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The structure of R$_3$PBr$_2$ compounds in the solid state and in solution; geometrical dependence on R, the crystal structures of tetrahedral ionic Et$_3$PBr$_2$ and molecular trigonal bipyramidal (C$_6$F$_5$)$_3$PBr$_2$

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Twenty-one triorganophosphorus dibromide compounds, R$_3$PBr$_2$ (R$_3$ = substituted aryl, mixed aryl–alkyl, triaryl or trialkyl) have been synthesized from diethyl ether solution and characterised by analytical and ^{31}P-{H} NMR data in CDCl$_3$ solution, the vast majority being reported for the first time. All but one of the compounds are ionic, [R$_3$PBr]Br in CDCl$_3$ solution, in keeping with analogous species containing iodine or chlorine, [R$_3$PX]X (X = I or Cl) according to ^{31}P-{H} NMR studies. In contrast, (C$_6$F$_5$)$_3$PBr$_2$ has a molecular five-co-ordinate trigonal bipyramidal structure both in CDCl$_3$ solution and in the solid state. The single crystal structure of this compound has been determined and it represents the only reported R$_3$PBr$_2$ species which contains a five-co-ordinate phosphorus atom. It has D_3 symmetry and perfect trigonal bipyramidal geometry. Why (C$_6$F$_5$)$_3$PBr$_2$ is the only R$_3$PBr$_2$ compound which adopts trigonal bipyramidal geometry is reasoned to be due to the very low basicity of the parent tertiary phosphine, which favours this geometry for the dihalogen adducts, a phenomenon previously observed for dichlorine adducts of tertiary phosphines and dihalogen adducts of tertiary arsines. The crystal structure of the first non-solvated trialkylphosphine dibromide compound, Et$_3$PBr$_2$, has also been determined and contains a tertrahedral phosphorus atom, exhibiting a long Br · · · Br contact, 3.303(2) Å, and is probably better described as ionic, [Et$_3$PBr]Br, with significant cation–anion interaction.

Introduction

Although compounds of formula R$_3$PX$_2$ (X = Cl, Br or I) have been recognised for over a century,[1] it is only recently that their precise structural nature has been elucidated. The interesting variety, and in some cases unexpected structures of such compounds in the solid state, has sparked considerable renewed interest in this area.[2–7] Perhaps surprisingly, no comprehensive study of compounds of formula R$_3$PBr$_2$ has ever been reported despite the fact that Ph$_3$PBr$_2$ is available commercially and has found significant use in synthetic organic chemistry, being widely used in many bromination reactions.[8]

