	2368vs, p	1709vw	1709s	1709vs, p
$2\nu_2$		1945vw			1515vw	
$2\nu_9$		1345vw			1180vw	
$2\nu_3$		1275vw			*ca.* 1282vw	
$\nu_8 + \nu_{11}$		1150vw			*ca.* 880vw	
$\nu_2 + \nu_4$		1100vvw		978vw	970vw	
$2\nu_{10}$		*ca.* 960vvw			*ca.* 830vw	
ν_8	1058m	1056s	1060m, dp	*ca.* 762s	760m	*ca.* 762m, dp?
ν_2	981s	981m	980w, p	*ca.* 760s	760m	*ca.* 760m, p?
$\nu_9(^{10}B)$	700sh	*ca.* 705w	*ca.* 700w, dp?	615sh	614sh	
$\nu_9(^{11}B)$	670m	680m	680m, dp?	598m	596m	597m, dp?
					587m	570sh, p?
$\nu_3(^{10}B)$		680m	*ca.* 690w, p?	655sh	657w	
$\nu_3(^{11}B)$	663m	*ca.* 660sh	665m, p	642s	642m	641m, p
ν_{10}	491s	492s	496m, dp		418s	
ν_4	232m	229m	230m, p		220vs	222s, p
ν_5		135m	133m, p		134s	132m p,
ν_{11}		127sh	*ca.* 127sh, dp?		123m	
ν_{12}		89s	*ca.* 87sh		89s	89w, dp

The Phosphine Vibrations.—The asymmetric, ν_7, and symmetric, ν_1, PH_3 stretching vibrations are readily

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[17] J. E. Drake and B. Rapp, *J.C.S. Dalton*, 1972, 2341.

assigned in all six adducts. However, the assignment of the asymmetric, ν_8, and symmetric, ν_2, PH_3 deformation modes is not so readily made. It is tempting to suggest that the more intense band in the Raman spectrum [Figure 3(A)] is probably ν_2; the assignment made in the recent work on PH_3,BCl_3.[12] However, we choose to reverse the previous assignment so that the higher-frequency band (1059 cm^{-1} in PH_3,BCl_3 and *ca.* the same value in the other PH_3 adducts) is the *e* mode, ν_8, and the lower-frequency band (*ca.* 980 cm^{-1} in all of the phosphine adducts) is the a_1 mode ν_2, because: (i) in the closely related compound NH_3BF_3,[18] the asymmetric deformation mode is in fact the more intense in the Raman spectrum and at higher frequency; (ii) the corresponding *e* and a_1 modes in free phosphine [13] are at 1122 cm^{-1} and 992 cm^{-1} respectively; (iii) as with PH_3,BH_3,[19] the lower-frequency band is clearly polarized; (iv) the dipole moment changes are greater for the *a* mode so it should be more intense in the i.r. spectrum (Figure 2) as is generally true for comparable SiH_3 derivatives; [20] (v) the natural consequences of the Teller–Redlich product rule [for a_1 modes $\nu(i)/\nu$ for PH_3 is 0·515 observed, 0·50 calc.; for PH_3,BBr_3 is 0·515 obs., 0·50 calc.; for PH_3,BI_3 is 0·527 obs., 0·50 calc.; while for *e* modes $\nu(i)/\nu$ for PH_3,BCl_3 is 0·39 obs., 0·37 calc.; for PH_3,BBr_3 is 0·38 obs. 0·36 calc.; and for PH_3,BI_3 is 0·38 obs., 0·36 calc.] requires that both ν_2 and ν_8 be placed close together, in all spectra, at *ca.* 760 cm^{-1}. [The accidental degeneracy is not without precedent since in SiH_3Me both the symmetric and asymmetric SiH_3 deformations are placed at *ca.* 945 cm^{-1} [21] and it is on deuteriation that they become separated]. The alternative assignment [12] does not allow as good a fit of the product rule when all the modes are considered. In PD_3,BI_3 the band at 760 cm^{-1} shows some evidence of splitting in the solution spectra in both effects as does the solution i.r. spectrum of PH_3,BCl_3. The asymmetry alters in the polarization run in the Raman spectrum of PD_3,BI_3 as would be expected for two almost coincident bands [Figure 3(B)]. The Raman spectrum of PH_3,BBr_3 (Figure 1) shows three bands in the PH_3 deformation region. The split band centred at 1059 cm^{-1} provides an excellent example of Fermi resonance ($2\nu_{10}$ = 1060 cm^{-1}).

