Raman Spectra and Isomerism of Some Bromophenylphosphoranes Ph_nPBr_{5-n} ($1 \leqslant n \leqslant 3$) and Their Salts

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A synthetic and Raman investigation of isomerism in the bromophenylphosphoranes has shown no evidence for ionic–covalent isomerism analogous to that in the chlorophenylphosphoranes. Two ionic modifications of $PhPBr_4$ have been identified by Raman spectroscopy, whereas Ph_2PBr_3 was found to exist in only one ionic form, $Ph_2PBr_2^+Br^-$. A recent proposal that Ph_3PBr_2 is a molecular four-co-ordinate species is disputed and evidence supporting an ionic formulation $Ph_3PBr^+Br^-$ is presented. Vibrational Raman assignments for the bromophenylphosphoranes and some of their tetrabromoborate and tetrabromoaluminate salts are given.

Previous studies of bromophenylphosphoranes have mainly involved ^{31}P NMR spectroscopy, both in solid and solution.[1-3] In these and earlier conductometric work[4,5] the structures were all inferred to be of the ionic type, $[Ph_nPBr_{4-n}]^+Br^-$ ($1 \leqslant n \leqslant 3$) similar to that of $[Me_nPBr_{4-n}]^+Br^-$,[6,7] analogous to the crystallographically well established phosphorus pentabromide $PBr_4^+Br^-$.[8-10] X-Ray diffraction data on these compounds are sparse with the exception of two very recent reports in which the structures of Ph_3PBr_2[11] and Ph_3PBr^+-Br_3^-[12] were established. In the former the data were interpreted in terms of a four-co-ordinate donor–acceptor complex, $Ph_3P{\cdot}Br_2$, rather than an ionic species, $Ph_3PBr^+Br^-$.

These systems appear to be in contrast to the chlorophenylphosphoranes, where normally $PhPCl_4$ and Ph_2PCl_3 are molecular, pseudo-trigonal-bipyramidal whereas Ph_3PCl_2 is ionic, $Ph_3PCl^+Cl^-$.[13-16] Recently however, both ionic and pseudotrigonal-bipyramidal isomers for each of these chlorophenylphosphoranes have been isolated and characterised by Raman spectroscopy.[17] This and the current interest[18,19] in the fine energetic balance between the possible forms of the organophosphorus halides (*e.g.* **I**, **II** and **III** for Ph_2PX_3) has prompted us to explore the possibility of isomerism in the analogous bromophenylphosphoranes Ph_nPBr_{5-n}. We report here a synthetic and Raman investigation of these and some salts of the type $[Ph_nPBr_{4-n}]^+[MBr_4]^-$ ($1 \leqslant n \leqslant 3$, M = Al or B).

Experimental

Most materials were moisture and air-sensitive and all manipulations were carried out in a dry-box filled with oxygen-free nitrogen. Triphenylphosphine (Aldrich) was used without prior purification. Dichloromethane and toluene were dried over $CaCl_2$ or activated 4 Å molecular sieves. The compounds $PhPBr_2$ and Ph_2PBr were prepared following the method of Lappert and co-workers[20] by reaction of the appropriate chlorophosphine with BBr_3 and subsequent exposure to vacuum at 90 °C to remove all traces of BCl_3 and any excess of BBr_3.

Preparations of one form of $PhPBr_4$ (type B), Ph_2PBr_3 and Ph_3PBr_2 were effected by direct bromination of the parent phosphine in toluene solution at 0 °C. Attempts to prepare pseudo-trigonal-bipyramidal species were carried out by the passage of bromine vapour over the surface of a gently stirred solution of the appropriate parent phosphine in toluene at 0 °C. This technique sometimes resulted in the isolation of another form of $PhPBr_4$ (type A) and sometimes in mixtures of both types A and B.

Complexes of the bromophenylphosphoranes with either boron or aluminium tribromide were prepared by reaction of stoichiometric amounts of each in dichloromethane. Bromide analyses of the compounds were carried out by alkaline hydrolysis and subsequent potentiometric titration with aqueous $AgNO_3$ using a silver electrode. Values are summarised in Table 1.

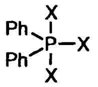
Raman spectra were recorded using a Coderg PHO spectrometer with excitation by the 514.5 nm line of a Coherent Radiation argon laser. All samples were contained in sealed glass capillary tubes.