Recent studies by us[2] and other workers[9] have established the diiodide compounds, R$_3$PI$_2$, as charge-transfer species, (R$_3$ = Ph$_3$, ^{2}PhMe$_2$[2] or Bu$^t_3$[9]). However, a sample of Ph$_3$PI$_2$ prepared from nitrobenzene, a more polar solvent, was claimed[10] to be ionic, [Ph$_3$PI]I, from solid state ^{31}P-{H} NMR spectroscopy, thus illustrating the structural dependence of R$_3$PI$_2$ compounds on the nature of the solvent in which they are prepared. The analogous dibromine compounds, R$_3$PBr$_2$, have received very little attention, especially in the solid state. Solution ^{31}P-{H} NMR studies regarding such compounds are limited to Ph$_3$PBr$_2$,[10] Bu$^n_3$PBr$_2$, Pr$^i_3$PBr$_2$,[11] as well as the nitrogen containing compounds (Et$_2$N)$_3$PBr$_2$, (Me$_2$N)$_3$PBr$_2$ and Me(Me$_2$N)$_2$PBr$_2$.[12] All the compounds were assigned an ionic structure [R$_3$PBr]Br, in acetonitrile solution. Such reports are in agreement with conductimetric studies by Harris and co-workers[13] who also assigned R$_3$PBr$_2$ compounds an ionic structure, [R$_3$PBr]Br, again in acetonitrile solution. Solid state investigations of R$_3$PBr$_2$ compounds are limited to an infrared study of Me$_3$PBr$_2$[14] and a solid state ^{31}P-{H} NMR study of Ph$_3$PBr$_2$ prepared from nitrobenzene.[10] Both compounds were assigned an ionic structure, [R$_3$PBr]Br (R = Me or Ph) in agreement with solution studies. More recently, a sample of Ph$_3$PBr$_2$ prepared from diethyl ether solution was examined crystallographically[3] and shown to adopt the four-co-ordinate charge-transfer structure Ph$_3$PBr–Br, previously established for the diiodo compound, Ph$_3$PI$_2$. However, this has been challenged by Gates and co-workers[15] who spectroscopically investigated Ph$_3$PBr$_2$, prepared from both dichloromethane and toluene solution; these workers compared the Raman spectrum of this material with those of the salts [Ph$_3$PBr][BBr$_4$] and [Ph$_3$PBr][AlBr$_4$]. The similarity between the Raman spectra led the authors to conclude that Ph$_3$PBr$_2$ is better described as ionic, [Ph$_3$PBr]Br, in the solid state despite the fact that the Br–Br distance, 3.12(1) Å, lies well within bonding distance if the van der Waals radius for two bromine atoms, 3.9 Å, is considered. Clearly triorgano-phosphorus and -arsenic dihalide compounds could conceivably be regarded as either molecular charge-transfer 'spoke' structures R$_3$EX–X (E = P or As; X = Br or I) which exhibit a weak donor–acceptor X–X bond or as ionic species, [R$_3$EX]X (E = P or As; X = Br or I), which exhibit significant cation–anion interactions; which of these structures is correct is probably dependent on the R, E and X variables for any given R$_3$EX$_2$ compound. It has been established by Raman spectroscopy that Ph$_3$AsI$_2$ does exist as a donor–acceptor charge-transfer compound, Ph$_3$AsI–I, similarly Ph$_3$PI$_2$ has been shown to be a donor-acceptor compound of [Ph$_3$PI]$^+$ and I$^-$. The perceived ambiguity regarding the solid-state structure of R$_3$EX$_2$ compounds indicates that a theoretical study of these compounds would certainly be worthwhile. No trigonal bipyramidal compound of formula R$_3$PBr$_2$ has been crystallographically characterised and the ionic structure of R$_3$PBr$_2$ compounds, [R$_3$PBr]Br, which has been suggested from several NMR, infrared and conductimetric studies, had never been confirmed crystallographically. However, very recently du Mont and co-workers[7] reported the crystal structure of the solvated compound $Pr^i{}_3PBr_2{\cdot}0.5CH_2Cl_2$. This molecule exhibits a long Br · · · Br contact [3.369(2) Å] and is essentially ionic; the bromide ions of two such ion pairs are 'bridged' by a CH_2Cl_2 molecule.

We are currently engaged on a comprehensive study of R_3EX_2 compounds ($E = P$ or As;[16] $X_2 = Cl_2$,[5] Br_2,[3] I_2[2] or IBr[4]). Our studies regarding the related chloro-compounds, R_3PCl_2,[5] have shown that the structure of such compounds is dependent on the nature of R and, in some cases, the nature of the solvent used for their preparation. In most cases the compounds are ionic both in the solid state and in solution, this being illustrated crystallographically for $Pr^n{}_3PCl_2$. In contrast, the compounds R_3PCl_2 [$R_3 = (C_6F_5)_3$ or $Ph_2(C_6F_5)$] are five-co-ordinate molecular trigonal bipyramidal species. Interestingly, Ph_3PCl_2 appears to represent a borderline case and is solvent dependent, Ph_3PCl_2 prepared from diethyl ether again being molecular trigonal bipyramidal whereas the same material prepared in the same way but using CH_2Cl_2 as a solvent produces the ionic solvated dinuclear species $[Ph_3PCl \cdots Cl \cdots ClPPh_3]Cl{\cdot}2CH_2Cl_2$.

The aims of the present study are therefore as follows: first to report a comprehensive study of R_3PBr_2 compounds which contain a wide variety of different R groups on the phosphorus atoms, secondly to characterise crystallographically the first five-co-ordinate trigonal bipyramidal R_3PBr_2 compound and thirdly to characterise crystallographically the first ionic solvent-free $[R_3PBr]Br$ compound to compare with du Mont's $Pr^i{}_3PBr_2{\cdot}0.5CH_2Cl_2$.[7] Considering the familiarity of R_3PBr_2 compounds to both inorganic and organic chemists alike, establishing their structures is of fundamental importance and is of considerable current interest.