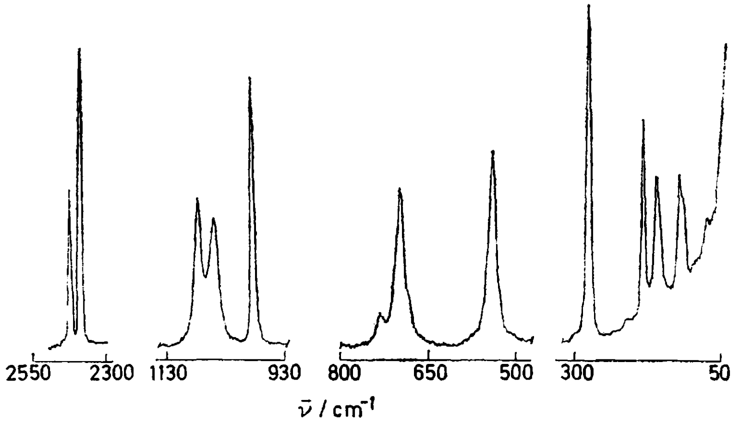

FIGURE 1 Raman spectrum of solid PH_3,BBr_3. The left-hand curve is taken at reduced intensity

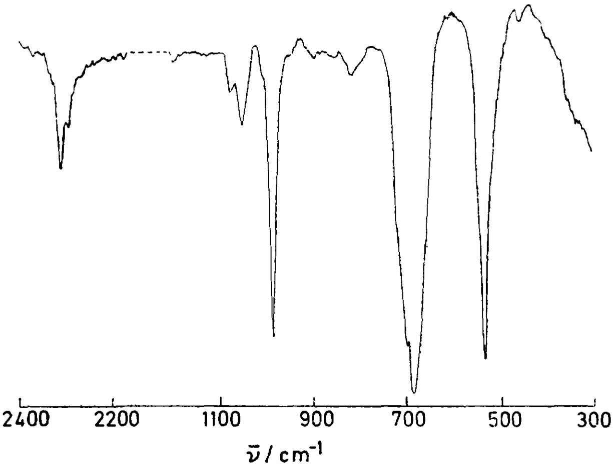

FIGURE 2 I.r. spectrum of PH_3,BBr_3 in iodomethane

The PH_3 rocking mode, ν_{10}, is a distinct band of medium intensity, depolarized in the Raman spectra of the adducts. The feature is very similar to that noted in PH_3,BD_3 [19] and for the SiH_3 rocking mode in the isoelectronic SiH_3Me.[21] The PH_3 rocking modes show a shift to lower frequency with increasing acidity of the acceptor species that parallels a similar trend in the PH_3 stretching modes. The trend to lower frequencies may indicate a progressive drift of charge away from the PH_3 group as the acceptor ability of the Lewis acid increases.

The Boron Trihalide Vibrations.—Deuteriation of phosphine causes only slight changes in the BX_3 fundamental frequencies.

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[18] R. C. Taylor, H. S. Gabelnick, K. Aida, and R. L. Amster, *Inorg. Chem.*, 1969, **8**, 605.

[19] J. Davis and J. E. Drake, *J. Chem. Soc.* (*A*), 1970, 2959.

[20] W. L. Jolly, *J. Amer. Chem. Soc.*, 1963, **85**, 3083.

[21] D. F. Ball, T. Carter, D. C. McKean, and L. A. Woodward, *Spectrochim. Acta*, 1964, **20**, 1721.

