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The reaction of some tertiary phosphines with two mole equivalents of diiodine to produce the iodophosphonium triiodides $[R_3PI]I_3$; influence of R in causing subtle variations in solid state structures

Wendy I. Cross, Stephen M. Godfrey, Charles A. McAuliffe, Robin G. Pritchard, Joanne M. Sheffield and Graeme M. Thompson

Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester, UK M60 1QD. E-mail: stephen.m.godfrey@umist.ac.uk

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A variety of R_3PI_4 compounds have been synthesized and characterised by elemental analysis, NMR and visible spectroscopy. Apart from Ph_3PI_4, all are reported for the first time. X-Ray crystallographic studies on two of these materials, $Pr^i_3PI_4$ and $(Pr^n_2N)_3PI_4$, revealed different solid-state structures which are, in turn, different to both the two polymorphs of Ph_3PI_4 and Fc_3PI_4 (Fc = ferrocenyl) the crystal structures of which have been previously reported. The compound $Pr^i_3PI_4$ exists as $[(IPPr^i_3)_2I_3]I_3$, which contains two $[IPPr^i_3]^+$ cations independently weakly linked to one of the two terminal iodine atoms of the same triiodide anion. The structure also contains a discrete triiodide anion. The compound $(Pr^n_2N)_3PI_4$ exhibits very little anion–cation interaction. Of the two molecules present in the asymmetric unit, one exhibits no anion–cation interaction, while the other shows only a very weak contact [d(I–I)] (cation–anion) = 3.944(2) Å.

Introduction

Although the formation of 1 : 1 tertiary phosphine dihalogen adducts, R_3PX_2 (X = Cl, Br or I), has been recognised for over a century[1] it is only recently that their solid-state structures have been elucidated. The geometrical nature of such compounds has been shown to be dependent on X, the halide, the organo substituents bound to the phosphorus and, in some cases, the relative permittivity (polarity) of the solvent employed for their preparation.[2–6] The structure of the diiodo compounds, R_3PI_2,[2,3] has revealed the same topology, R_3P–I–I, regardless of the nature of R, although it has been noted that the organo substituents do influence the iodine–iodine bond length in the resultant compound. Thus, for example, Ph_3PI_2 exhibits d(I–I) of 3.142(2) Å,[2] whereas $PhMe_2PI_2$ shows d(I–I) of 3.409(2) Å. The nature of R for a given PR_3 will obviously affect its basicity and thus its donor power towards I_2, which is in turn reflected in d(I–I) for the resultant charge-transfer complex. The analogous bromide complexes, R_3PBr_2,[4] do exhibit geometrical dependence on R. Where R = Et an ionic compound results, $[Et_3PBr]Br$, which contains a tetrahedral phosphorus centre; in contrast, however, where $R = C_6F_5$, a trigonal bipyramidal compound results $(C_6F_5)_3PBr_2$. A similar situation is observed for the dichloro adducts, R_3PCl_2,[5,6] being ionic, $[R_3PCl]Cl$ ($R = Pr^n$ or Pr^i) or trigonal bipyramidal [$R_3 = (C_6F_5)_3$ or $Ph_2(C_6F_5)$].

Despite the current interest in the 1 : 1 adducts formed between tertiary phosphines and dihalogens, much less has been reported concerning the 1 : 2, R_3PX_4 adducts, despite the fact that these too have been known for over a century.[1] The formation of 1 : 2 tertiary phosphine tetraiodides, R_3PI_4, has been extensively studied conductimetrically by Harris and coworkers.[7] Solutions of these species in acetonitrile gave conductance values very close to that expected for a 1 : 1 electrolyte. This observation led the authors to conclude that the adducts were ionic, $[Ph_3PI]I_3$, in MeCN, the presence of the triiodide anion being detected using visible spectroscopy. The only crystal structures reported for a 1 : 2 tertiary phosphine–dihalogen adduct have appeared quite recently. The first report of an iodophosphonium triiodide was by Gridunova *et al.*[8] who described R_3PI_4 (R = ferrocenyl). Additionally, Cotton and Kibala[9] reported that the product from the reaction of triphenylphosphine with two equivalents of diiodine is solvent dependent. If the reaction is performed in CH_2Cl_2 (high relative permittivity) the compound $[(IPPh_3)_2I_3]I_3$ results. The crystal structure of this material reveals parallel zigzag chains of $[(IPPh_3)_2I_3]^+$ cations sandwiched between layers of I_3^- anions. In contrast, however, the same reaction performed in toluene produces the compound $[IPPh_3]I_3$. The crystal structure[9] of this material reveals a strong interaction between the $[IPPh_3]^+$ cation and a triiodide anion, the distance between the terminal iodine atom of I_3^- and the iodine atoms of $[IPPh_3]^+$ being 3.551(1) Å. The individual $[IPPh_3]I_3$ units are further linked into a polymer by weak interactions between the triiodine anions [d(I–I) = 3.741(1) Å]. A similar structural arrangement is also observed for the related compound triferrocenyliodophosphonium triiodide[8] in which the I–I cation–anion interactions are 3.736(1) Å and the triiodide anions are again weakly linked in the solid state, d(I–I) = 4.139(1) Å.