Results and discussion

All of the triorganophosphorus dibromides synthesized for this study were prepared by the reaction of equimolar quantities of tertiary phosphine and dibromine in diethyl ether, eqn. (1)

$$R_3P + Br_2 \xrightarrow[\text{r.t.}]{\text{Et}_2\text{O, N}_2} R_3PBr_2 \qquad (1)$$

(r.t. = room temperature). Reaction times were dependent on the tertiary phosphine; triaryl tertiary phosphines took *ca.* 3 d to reach complete reaction with dibromine whereas the corresponding trialkyl tertiary phosphines reacted with dibromine in a matter of hours. In all cases a white flocculent solid was produced which was isolated by standard Schlenk techniques.

All the products described are very moisture sensitive, especially those containing parent trialkyl tertiary phosphines, which smoke profusely when exposed to the atmosphere, therefore strictly anhydrous conditions must be adhered to during their synthesis and subsequent manipulation. Elemental analyses of the compounds, together with their ^{31}P-{H} NMR chemical shifts recorded in $CDCl_3$ solution, are presented in Table 1.

With one notable exception, $(C_6F_5)_3PBr_2$, all of the R_3PBr_2 compounds exhibit high positive ^{31}P-{H} NMR resonances. Such resonances are indicative of an ionic structure in $CDCl_3$ solution, irrespective of their solid state structure. Furthermore, the values recorded herein are in good agreement with the limited studies regarding such compounds performed by previous workers.[10–12] Of the compounds described here only Ph_3PBr_2,[10] $Bu^n{}_3PBr_2$,[11] and $(Me_2N)_3PBr_2$ [12] have previously been the subject of a solution ^{31}P-{H} NMR spectroscopic study; the present values for these compounds δ 49.2, 102.5 and 48.2, are in good agreement with the previously reported values of δ 48.3, 105.0 and 47.0 respectively. Previous workers[10–12] also assigned an ionic structure, $[R_3PBr]Br$, in solution to these compounds.

Table 1 Analytical and spectroscopic data for the compounds R_3PBr_2

	Analysis (%)[a]			
Compound	C	H	Br	^{31}P-{H}, δ[b]
$(C_6F_5)_3PBr_2$	31.0 (31.2)	0.0 (0.0)	23.2 (23.1)	−59.1
$(p\text{-}FC_6H_4)_3PBr_2$	45.4 (45.4)	2.8 (2.5)	33.2 (33.6)	47.0
$(p\text{-}FC_6H_4)Ph_2PBr_2$	47.3 (47.2)	3.1 (2.8)	34.9 (34.9)	44.3
$(p\text{-}ClC_6H_4)_3PBr_2$	40.8 (41.1)	2.4 (2.3)	30.3 (30.4)	48.1
$(m\text{-}MeC_6H_4)_3PBr_2$	55.4 (54.3)	4.9 (4.5)	33.3 (34.5)	45.9
$(o\text{-}MeC_6H_4)Ph_2PBr_2$	51.6 (52.3)	3.9 (4.2)	33.4 (33.9)	54.4
$(p\text{-}MeC_6H_4)Ph_2PBr_2$	48.7 (48.4)	3.9 (4.2)	33.4 (33.9)	52.3
Ph_3PBr_2	51.5 (51.2)	3.8 (3.6)	37.7 (37.9)	49.2
$Ph_2(C_5H_4N)PBr_2$	49.4 (49.1)	7.7 (7.5)	36.1 (36.4)	64.4
$Ph_2(C_6H_{11})PBr_2$	51.5 (50.5)	5.1 (4.9)	36.0 (37.4)	72.2
$Ph_2Pr^nPBr_2$	46.1 (46.4)	4.2 (4.4)	39.9 (41.2)	55.0
Ph_2MePBr_2	43.3 (43.3)	3.5 (3.6)	44.5 (44.4)	63.0
$PhMe_2PBr_2$	31.9 (32.2)	3.8 (3.7)	53.7 (53.7)	67.7
$PhBu^n{}_2PBr_2$	43.8 (43.8)	6.3 (6.5)	41.8 (41.7)	83.7
$PhPr^n{}_2PBr_2$	40.3 (40.7)	5.4 (5.4)	45.2 (45.1)	81.2
$Bu^n{}_3PBr_2$	39.5 (39.8)	7.2 (7.5)	43.8 (44.2)	102.5
$Pr^n{}_3PBr_2$	33.6 (33.7)	6.9 (6.6)	49.6 (50.0)	101.6
Et_3PBr_2	26.1 (25.9)	5.6 (5.4)	57.1 (57.5)	100.0
$(PhCH_2)_3PBr_2$	54.3 (54.3)	4.6 (4.5)	34.1 (34.5)	89.8
$(C_6H_{11})_3PBr_2$	48.5 (49.1)	8.3 (7.5)	35.8 (36.4)	105.5
$(Me_2N)_3PBr_2$	22.0 (22.3)	5.9 (5.6)	49.0 (49.5)	48.2

[a] Calculated values in parentheses. [b] Shifts recorded in $CDCl_3$ relative to concentrated phosphoric acid standard.