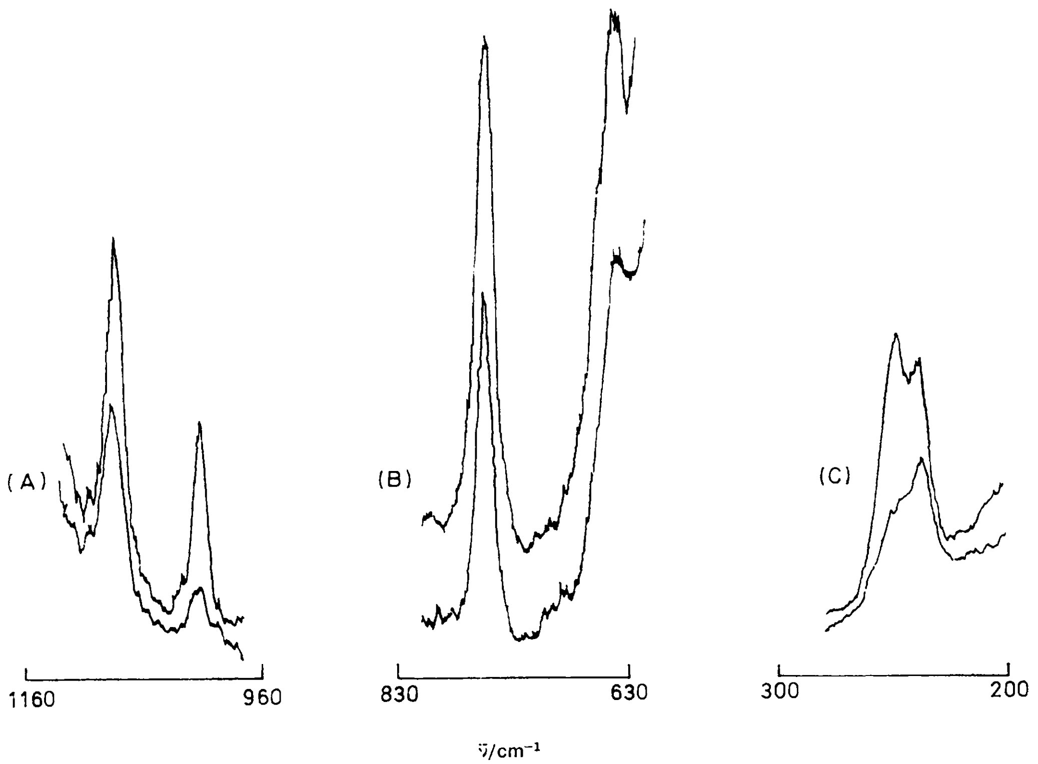

Figure 3 Selected regions of the Raman spectra of PH_3,BCl_3 in CH_2Cl_2 [(A) and (C)] and of PD_3,BI_3 in MeI(B)

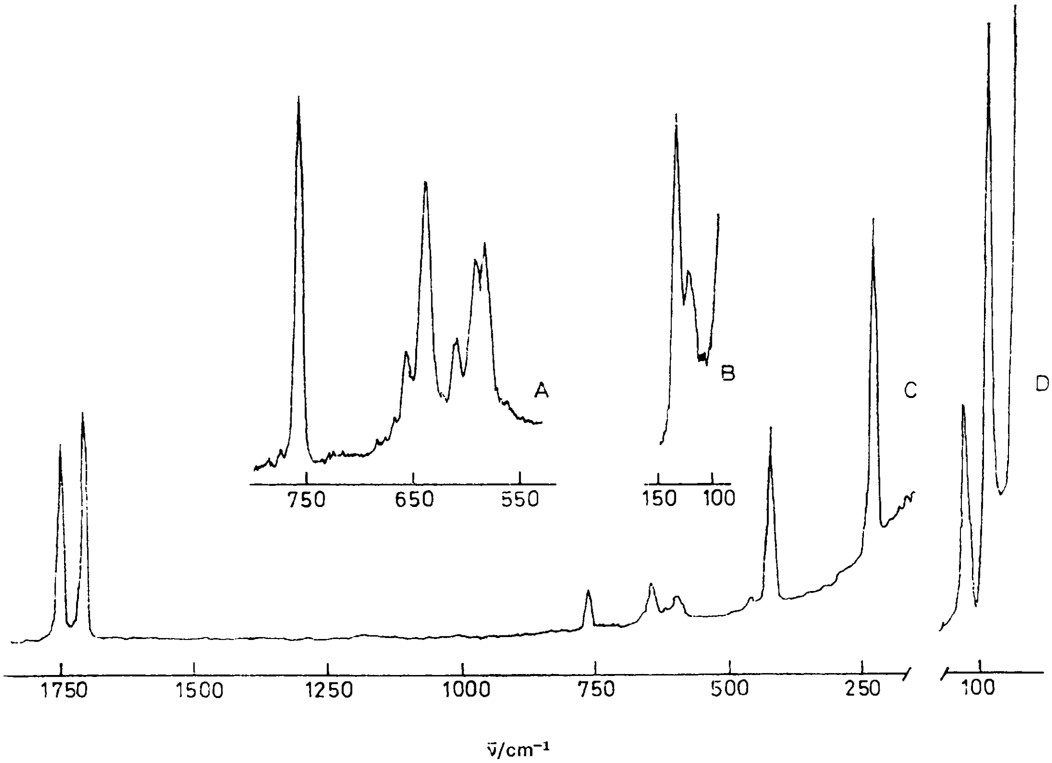

Figure 4 Raman spectrum of solid PD_3,BI_3. In A the intensity has been multiplied by 100, in B the intensity has been doubled, in C the intensity has been multiplied by 10, and in D it has been multiplied by unity

The BX_3 symmetric stretch, ν_4, is a very intense Raman band fully polarized in all six species. Its position is consistently at a slightly lower frequency than the corresponding mode in the free boron trihalide,[22] a feature which has been noted for other BX_3 adducts.[4,5] The asymmetric BX_3 stretch ν_9, is less readily assigned since it occurs in a ' crowded ' region of the spectrum (550—750 cm^{-1}). However, by comparison with other BX_3 adducts,[3,5] very strong absorptions in the i.r. spectra are matched by relatively weak features in the Raman spectra and assigned to ν_9. Further, as the calculations confirm, there is considerable separation between $\nu_9(^{10}B)$ and $\nu_9(^{11}B)$ which aids the assignments. In PD_3,BI_3 (Figure 4) there is some evidence that the degeneracy of this mode is lifted.