Results and Discussion

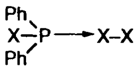
Tetrabromophenylphosphorane.—Addition of bromine to phenylphosphorus dibromide in dichloromethane yields a compound (type B) the Raman spectrum of which is shown in Fig. 1(*b*). Comparison of this with the spectrum of its tetrabromoborate salt [Fig. 1(*c*)] shows good correspondence (apart from the well established tetrabromoborate bands at 117 and 164 cm^{-1})[21] and confirms that the compound is ionic, $PhPBr_3^+Br^-$, in accord with previous conductometric and

$Ph_2PX_2^+ X^-$

I (ionic)



II (pseudo-trigonal bipyramidal)



III (donor-acceptor)

Table 1 Bromide analysis for bromophenylphosphoranes and derivatives

Compound	Analysis (%) Found	Analysis (%) Calculated
$PhPBr_3^+Br^-$		
type A	74.45	74.75
type B	74.60	
$PhPBr_3^+BBr_4^-$	82.60	82.50
$Ph_2PBr_2^+Br^-$	56.15	56.50
$Ph_2PBr_2^+BBr_4^-$	70.55	71.00
$Ph_3PBr^+Br^-$	37.80	37.85
$Ph_3PBr^+BBr_4^-$	58.80	59.40
$Ph_3PBr^+AlBr_4^-$	57.65	58.00

NMR studies.[2–5] Vibrational assignments on the basis of a C_{3v} $PhPBr_3^+$ cation (Table 2) were aided by comparison with $MePBr_3^+Br^-$.[7] Attempts were made to prepare an isomeric pseudo-trigonal-bipyramidal form of $PhPBr_4$ by using a variation of the technique employed successfully for the analogous chlorophenylphosphoranes, namely slow passage of bromine vapour over a gently stirred solution of $PhPBr_2$ in toluene. This usually resulted in an identical form (as monitored by the Raman spectrum) to that isolated by direct bromination as described above. On several occasions, however, a compound with identical bromine analysis but different Raman spectrum was obtained [Fig. 1(*a*)]. The pattern of the bands was not consistent with a pseudo-trigonal-bipyramidal form but rather with a slightly different ionic form, presumably present as a different crystal modification (type A). In some preparations a mixture of both types (A and B) was found. Similar isomers of ionic modifications have been noted previously in related systems such as $MePCl_4$ and Me_2PCl_3.[7,24] Reactions of both forms with BBr_3 produced compounds having identical Raman spectra.

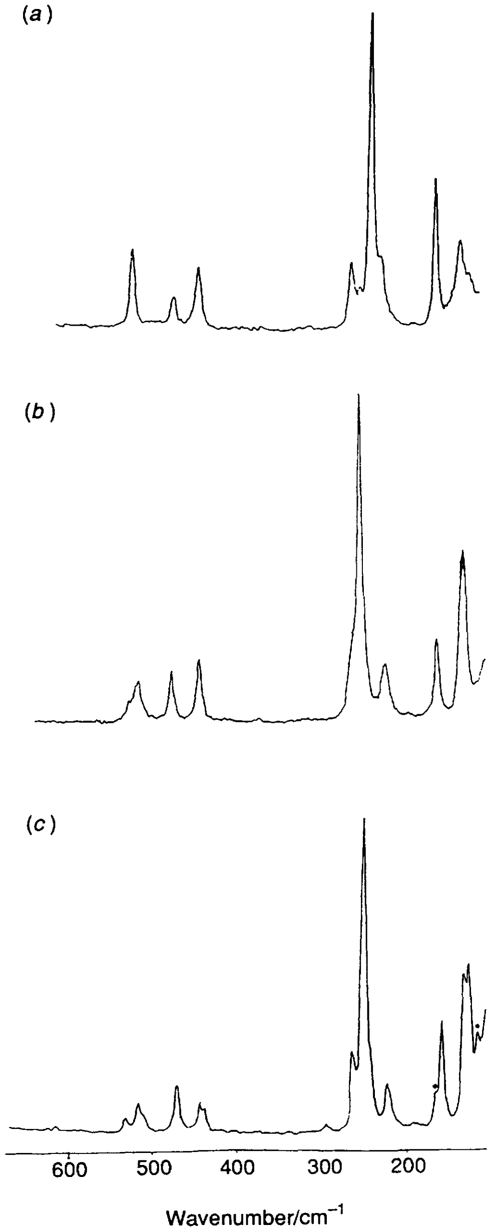


Fig. 1 Raman spectra of $PhPBr_3^+Br^-$ types A (*a*) and B (*b*) and $PhPBr_3^+BBr_4^-$ (*c*) (•, anion bands)