The chemical shifts recorded in Table 1 are also similar to those previously observed for analogous R_3PI_2[1] and R_3PCl_2[5] compounds which have also been shown to adopt the ionic $[R_3PX]X$ (X = Cl or I) structure in $CDCl_3$ solution.

We have previously observed[2,5] that the $CDCl_3$ solution ^{31}P-{H} NMR shifts for $[R_3PCl]Cl$ are more positive than those of $[R_3PI]I$. In keeping with this phenomenon, the values recorded here for $[R_3PBr]Br$ are intermediate between those recorded for $[R_3PCl]Cl$ and $[R_3PI]I$, for a given parent tertiary phosphine. The ^{31}P-{H} NMR resonance for $(C_6F_5)_3PBr_2$, δ −59.1, is clearly anomalous and is particularly interesting since it arises from the R_3PBr_2 compound which contains the more acidic (or least basic) parent tertiary phosphine. In addition, this value is similar to the chemical shift in the ^{31}P-{H} NMR of $(CF_3)_3PBr_2$, δ −64.5, recorded by Cavell *et al.*,[17] who assigned a trigonal bipyramidal structure to this R_3PBr_2 compound. However, no five-co-ordinate R_3PBr_2 species has been crystallographically characterised. Consequently we decided to investigate the structure of $(C_6F_5)_3PBr_2$ by single crystal X-ray diffraction.

Recrystallisation of $(C_6F_5)_3PBr_2$ from dichloromethane solution at room temperature produced a large quantity of huge colourless crystals on standing for *ca.* 7 d. Of these, one was selected for analysis by X-ray diffraction. In contrast to all previous reports regarding compounds of formula R_3PBr_2, which relate to phosphorus in tetrahedral geometry, $(C_6F_5)_3PBr_2$ is trigonal bipyramidal, with a five-co-ordinate phosphorus atom, Fig. 1. In addition to being the first reported trigonal bipyramidal R_3PBr_2 compound, $(C_6F_5)_3PBr_2$ is also only the second non-solvated R_3PBr_2 compound to be studied crystallographically. The reason why $(C_6F_5)_3PBr_2$ adopts this geometry in contrast to all the other reported R_3PBr_2 compounds reported herein must be due to the very low basicity of the parent tertiary phosphine. It exhibits crystallographically imposed (space group $R\bar{3}c$) trigonal bipyramidal geometry (D_3 symmetry) with d(P–Br) of 2.4105(9) Å, significantly longer than that exhibited by Ph_3PBr_2, 2.181(2) Å[3], as expected with the higher co-ordination number at the phosphorus atom.

In addition to crystallographically characterising the first trigonal bipyramidal R_3PBr_2 compound, we were also interested in crystallographically characterising an R_3PBr_2 compound which adopts an ionic structure but doesn't contain a dichloro-