The BX_3 deformation bands ν_5 and ν_{11} occur in close proximity to one another in the spectra of all adducts but especially in those of PH_3,BCl_3 and PH_3,BI_3 (Figure 4, of PD_3,BI_3 150—100 cm^{-1}). The Raman spectrum of a solution of the former [Figure 3(C)] clearly shows the polarized nature of the band at higher frequency which is therefore assigned to the symmetric mode, ν_5. (This is again in direct contrast with the recent assignment of PH_3,BCl_3.[12]) Further, a comparison of these bands in the spectrum of solid PH_3,BBr_3 (Figure 1) shows the band at 183 cm^{-1} ν_5 is rather sharp (a_1) and that at 161 cm^{-1}, ν_{11}, somewhat broader (e) providing additional evidence for our assignment.[23] Finally, this order is consistent with observations in other boron trihalide adducts.[2,4,5]

The BX_3 rocking modes, ν_{12}, are seen as the lowest-frequency fundamentals in the solution spectra of all the adducts where they are clearly depolarized bands. In the recent study of PH_3,BCl_3 a band at 154 cm^{-1} was apparently assigned as a lattice vibration and one at 179 cm^{-1} as the fundamental.[12] However, in the solution spectrum we observe a single peak at 148 cm^{-1} and none in the 180 cm^{-1} region. The 148 cm^{-1} band, assigned as ν_{12}, exhibits some splitting in the spectrum of solid PH_3,BCl_3. This partial lifting of degeneracy can be attributed to lattice effects and is also evident, but less so, in the corresponding band of the spectrum of solid PH_3,BBr_3 (Figure 1). The presence of other bands in the region of the spectrum below 85 cm^{-1} are also attributed to lattice effects.

The Phosphorus–Boron Stretching Frequency. The P–B stretch, ν_3, is assigned to a band which is a partially polarized, medium intensity peak in the Raman spectra. As with ν_9, there is evidence of a separation of $\nu_3(^{10}B\text{–}P)$ and $\nu_3(^{11}B\text{–}P)$. This places the P–B stretch at an appreciably higher frequency than in PH_3,BH_3,[8,10] (Tables 2—4) and at a fairly consistent value for all of the phosphine adducts. The rather large shift on deuteriation is not surprising in view of the degree of participation by the PH_3 group indicated by the calculations.

The difficulty of obtaining good polarization data is demonstrated by the spectrum of PD_3,BI_3 in the 630—830 cm^{-1} region [Figure 3(B)] where the P–B stretching mode appears as an apparently polarized shoulder on a solvent peak. Extensive mixing involving the donor–acceptor bond has been observed for the adduct H_3N,BF_3 where the similar masses of the NH_3 moiety and the fluorine atoms produces appreciable mixing of the N–B stretching mode.[2]

Normal Co-ordinate Analysis.—Normal co-ordinate analysis was carried out using a computer programme written by one of us.[24] The normal equations were expressed in mass-weighted Cartesian co-ordinates by a method similar to that recently described by Gwinn.[25] A set of trial force constants were refined by the usual least-squares criterion to produce the best agreement between the observed and calculated frequencies.

TABLE 5

Assumed structures of PH_3,BX_3 (X = Cl, Br, I)

	X = Cl	Br	I
r(P–H)/Å	1·40	1·40	1·40
∠HPB [c]	111·5°	111·2°	110·7°
∠HPH	105·5°	106°	105°
r(P–B)/Å [a]	1·90	1·90	1·90
r(B–X)/Å [b]	1·84	2·02	2·265
∠PBX	109·5	110·1°	110·7°
∠XBX [c]	109·5°	108·3°	108·2°

[a] J. R. Durig, Y. S. Li, L. A. Carriera, and J. D. Odom, *J. Amer. Chem. Soc.*, 1973, **95**, 2491. [b] Ref. 4. [c] See text.

The Cartesian co-ordinates were calculated from the sets of geometric parameters given in Table 5 according to the Euclidean construction devised by Hilderbrandt.[26]

A total of 22 observed frequencies were available (11 for each isotopic species) but since the deuterium substitution affected mainly the PH_3 group this was of little practical value as far as the $-PBX_3$ skeleton was concerned. Moreover, anharmonicity corrections were not obtainable and the assignment of ν_2 in PD_3,BX_3 was uncertain. Thus the force field for the PH_3,BX_3 species was calculated and tested by using the same values of the force constants to calculate frequencies for PD_3,BX_3. The modified valence force field approximation was not expected to give unambiguous results owing to the impossibility of selecting a unique set of force constants; therefore a modified Urey–Bradley[27] force field was adopted. The 11 force constants thus calculated are labelled according to the formulation given by Shimanouchi.[28,29] The modification consisted of neglecting the non-bonded interaction constants involving hydrogen and including two valence force constants as follows: the stretch–bend interaction $F_{\mathrm{HPB/PB}}$ (which was needed to provide good agreement with ν_3 of PD_3,BX_3), and the bend–bend interaction

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[22] T. Wentick and V. H. Tiensu, *J. Chem. Phys.*, 1958, **28**, 826.