The interaction of the related compounds R_2PI and RPI_2 with diiodine has also recently been reported and a very interesting variety of layer and helical type structures in the solid state have been established *via* X-ray crystallography.[10,11] Finally, of relevance to the present study is the recent report of the crystal structure of bromotriphenylphosphonium tribromide, $[BrPPh_3]Br_3$.[12] In contrast to the analogous iodine containing species, described above, no cation–anion interactions are observed, the compound existing as discrete $[BrPPh_3]^+$ cations and tribromide anions.

In view of the renewed interest in the products formed from the reaction of tertiary phosphines with dihalogens and the fact that relatively little information is available concerning the products formed from the reaction of two mole equivalents of diiodine with PR_3, we decided to investigate the products formed from these reactions upon changing the R substituents on the tertiary phosphine. Additionally, we were interested in

Table 1 Analytical and spectroscopic data for the compounds R_3PI_4

		Analytical data, % Found (% Calc.)				
Compound	Colour	C	H	I	uv/vis band/nm	^{31}P-{H} NMR, δ^a
Et_3PI_4	Blue-grey	11.5 (11.8)	2.6 (2.4)	80.8 (81.2)	365.0, 295.0	59.7
$Pr^n{}_3PI_4$	Purple	16.8 (16.2)	3.3 (3.1)	74.5 (76.1)	365.5, 295.0	87.9
$Pr^i{}_3PI_4$	Red	16.3 (16.2)	3.1 (3.1)	75.8 (76.1)	365.0, 295.0	89.4
$Bu^i{}_3PI_4$	Burgundy	20.3 (20.3)	3.8 (3.8)	71.2 (71.6)	365.5, 295.5	9.1
Ph_2MePI_4	Purple	22.9 (22.0)	1.7 (1.8)	68.0 (71.8)	365.5, 297.5	57.9
Ph_2EtPI_4	Purple	25.3 (23.3)	2.9 (2.1)	68.2 (70.4)	365.0, 295.0	57.9
Ph_3PI_4	Purple	28.1 (28.1)	2.0 (1.9)	65.7 (65.9)	365.0, 295.0	48.8
$[2,4,6\text{-}(CH_3O)_3C_6H_2]_3PI_4$	Brown	31.3 (31.2)	3.3 (3.2)	48.7 (48.8)	358.5, 297.5	−60.1
$[2,6\text{-}(CH_3O)_2C_6H_3]_3PI_4$	Brown	30.6 (30.3)	2.8 (2.8)	53.0 (53.5)	366.5, 296.0	−61.3
$(PhCH_2)_3PI_4$	Brown	31.3 (31.0)	2.9 (2.6)	62.0 (62.6)	365.0, 296.0	76.5
$(Me_2N)_3PI_4$	Burgundy	11.1 (10.7)	2.8 (2.7)	75.1 (75.7)	366.0, 295.0	25.3
$(Pr^n{}_2N)_3PI_4$	Brown	26.7 (25.7)	5.4 (5.0)	59.0 (60.5)	365.5, 292.0	26.0

[a] All shifts recorded in $CDCl_3$ solution relative to concentrated phosphoric acid as standard.

crystallographically characterising some examples of R_3PI_4 derivatives containing alkyl or amino groups on the tertiary phosphine to compare to Cotton and Kibala's[9] triphenylphosphine derivatives and du Mont's diiodine adducts of RPI_2 and R_2PI_2.[10,11]