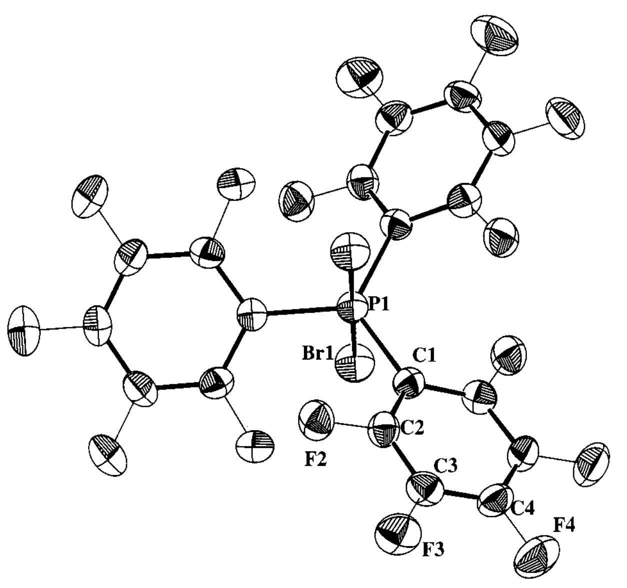

Fig. 1 Molecular structure of $(C_6F_5)_3PBr_2$ (the molecule has crystallographically imposed D_3 symmetry). Selected bond lengths (Å) and angles (°): Br(1)–P(1) 2.4105(9), P(1)–C(1) 1.819(7); C(1)–P(1)–C(1) 120, C(1)–P(1)–Br(1) 90, Br(1)–P(1)–Br(1) 180, C(2)–C(1)–P(1) 121.6(3).

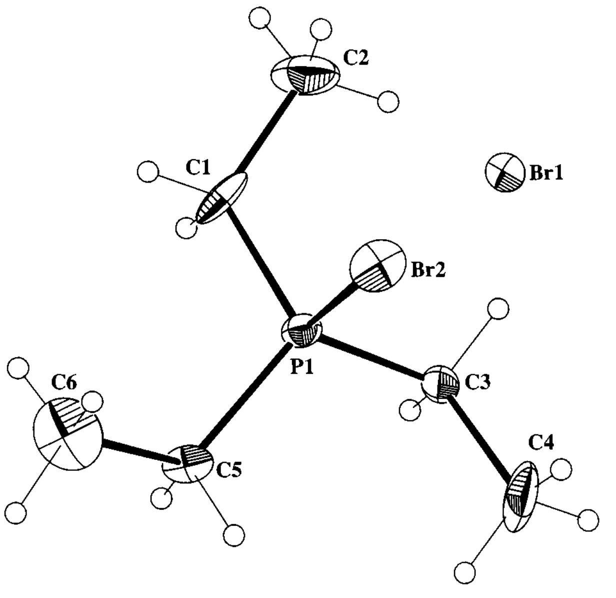

Fig. 2 Molecular structure of $[Et_3PBr]Br$ (only one of each of the disordered methylene groups is illustrated for clarity). Selected bond lengths (Å) and angles (°): Br(2)–Br(1) 3.303(2), Br(2)–P(1) 2.173(3); Br(1)–Br(2)–P(1) 177.5(1).

methane solvent molecule since, as observed in $[Ph_3PCl\cdots Cl\cdots ClPPh_3]Cl\cdot 2CH_2Cl_2$ and $Pr^i_3PBr_2\cdot 0.5CH_2Cl_2$, the long-range electrostatic interactions between the solvent and the ionic molecule influence the product formed. Consequently, we recrystallised a sample of Et_3PBr_2 previously prepared in Et_2O from Et_2O (and not CH_2Cl_2 to avoid its possible inclusion in the structure) at room temperature. On standing for *ca.* 6 d a number of colourless crystals formed which were removed from the reaction vessel in an inert atmosphere and plunged into an inert oil. From these, a suitable crystal was chosen for examination by single crystal X-ray diffraction. The crystal structure of Et_3PBr_2 is illustrated in Fig. 2. The structure represents the first crystallographically characterised non-solvated trialkylphosphine dibromide compound and contains the phosphorus atom in tetrahedral geometry, as expected. A long contact [3.303(2) Å] exists between the two bromine atoms and the structure is probably best described as ionic, $[Et_3PBr]Br$ with cation–anion interaction. This interaction is similar to that exhibited by $Pr^i_3PBr_2\cdot 0.5CH_2Cl_2$, 3.369(2) Å, reported by du Mont and co-workers.[7]

Conclusion

The results reported here clearly show that all of the R_3PBr_2 compounds except one ionise in $CDCl_3$ solution to produce $[R_3PBr]Br$, from ^{31}P-{H} NMR studies. However when a very weakly basic parent tertiary phosphine is employed, $(C_6F_5)_3P$, a trigonal bipyramidal R_3PBr_2 compound is revealed in the solid state which also persists in $CDCl_3$ solution. The geometrical dependence of R_3PBr_2 compounds on R is therefore clearly illustrated. This phenomenon has previously been observed for R_3AsBr_2 [15] and R_3PCl_2 [5] compounds.