[23] G. Herzberg, ref. 16, p. 491.

[24] J. L. Hencher, Ph.D. Thesis, McMaster University, 1965.

[25] W. D. Gwinn, *J. Chem. Phys.*, 1971, **55**, 477.

[26] R. L. Hilderbrandt, *J. Chem. Phys.*, 1969, **51**, 1654.

[27] H. C. Urey and C. A. Bradley, *Phys. Rev.*, 1931, **38**, 1969.

[28] T. Shimanouchi, *J. Chem. Phys.*, 1949, **17**, 245.

[29] T. Shimanouchi, *Pure Appl. Chem.*, 1963, **1**, 131.

$F_{\mathrm{XBX/PBX}}$ (which was needed to ensure that ν was greater than ν_{11}). These were determined by trial and error and constrained. Following the usual procedure,[28,29] the linear non-bonded force constants, F'_{ij} were approximated by $F'_{ij} = -(\frac{1}{10})F_{ij}$, where F_{ij} is the quadratic force constant for the repulsive potential between atoms i and j.

The $-BX_3$ group structures (Table 5) were taken directly from the trimethylamine adducts. The PB bond length was estimated to be 1·90 Å; a value comparable with that in $MePH_2,BH_3$.[30] Although the geometrical parameters initially assumed for the PH_3 group were those from PH_3,BH_3, they were later modified as indicated below. The calculations were not sensitive to the values assumed for the $-PBX_3$ skeleton.

TABLE 6

Calculated frequencies and potential energy distribution [a] of PH_3,BCl_3 and PD_3,BCl_3

		PH_3,BCl_3		PD_3,BCl_3		
		obs.	calc.	obs.	calc.	
A	ν_1	2413	2413	1743	1718	$100K_{\mathrm{PH}}$ [b] $(100K_{\mathrm{PH}})$
	ν_2	988	993	780	778	$51H_{\mathrm{HH}} + 38H_{\mathrm{HB}} + 6F_{\mathrm{PB/HPB}}$ $(22K_{\mathrm{PB}} + 30H_{\mathrm{HH}} + 22H_{\mathrm{BH}} + 12F_{\mathrm{PB/HPB}})$
	ν_3	675 [700] [c]	674 [701]	633 [650]	635 [655]	$41K_{\mathrm{PB}} + 27K_{\mathrm{BX}} + 13F_{\mathrm{XBX/PBX}}$ $(22K_{\mathrm{PB}} + 24K_{\mathrm{BX}} + 24H_{\mathrm{HH}} + 18H_{\mathrm{BH}} - 11F_{\mathrm{PB/HPB}})$
	ν_4	399	399	395	393	$16K_{\mathrm{PB}} + 29K_{\mathrm{BX}} + 37F_{\mathrm{XX}}$ $(15K_{\mathrm{PB}} + 27K_{\mathrm{BX}} + 39F_{\mathrm{XX}})$
	ν_5	254	254	247	246	$16K_{\mathrm{PB}} + 10H_{\mathrm{XX}} + 23F_{\mathrm{XX}} + 36F_{\mathrm{PX}} + 16F_{\mathrm{XBX/PBX}}$ $(18K_{\mathrm{PB}} + 10H_{\mathrm{XX}} + 21F_{\mathrm{XX}} + 37F_{\mathrm{PX}} + 15F_{\mathrm{XBX/PBX}})$
E	ν_7	2447	2447	1787	1765	$100K_{\mathrm{PH}}$ $(100K_{\mathrm{PH}})$
	ν_8	1059	1057	*ca.* 760	760	$93H_{\mathrm{HH}} + 7H_{\mathrm{BH}}$ $(10K_{\mathrm{BX}} + 80H_{\mathrm{HH}} + 9H_{\mathrm{BH}})$
	ν_9	730 [750]	731 [757]	714	709 [731]	$69K_{\mathrm{BX}} + 22H_{\mathrm{BH}}$ $(73K_{\mathrm{BX}} + 16H_{\mathrm{HH}})$
	ν_{10}	556	556	440	425	$23K_{\mathrm{BX}} + 70H_{\mathrm{BH}}$ $(9K_{\mathrm{BX}} + 84H_{\mathrm{BH}})$
	ν_{11}	242	242	238	242	$29H_{\mathrm{XX}} + 70F_{\mathrm{XX}}$ $(29H_{\mathrm{XX}} + 71\mathrm{F}_{\mathrm{XX}})$
	ν_{12}	148	148	144	141	$100F_{\mathrm{PX}}$ $(100F_{\mathrm{PX}})$

[a] Contribution greater than 9%. [b] P.E.D. for PD_3,BCl_3 in parentheses. [c] [ ] give values for ^{10}B.