Results and discussion

All of the triorganophosphorus tetraiodides synthesized for this study were prepared by the reaction of one mole of tertiary phosphine with two mole equivalents of diiodine in diethyl ether, eqn. (1) (r.t. = room temperature). In each case the yield

$$R_3P + 2I_2 \xrightarrow[ca.\ 2\ \text{d, r.t.}]{Et_2O,\ N_2} R_3PI_4 \qquad (1)$$

of the trioganophosphorus tetraiodide compound was quantitative, Table 1. In contrast to the analogous R_3PI_2 compounds, which are yellow, all of the R_3PI_4 compounds have a deep red-brown colouration due to the presence of the I_3^- anion. The presence of this anion was confirmed using visible spectroscopy, Table 1. The visible spectra were recorded in dichloromethane solution and the peak positions are essentially independent of R thus indicating any cation–anion interaction present in the solid state is lost in solution, as expected. We were interested crystallographically to characterise some of our R_3PI_4 compounds to compare to Cotton and Kibala's[9] two polymorphs of Ph_3PI_4. Specifically, we were interested to investigate whether varying the R groups on a given R_3PI_4 compound affects the solid state structure of the materials, a phenomenon we have previously observed in R_3PX_2 compounds (X = Cl, Br or I).[2–5]

Consequently, we decided crystallographically to characterise two R_3PI_4 compounds containing different R groups which are also, in turn, different to the Ph_3PI_4 compounds previously described. Initially we decided to prepare crystals of an R_3PI_4 compound containing a trialkyl parent tertiary phosphine, since the greater basicity of the tertiary phosphine may well influence the solid-state structure of the resultant R_3PI_4 compound. Crystals of $Pr^i{}_3PI_4$ were prepared by recrystallisation of the bulk solid from diethyl ether–dichloromethane (1 : 1) solution at 50 °C. On standing at room temperature, large red-brown crystals appeared in the reaction vessel after *ca.* 3 d. One of these was selected for analysis by single crystal X-ray diffraction. The crystal structure of $Pr^i{}_3PI_4$ is illustrated in Fig. 1; selected bond lengths and angles are displayed in Table 2. The structural analysis reveals a different structural type for a R_3PI_4 compound when compared to the two polymorphs of Ph_3PI_4 described by Cotton and Kibala.[9] For $Pr^i{}_3PI_4$, weak interactions are observed between the iodine atoms of two $[Pr^i{}_3PI]^+$ moieties and each of the terminal iodine atoms of a single I_3^- anion, Scheme 1 [d(I3–I7) = 3.716(1); d(I1–I4) = 3.680(1) Å], van der Waals radius for two iodine atoms = 4.3 Å. The structure also contains a discrete I_3^- anion, and overall, the ionic material is probably better represented as $[(Pr^i{}_3PI)_2I_3]^+[I_3]^-$. This connectivity is subtly different to both of the isomers of Ph_3PI_4, previously described.[9] In one of these isomers, $[(Ph_3PI)_2I_3]^+[I_3]^-$, the two Ph_3PI^+ moieties both interact with only one of the terminal iodine atoms of an I_3 fragment. The second isomer of Ph_3PI_4, $[Ph_3PI]^+[I_3]^-$, again shows interaction of a Ph_3PI^+ moiety with a terminal iodine atom of an I_3 fragment, however this terminal iodine atom of the I_3 fragment also interacts with the same terminal iodine atom of the I_3 fragment of an adjacent molecule thus forming a weakly linked polymeric structure. No discrete I_3 anion is observed in this structure.