Tribromodiphenylphosphorane.—Bromination of diphenylphosphorus bromide in toluene yielded a pale yellow solid with a bromine analysis corresponding to Ph_2PBr_3, the Raman spectrum of which is shown in Fig. 2(*a*). The spectrum of its tetrabromoborate salt [Fig. 2(*b*)] clearly shows the bands (240, 163 and 125 cm^{-1})[21] characteristic of BBr_4^-. Apart from these the close correspondence of the spectra strongly suggests that tribromodiphenylphosphorane has an ionic formulation, $Ph_2PBr_2^+Br^-$, in agreement with the earlier ^{31}P NMR studies.[2] Assignments on the basis of a C_{2v} $C_2PBr_2^+$ skeleton are shown in Table 3. Numerous attempts to prepare a pseudo-trigonal-bipyramidal form by passage of bromine vapour over the surface of the diphenylphosphorus bromide in toluene all resulted in products with an identical Raman spectrum to that above.

Dibromotriphenylphosphorane.—Reaction of equivalent quantities of triphenylphosphine and bromine in either toluene

Table 2 Raman wavenumbers (cm^{-1}) for $PhPBr_3^+Br^-$ (types A and B) and $PhPBr_3^+BBr_4^-$

$PhPBr_3^+Br^-$			
type A	type B	$PhPBr_3^+BBr_4^-$	Assignment for cation
513(24)	510(12)	513(7)	y(b_2) X-sensitive[a]
465(9)	470(14)	470(13)	ν_4(e) asym. P–Br str.
438(19)	438(17)	437(8) 440(10)	t(a_1) Ph–P str. X-sensitive[a]
238(100)	250(100)	250(100)	ν_2(a_1) sym. P–Br str.
224(22)	222(16)	222(12)	ν_5(e) CPBr def.
160(40)	160(23)	158(29)	ν_3(a_1) sym. PBr_3 def.
132(18)	127(42)	126(27) 132(32)	ν_6(e) PBr_2 def.
		245–240[b] 164(11) 117(7)	Anion

Relative intensities are given in parentheses. [a] Refs. 22 and 23. [b] This vibration is obscured by $\nu_2(a_1)$ of the symmetric P–Br stretch.

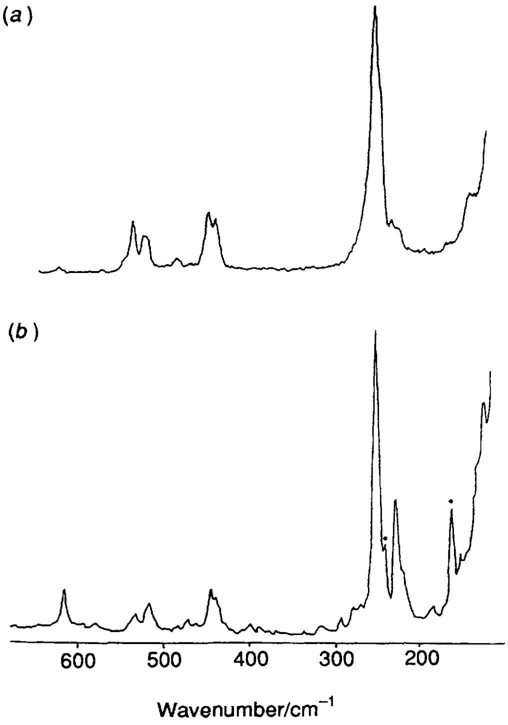


Fig. 2 Raman spectra of $Ph_2PBr_2^+Br^-$ (*a*) and $Ph_2PBr_2^+BBr_4^-$ (*b*) (•, anion bands)