In the course of the least-squares analysis, it was observed that the standard deviation depended significantly on the value assumed for the HPB angle. Refinement to give a minimum standard deviation gave an average value of *ca.* 111·5°. This makes the angle HPH about 105·5° which is larger than in PH_3,BH_3 and $MePH_2,BH_3$ (99·4 ± 0·4°). As expected, the trend in H_{HH} (0·644 erg rad^{-1} in phosphine,[31] 0·528 erg rad^{-1} in PH_3,BH_3,[10,32] and 0·5 erg rad^{-1} in PH_3,BX_3) follows the increase in angle.

The suggestion of a bond angle at HPH of *ca.* 105·5° is also consistent with conjectures made on the basis of n.m.r. parameters,[17] The J_{PH} coupling constant, presumably strongly dependent on the degree of *s*-character in the P–H bond, has the values of 182 Hz for PH_3,[33] 366 Hz for PH_3,BH_3,[8] 420, 430, and 436 Hz for PH_3,BCl_3, PH_3,BBr_3 and PH_3,BI_3 respectively[17] and 548 Hz for PH_4^+.[34] This trend is of course consistent with an increase in *s*-character as the bond angle ' opens up ' from its *ca.* 93° in PH_3 through to *ca.* 109° in PH_4^+. The relatively large changes in J_{PH} presumably reflect changes in *s*-character related to significant changes in bond angles. The smaller changes in the sequence PH_3,BX_3, X = Cl, Br, and I, may be related less to angle changes than to the increasing electron-withdrawing power of the stronger Lewis acids. Thus BI_3, with the greatest effective electronegativity, presumably uses more *p*-character from the phosphorus orbital[35] and hence leaves more *s*-character in the P–H bond.

The calculated frequencies and potential-energy distributions (in Urey–Bradley space) are presented in Tables 6—8. The ^{10}B substituted frequencies are included in brackets. The excellent fit to the frequencies for the PH_3,BX_3 species, combined with the remarkably good transfer of the force constants to the PD_3,BX_3 analogues indicates that the force-field model is a reasonable one. The potential-energy distribution reveals that there is no pure P–B bond stretching frequency. It is involved in all the symmetric modes except ν_1, and the degree of this involvement differs in PH_3,BX_3 and PD_3,BX_3. The effect of deuteriation is very evident in ν_2 and ν_3. In the hydrides ν_2 is predominantly PH_3 symmetric bending and ν_3 is symmetric

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TABLE 7

Calculated frequencies and potential energy distribution[a] of PH_3,BBr_3 and PD_3,BBr_3

		PH_3,BBr_3		PD_3,BBr_3		
		obs.	calc.	obs.	calc.	
A	ν_1	2390	2394	1726	1705	$100K_{\mathrm{PH}}$[b] ($100K_{\mathrm{PH}}$)
	ν_2	980	985	*ca.* 765	764	$57H_{\mathrm{HH}} + 39H_{\mathrm{BH}}$ ($25K_{\mathrm{PB}} + 34H_{\mathrm{HH}} + 23H_{\mathrm{HB}}$)
	ν_3	685 [695][c]	685 [714]	640	649 [666]	$54K_{\mathrm{PB}} + 19K_{\mathrm{BX}} + 8H_{\mathrm{PX}} + 9F_{\mathrm{XBX/PBX}}$ ($30K_{\mathrm{PB}} + 15K_{\mathrm{BX}} + 24H_{\mathrm{HH}} + 16H_{\mathrm{BH}}$)
	ν_4	281	281	276	273	$20K_{\mathrm{PB}} + 34K_{\mathrm{BX}} + 10F_{\mathrm{XX}} + 33F_{\mathrm{PX}}$ ($20K_{\mathrm{PB}} + 35K_{\mathrm{BX}} + 10F_{\mathrm{XX}} + 30F_{\mathrm{PX}}$)
	ν_5	183	183	182	180	$12K_{\mathrm{BX}} + 13H_{\mathrm{PX}} + 40F_{\mathrm{XX}} + 12F_{\mathrm{PX}} + 15F_{\mathrm{XBX/PBX}}$ ($11K_{\mathrm{BX}} + 13H_{\mathrm{PX}} + 39F_{\mathrm{XX}} + 13F_{\mathrm{PX}} + 16\mathrm{F}_{\mathrm{XBX/PBX}}$)
E	ν_7	2428	2426	1773	1751	$100K_{\mathrm{PH}}$ ($100K_{\mathrm{PH}}$)
	ν_8	1060[d]	1059	760	757	$93H_{\mathrm{HH}} + 7H_{\mathrm{BH}}$ ($90H_{\mathrm{HH}} + 7H_{\mathrm{BH}}$)
	ν_9	700 [722]	702 [726]	665 [678]	676 [705]	$55K_{\mathrm{BX}} + 32H_{\mathrm{BH}}$ ($71K_{\mathrm{BX}} + 11H_{\mathrm{BH}}$)
	ν_{10}	530	527	428	406	$32K_{\mathrm{BX}} + 61H_{\mathrm{BH}}$ ($15K_{\mathrm{BX}} + 80H_{\mathrm{BH}}$)
	ν_{11}	160	160	155	152	$45H_{\mathrm{PX}} + 49F_{\mathrm{PX}}$ ($45H_{\mathrm{PX}} + 49F_{\mathrm{PX}}$)
	ν_{12}	116	115	112	115	$19H_{\mathrm{XX}} + 80F_{\mathrm{XX}}$ ($19H_{\mathrm{XX}} + 79F_{\mathrm{XX}}$)