The solid state structure of Et_3PBr_2, prepared and recrystallised from Et_2O, is interesting to compare to the solvated $Pr^i_3PBr_2\cdot 0.5CH_2Cl_2$.[7] Both structures exhibit long Br–Br contacts [3.303(2) and 3.369(2) Å, respectively] and are essentially ionic.

Experimental

All of the compounds reported here are moisture sensitive, some intensely so, decomposing in a few seconds if exposed to the atmosphere. Consequently, strictly anaerobic and anhydrous conditions were employed for their synthesis. Any subsequent manipulations were carried out inside a Vacuum Atmospheres HE-493 glove-box. Diethyl ether (BDH) was dried by standing over sodium wire for *ca.* 1 d and subsequently refluxed over CaH_2 in an inert atmosphere and distilled directly into the reaction vessel. Anhydrous CH_2Cl_2 was obtained commercially (Aldrich) and used as received. Tertiary phosphines were either synthesized by standard Grignard techniques, R_3P [$R_3 = (p\text{-}FC_6H_4)_3$, $(p\text{-}FC_6H_4)Ph_2$, $(p\text{-}ClC_6H_4)_3$, $(m\text{-}MeC_6H_4)_3$, $(o\text{-}MeC_6H_4)Ph_2$, $(p\text{-}MeC_6H_4)Ph_2$, $PhBu^n_2$, $PhPr^n_2$ or $Ph_2(C_6H_{11})$] or obtained commercially, R_3P [$R_3 = (C_6F_5)_3$, Ph_3, $Ph_2(C_5H_4N)$, Ph_2Pr^n, Ph_2Me, $PhMe_2$, Bu^n_3 or Pr^n_3 (Aldrich); $R = Et_3$, $(CNCH_2CH_2)_3$, $(PhCH_2)_3$ or $(C_6H_{11})_3$, (Strem); $R = Me_2N$ (Lancaster)]. The purity of all the tertiary phosphines used was confirmed by elemental analysis and ^{31}P-{H} NMR spectroscopy prior to use. Dibromine was obtained commercially (Aldrich) and used as received.

All the R_3PBr_2 compounds were synthesized in a similar way, that of Ph_3PBr_2 being typical. Triphenylphosphine (2.00 g, 7.63 mmol) was suspended in Et_2O (*ca.* 75 cm^3) and subsequently dibromine (1.22 g, 0.39 cm^3, 7.63 mmol) was added. After reaction completion, the resultant white solid was isolated using standard Schlenk techniques. The solids were then transferred to pre-dried argon-filled ampoules which were flame sealed.

Elemental analyses were performed by the analytical laboratory of this department. The ^{31}P-{H} NMR spectra were recorded as $CDCl_3$ solutions on a Bruker AC200 high-resolution multiprobe spectrometer relative to concentrated phosphoric acid as standard.

Crystallography

Crystals of $(C_6F_5)_3PBr_2$ were mounted in Lindemann tubes under an atmosphere of dry argon. Crystals of Et_3PBr_2 were submerged in an inert oil under anaerobic conditions and a suitable crystal was chosen by examination under the microscope. The crystal, with its protective coating of oil, was then mounted on a glass fibre and transferred to the diffractometer and cooled to *ca.* 183(2) K in the cold gas stream derived from liquid nitrogen. Measurements were performed on a MAC 3 CAD 4 diffractometer employing graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) and ω–2θ scans. Both

Table 2 Crystal data and details of refinement for R_3PBr_2

	$(C_6F_5)_3PBr_2$	$[Et_3PBr]Br$
M	691.97	277.97
T/K	293(2)	183(2)
Crystal system	Rhombohedral	Orthorhombic
Space group	$R\bar{3}c$ (no. 167)	$Pbca$ (no. 61)
a/Å	11.539(3)	16.387(6)
b/Å	—	14.585(2)
c/Å	26.389(5)	9.369(2)
U/Å^3	3043(1)	2239(1)
Z	6	8
D_c/g cm^{-3}	2.266	1.649
F(000)	1968	1088
μ/cm^{-1}	42.17	73.20
Total data measured	596	1746
Maximum 2θ/°	49.8	50.0
No. unique reflections	596	1746
No. observed reflections [$I > 2.00\sigma(I)$]	596	1746
No. parameters	58	95
Final R	0.0317	0.063
Final R'	0.0529	0.012

structures were solved by direct methods. Unit-cell dimensions were derived from the setting angles of 25 accurately centred reflections. Lorentz-polarisation corrections were applied. Details of the X-ray measurements and subsequent structure determinations are presented in Table 2. Hydrogen atoms were confined to chemically reasonable positions. In the structure of $[Et_3PBr]Br$ each of the methylene groups is disordered over two semi-populated sites.