or dichloroethane produced identical solids the bromide analysis of which corresponded to Ph_3PBr_2. Raman spectra of this compound and its tetrabromoborate salt are shown in Fig. 3. Vibrational assignments, including $Ph_3PBr^+AlBr_4^-$, are presented in Table 4. The presence of each anion is confirmed by characteristic bands (for BBr_4^- at 166 and 116 cm^{-1}, and at 398, 211 and 114 cm^{-1} for $AlBr_4^-$).[21] Apart from the anion bands there is a good correspondence between the spectra of the salts and that for Ph_3PBr_2 which strongly suggests that the latter should be considered as an ionic species, $Ph_3PBr^+Br^-$, in agreement with earlier ^{31}P NMR and conductometric studies.[1,2,4,5] For these species there is a small low-frequency shift in the P–Br stretching vibration on passing from the salts with polyatomic anions to one containing a single halide ion (*i.e.* from 251 and 245 cm^{-1} in the $AlBr_4^-$ and BBr_4^- salts respectively to 239 cm^{-1} in Ph_3PBr_2). In a number of other systems[26,27] this is associated with a significant interaction between the single halide anion and the halogen atoms of the halogenophosphonium cation leading to a slight lengthening of the phosphorus–halogen bonds and consequent reduction in force constant and frequency.

The ionic nature of Ph_3PBr_2 has been challenged recently on the basis of the structure and bond lengths determined by X-ray diffraction.[11] It was proposed that the compound has a four-co-ordinate molecular structure of type **III**, which would be quite novel for such a phosphorus system. The difference between an ionic (type **I**) and a molecular donor–acceptor complex of type **III** lies only in the relative P–Br and Br–Br distances. In our view it is quite unnecessary to invoke the novel four-co-ordinate molecular formulation to explain the structure and we consider that it is best regarded as ionic for the following reasons.

(*i*) The good correspondence between the Raman spectra of Ph_3PBr_2 and the salts $Ph_3PBr^+MBr_4^-$ (M = Al or B) as discussed above.

(*ii*) McAuliffe and co-workers[11] report that the compound exhibits an intense Raman band at 239 cm^{-1}, assignable to ν(P–Br) but that unambiguous identification of ν(Br–Br) was not possible. Our spectrum [Fig. 3(*a*)] shows that the strongest band clearly arises mainly from the ν(P–Br) vibration. However, in our experience the perturbed ν(Br–Br) scatter which would arise from a relatively weakly bonded donor–Br_2 species is very intense and usually lies in the region of 250–300 cm^{-1}, *e.g.* in $Me_2S{\cdot}Br_2$.[28] No such band occurs in the Raman spectrum of Ph_3PBr_2.

(*iii*) Most importantly, the bond lengths reported by McAuliffe and co-workers[11] are very close to what would be predicted for an ionic form in which there is significant cation–anion interaction of the type $\geqslant P^+Br \cdots Br^-$, as discussed above. Such interactions are common and we have observed their presence in a number of halogenophosphonium compounds.[7,26,27] This type of interaction is certainly present in PBr_5 which was first established as an ionic species, $PBr_4^+Br^-$, over fifty years ago.[8] It is seen in Table 5 that there is a quite striking similarity between P–Br and $Br \cdots Br^-$ distances in $PBr_4^+Br^-$, in $PBr_4^+Br_3^-$[29] and in those determined by McAuliffe and co-workers for the Ph_3PBr_2 structure.

The almost identical P–Br distances in $PBr_4^+Br^-$, $PBr_4^+Br_3^-$, $Ph_3PBr^+Br_3^-$ and Ph_3PBr_2 strongly support an ionic formulation, $Ph_3PBr^+Br^-$, for the latter. The Br–Br distance of 3.12 Å