[a] Contributions greater than 8%. [b] P.E.D. for PD_3,BBr_3 in parentheses. [c] [ ] gives value for ^{10}B. [d] Average of Fermi resonance doublet.

TABLE 8

Calculated frequencies and potential energy distribution[a] of PH_3,BI_3 and PD_3,BI_3

		PH_3,BI_3		PD_3,BI_3		
		obs.	calc.	obs.	calc.	
A	ν_1	2362	2362	1709	1681	$100K_{\mathrm{PH}}$ ($100K_{\mathrm{PH}}$)
	ν_2	980	977	*ca.* 760	750	$51H_{\mathrm{HH}} + 46H_{\mathrm{BH}}$ ($24K_{\mathrm{PB}} + 35H_{\mathrm{HH}} + 32H_{\mathrm{HB}}$)[b]
	ν_3	662 [680][c]	662 [690]	641 [657]	632 [655]	$66K_{\mathrm{PB}} + 14K_{\mathrm{BX}}$ ($43K_{\mathrm{PB}} + 12K_{\mathrm{BX}} + 17H_{\mathrm{HH}} + 15H_{\mathrm{BH}}$)
	ν_4	229	230	222	222	$15K_{\mathrm{PB}} + 34K_{\mathrm{BX}} + 32F_{\mathrm{PX}}$ ($15K_{\mathrm{PB}} + 34K_{\mathrm{BX}} + 31F_{\mathrm{PX}}$)
	ν_5	133	133	133	132	$15K_{\mathrm{BX}} + 9H_{\mathrm{PX}} + 51F_{\mathrm{XX}} + 12F_{\mathrm{XBX/PBX}}$ ($14K_{\mathrm{BX}} + 9H_{\mathrm{PX}} + 50F_{\mathrm{XX}} + 12F_{\mathrm{XBX/PBH}}$)
E	ν_7	2397	2397	1752	1730	$100K_{\mathrm{PH}}$ ($100K_{\mathrm{PH}}$)
	ν_8	1056	1057	762	754	$92H_{\mathrm{HH}} + 8H_{\mathrm{BH}}$ ($92H_{\mathrm{HH}} + 8H_{\mathrm{BH}}$)
	ν_9	*ca.* 780 [700]	679 [689	600 [614]	602 [614]	$19K_{\mathrm{BX}} + 69H_{\mathrm{BH}}$ ($52K_{\mathrm{BX}} + 31H_{\mathrm{BH}}$)
	ν_{10}	492	491	416	409	$65K_{\mathrm{BX}} + 23H_{\mathrm{BH}}$ ($32K_{\mathrm{BX}} + 61H_{\mathrm{BH}}$)
	ν_{11}	127	125	123	118	$41H_{\mathrm{PX}} + 53F_{\mathrm{PX}}$ ($41H_{\mathrm{PX}} + 53F_{\mathrm{PX}}$)
	ν_{12}	89	89	89	89	$24H_{\mathrm{XX}} + 74F_{\mathrm{XX}}$ ($23H_{\mathrm{XX}} + 73F_{\mathrm{XX}}$)

[a] Contributions greater than 8%. [b] P.E.D. for PD_3,BI_3 in parentheses. [c] [ ] gives values for ^{10}B.

TABLE 9

Urey–Bradley force constants for PH_3,BX_3[a]

	X = Cl		X = Br		X = I	
K_{PH}	3·38 (1)[b] 3·47 (2)[c]		3·33 (1) 3·41 (1)		3·246 (3) 3·34 (1)	
K_{PB}	1·23 (8)		1·40 (6)		1·52 (2)	
K_{BX}	1·74 (5)	1·808[d] 3·021[e]	1·61 (7)	1·490[d] 2·397[e]	1·15 (2)	1·025[d] 1·824[e]
H_{HH}	0·492 (6)		0·550 (4)		0·483 (1)	
H_{BH}	0·42 (1)		0·402 (2)		0·471 (3)	
H_{PX}	0·01 (7)		0·42 (8)		0·28 (2)	
H_{XX}	0·3 (1)		0·1 (2)		0·21 (5)	
F_{XX}	0·54 (8)	0·643[d] 0·539	0·31 (9)	0·466[d] 0·422[e]	0·27 (3)	0·336[d] 0·190[e]
F_{PX}	0·32 (8)		0·26 (4)		0·19 (1)	
$F_{\mathrm{PB/HPB}}$	−0·114 (c)		−0·041 (c)		−0·016 (c)	
$F_{\mathrm{XBX/PBX}}$	−0·14 (c)		−0·12 (c)		−0·09 (c)	

[a] Force constants in mdyne $Å^{-1}$. All bending constants weighted by 1 Å. Uncertainties in parentheses. [b] Calculated for the hydride. [c] Calculated for the deuteride. [d] K_{CX} calculated for CX_4, see ref. 31. [e] K_{BX} calculated for BX_3, see ref. 31.