Neutral atom scattering factors were taken from ref. 18. Anomalous dispersion effects were taken from ref. 19. All calculations were performed using SHELXS 86 and SHELXL 93 crystallographic software packages.[20,21]

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References

1 A. M. Liebigs, *Ann. Chem.*, 1876, **181**, 256.

2 S. M. Godfrey, D. G. Kelly, A. G. Mackie, C. A. McAuliffe, R. G. Pritchard and S. M. Watson, *J. Chem. Soc., Chem. Commun.*, 1991, 1163; N. Bricklebank, S. M. Godfrey, A. G. Mackie, C. A. McAuliffe, R. G. Pritchard and P. J. Kobryn, *J. Chem. Soc., Dalton Trans.*, 1993, 101; N. Bricklebank, S. M. Godfrey, H. P. Lane, C. A. McAuliffe, R. G. Pritchard and J. M. Moreno, *J. Chem. Soc., Dalton Trans.*, 1995, 2421.

3 N. Bricklebank, S. M. Godfrey, A. G. Mackie, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Chem. Commun.*, 1992, 355.

4 N. Bricklebank, S. M. Godfrey, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.,* 1993, 2261.

5 S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard and J. M. Sheffield, *Chem. Commun.*, 1996, 2521; S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard, J. M. Sheffield and G. M. Thompson, *J. Chem. Soc., Dalton Trans.*, 1997, 4823.

6 M. A. H. A. Al-Juboori, P. N. Gates and A. S. Muir, *J. Chem. Soc., Chem. Commun.*, 1991, 1270.

7 F. Ruthe, W. W. du Mont and P. G. Jones, *Chem. Commun.*, 1997, 1947.

8 G. A. Wiley, B. M. Rein and R. L. Hershkowitz, *Tetrahedron Lett.*, 1964, 2509; A. G. Anderson and F. J. Freenor, *J. Am. Chem. Soc.*, 1964, **86**, 5037; *J. Org. Chem.*, 1972, **27**, 626.

9 W. W. du Mont, M. Bätcher, S. Pohl and W. Saak, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 912.

10 K. B. Dillon and T. C. Waddington, *Nature* (*London*) *Phys. Sci.*, 1971, **230**, 158.

11 G. A. Wiley and W. R. Stine, *Tetrahedron Lett.*, 1967, **24**, 2321.

12 R. Bartsch, O. Stelzer and R. Schmutzler, *Z. Naturforsch, Teil B*, 1981, **36**, 1349; *J. Fluorine Chem.*, 1982, **20**, 85.

13 A. D. Beveridge and G. S. Harris., *J. Chem. Soc.*, 1964, 6077; A. D. Beveridge, G. S. Harris and F. Inglis, *J. Chem. Soc. A*, 1966, 520; A. D. Beveridge, G. S. Harris and D. S. Payne, *J. Chem. Soc. A*, 1966, 726; G. S. Harris and M. F. Ali, *Tetrahedron Lett.*, 1968, 37; *Inorg. Nucl. Chem. Lett.*, 1968, **4**, 5; M. F. Ali and G. S. Harris, *J. Chem. Soc., Dalton Trans.*, 1980, 1545; G. S. Harris and J. S. McKechnie, *Polyhedron*, 1985, **4**, 115.

14 J. Goubeau and R. Baumgartner, *Z. Electrochem.*, 1960, **64**, 598.

15 M. A. H. A. Al-Juboori, P. N. Gates and A. S. Muir, *J. Chem. Soc., Dalton Trans.*, 1994, 1441.

16 N. Bricklebank, S. M. Godfrey, H. P. Lane, C. A. McAuliffe, R. G. Pritchard and J. M. Moreno, *J. Chem. Soc., Dalton Trans.*, 1995, 3873.

17 R. G. Cavell, J. A. Gibson and K. I. The, *J. Am. Chem. Soc.*, 1977, **99**, 784.

18 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, Table 2.2A.

19 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, Table 2.3.1.

20 G. M. Sheldrick, SHELXS 86, in *Crystallographic Computing 3*, ed. G. M. Sheldrick, Oxford University Press, 1985, p. 175.

21 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.

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