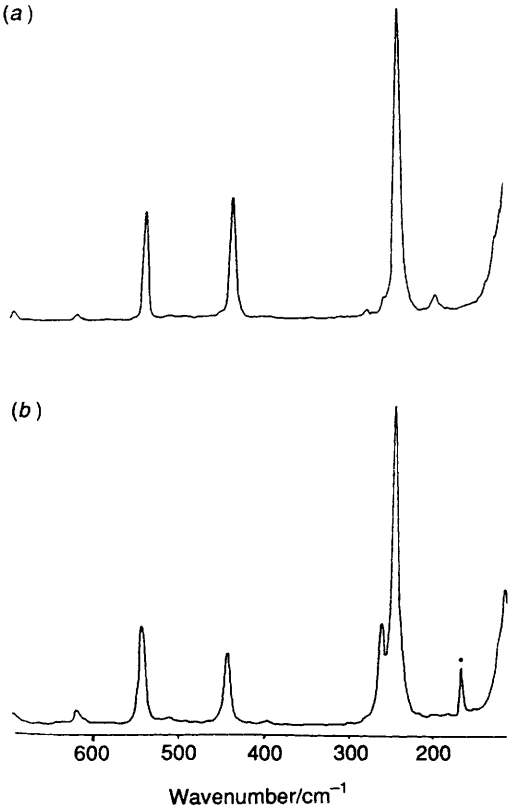


Fig. 3 Raman spectra of $Ph_3PBr^+Br^-$ (*a*) and $Ph_3PBr^+BBr_4^-$ (*b*) (•, anion bands)

Table 3 Raman wavenumbers (cm^{-1}) for $Ph_2PBr_2{}^+Br^-$ and $Ph_2PBr_2{}^+BBr_4^-$

$Ph_2PBr_2{}^+Br^-$	$Ph_2PBr_2{}^+BBr_4^-$	Assignment for cation
530(12)	530(5)	y(b_2) X-sensitive[a]
513(8)	513(7)	
443(16)	443(11)	ν_8(b_2) asym. P–Br str.
438(18)	438(8)	t(a_1) Ph–P str. X-sensitive[a]
250(71)	250(80)	ν_2(a_1) sym. P–Br str.
230(11)	230(31)	ν_3(a_1) sym. PC_2 def.
220(8)	220(14)	ν_9(b_2) PBr_2 def.
140(7)	—[b]	ν_4(a_1) sym. PBr_2 def.
	245–240[c]	Anion
	163(21)	
	125(8)	

[a] Refs. 22 and 23. [b] Not observed. [c] This vibration is almost entirely overlapped by the ν_2(a_1) symmetric P–Br stretch.

Table 4 Raman wavenumbers (cm^{-1}) for triphenylbromophosphonium compounds

$Ph_3PBr^+Br^-$	$Ph_3PBr^+BBr_4^-$	$Ph_3PBr^+AlBr_4^-$[a]	Assignment for cation
537(31)	540(26)	541w	y(b_2) X-sensitive[b]
436(35)	441(20)	442w	t(a_1) Ph–P str. X-sensitive[b]
260(32)	260(5)	275m	ν_3(a_1) sym. PC_3 def.
239(96)	245(92)	251ms	ν_2(a_1) sym. P–Br str.
	245–240[c]	398w	Anion
	166(14)	211m	
	116(8)	114w	

[a] Some decomposition in the laser beam; hence relative intensities are not listed. [b] Refs. 22 and 25. [c] This vibration is obscured by the ν_2(a_1) symmetric P–Br stretch.

Table 5 Comparison of P–Br and Br–Br bond lengths (Å) in bromophosphoranes

	$PBr_4^+Br^-$ [8–10]	$PBr_4^+Br_3^-$ [29]	$Ph_3PBr^+Br_3^-$ [12]	Ph_3PBr_2 [11]
$\geqslant$P–Br	2.13–2.17	2.16–2.18	2.13–2.14	2.18 (P–Br)
$\geqslant P^+Br\cdots Br^-$	3.06–3.19	3.10–3.40	3.49–3.54	3.12 (Br–Br)

in Ph_3PBr_2 is the same as the average value for this distance in $PBr_4^+Br^-$, again supporting an ionic formulation. The somewhat longer $\geqslant P^+Br\cdots Br^-Br_2$ distances of 3.10–3.40 Å in $PBr_4^+Br_3^-$ and 3.49–3.54 Å in $Ph_3PBr^+Br_3^-$ are probably a reflection of weaker interactions as the Br^- is also attached to Br_2 in the almost linear unsymmetrical Br_3^- ion.

Conclusion

No evidence was found for pseudo-trigonal-bipyramidal isomers of the three bromophenylphosphoranes, although $PhPBr_4$ exists in two ionic modifications at room temperature. In our opinion, the evidence for the ionic formulation of $Ph_3PBr^+Br^-$ is overwhelming, in contrast to the interpretation as a four-co-ordinate 'spoke' structure by McAuliffe and co-workers.[11]

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