PBX_3 stretching. The corresponding modes in the deuterides are mixtures of these motions. The interaction constant $F_{PB/HPB}$ has a considerably greater effect in the deuterides where it prevents the two modes of the same symmetry from having similar frequencies. The value of $F_{PB/HPB}$ was systematically adjusted so that satisfactory values were obtained for ν_3 and ν_{10} of the deuteriated species. In each case ν_2 was calculated to be in the range 750—775 cm^{-1}. A somewhat higher ν_2 frequency could be obtained by using a larger $F_{PB/HPB}$ but only if poorer agreement with ν_3 and ν_{10} were accepted. Attempts to assign ν_2 in the range 600—700 cm^{-1} failed because it was then impossible to calculate a reasonable value of ν_2 in the hydride.

The force constants of the modified Urey–Bradley force field and their calculated uncertainties are presented in Table 9 along with related constants of the CX_4 and BX_3 molecules.[31] The values of K_{BX} in the PH_3,BX_3 molecules are much smaller than in BX_3 as has been observed in the acetonitrile[5] and trimethylamine[4] adducts and are comparable with the K_{CX} values. Although the F_{XX} values in PH_3,BX_3 are uncertain, they are definitely smaller than in the CX_4 molecules. In view of the known inverse relationship between F_{XX} and $r(X \cdots X)$,[31] $r(B–X)$ must be longer than the corresponding $r(C–X)$ if the structure at boron is tetrahedral. This is known to be the case in the trimethylamine adducts[4] where (B–Cl) = 1·8 Å is larger than (C–Cl) = 1·766 Å found in CCl_4. The bromides and iodides exhibit the same effect. The values of K_{PB} increase in the sequence $PH_3,BCl_3 < PH_3,BBr_3 < PH_3,BI_3$ which is consistent with the generally accepted order of increasing Lewis acidity of $BCl_3 < BBr_3 < BI_3$. The F matrix elements calculated from the Urey–Bradley force field presented in Table 10 also follow this trend. The F matrix element for PB in PH_3,BCl_3, 1·83 mdyne Å^{-1}, agrees reasonably well with the modified valence force field determination, 1·96 mdyne Å^{-1}.[12] Both these values are smaller than those reported for PH_3,BH_3 (2·04 mdyne Å^{-1}).

The value of K_{PH} in all three molecules is greater than in phosphine for which it is 3·11 mdyne Å^{-1}.[31] This is the opposite trend from that observed in the ammonia adduct, NH_3,BF_3 where K_{NH} = 5·85 mdyne Å^{-1},[18] is smaller than 6·467 mdyne Å^{-1} calculated for NH_3.[31] In the latter case it is assumed that the NH bond order decreases as the BN order increases. By contrast, the PH bonds in PH_3,BX_3 appear to be stiffer than in PH_3. The latter effect must be related to the much greater structural reorganization required to form the phosphine adducts (∠HPH = 93·3° in PH_3, 105° in PH_3,BX_3). In ammonia ∠HNH is already *ca.* 107°. In the sequence PH_3,BCl_3, PH_3,BBr_3, PH_3,BI_3 there is no marked change in hybridization of the $-PH_3$ group. The reduction of K_{PH} through this sequence is therefore compatable with the normal effect of increased strength of the co-ordinate bond in ammonia adducts.[36]

TABLE 10

Non-zero elements of the F matrix [a, b]

	Cl	Br	I
PH	3·47 [c]	3·41 [c]	3·34 [c]
∠HPH	0·492	0·500	0·483
∠HPB	0·42	0·407	0·471
PB	1·83	1·92	1·92
BX	2·63	2·16	1·59
∠PBX	0·46	0·81	0·60
∠XBX	1·05	0·61	0·77
Interaction constants			
PB–BX	0·23	0·18	0·13
PB–PBX	0·24	0·22	0·17
BX–BX	0·38	0·21	0·19
BX–PBX	0·26	0·22	0·15
BX–XBX	0·42	0·26	0·27
PB–HPB	−0·114	−0·041	−0·016
PBX–XBX	−0·14	−0·12	−0·09

[a] Force constants in mdyne Å^{-1}. All bending constants weighted by 1 Å. [b] Calculated from the Urey–Bradley constants presented in Table 9. [c] Calculated for the deuteride.

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