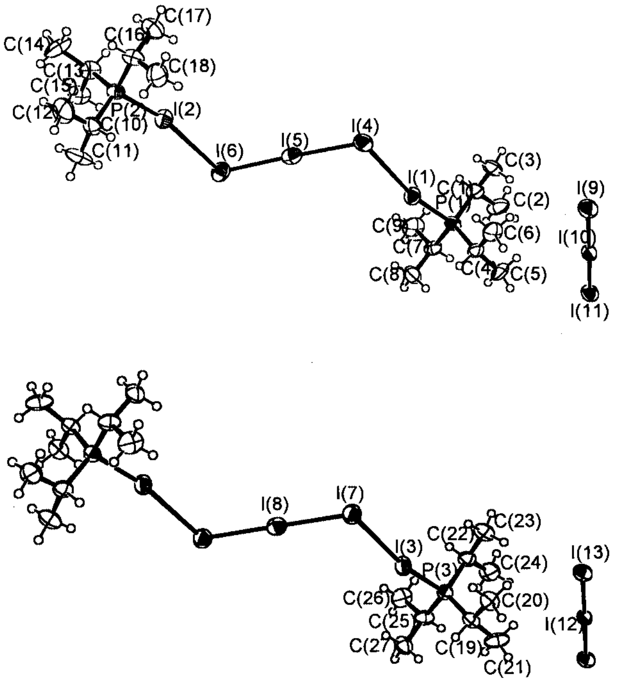


Fig. 1 The crystal structure of $[(IPPr^i{}_3)_2I_3]I_3$; hydrogen atoms are omitted for clarity.

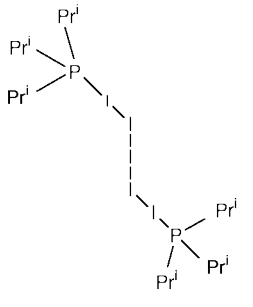
In order to gain further information regarding the nature of R_3PI_4 compounds, we also decided crystallographically to characterise $(Pr^n{}_2N)_3PI_4$ since this contains a very sterically hindered (large cone angle) and very basic parent tertiary phosphine in contrast to $Pr^i{}_3PI_4$ and the two isomers of Ph_3PI_4, previously described. These factors may combine to again affect the solid-state structure of this R_3PI_4 compound, leading to subtle differences in atom connectivity. Crystals of $(Pr^n{}_2N)_3PI_4$ were prepared in an identical way to that described for $Pr^i{}_3PI_4$.

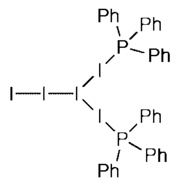
Table 2 Selected bond lengths (Å) and angles (°) for $Pr^i_3PI_4$

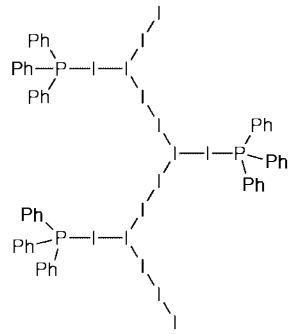
I(3)–I(7)	3.716(2)	I(4)–I(5)	2.905(2)
I(2)–I(6)	3.683(2)	I(5)–I(6)	2.925(2)
I(1)–I(4)	3.680(2)	I(7)–I(8)	2.922(1)
I(2)–P(1)	2.383(5)	I(9)–I(10)	2.878(1)
I(2)–P(2)	2.393(5)	I(11)–I(12)	2.878(2)
I(3)–P(3)	2.387(4)	I(12)–I(13)	2.898(2)
I(4)–I(5)–I(6)	176.72(6)	I(11)–I(12)–I(13)	178.50(6)
I(7)–I(8)–I(7)	180.0	C(1)–P(1)–I(1)	105.7(6)

Table 3 Selected bond lengths (Å) and angles (°) for $(Pr^n_2N)_3PI_4$

I(5)–I(6)	3.944(2)	P(1)–N(1)	1.592(12)
I(1)–P(1)	2.436(4)	P(1)–N(3)	1.603(12)
I(3)–I(4)	2.904(1)	P(1)–N(2)	1.612(11)
I(5)–P(2)	2.452(4)	P(2)–N(5)	1.600(11)
I(6)–I(7)	2.895(1)	P(2)–N(6)	1.603(12)
I(7)–I(8)	2.880(2)	P(2)–N(4)	1.612(12)
I(1)···I(2)	4.620(4)		
I(2)–I(3)–I(4)	176.88(6)	N(1)–P(1)–I(1)	107.2(5)
I(8)–I(7)–I(6)	178.57(7)		







The crystal structure is illustrated in Fig. 2; selected bond lengths and angles are displayed in Table 3. Two crystallographically independent molecules are present in the asymmetric unit. In one $(Pr^n_2N)_3PI_4$ molecule no interaction is observed between the $[(Pr^n_2N)_3PI]^+$ cation and the I_3^- anion [d(I–I) = 4.620(1) Å]. This molecule represents the first example of an R_3PI_4 species with no interactions between the $[R_3PI]^+$-cation and the I_3^- anion to be reported. The second molecule in the asymmetric unit of $(Pr^n_2N)_3PI_4$ exhibits a very weak interaction between the $[(Pr^n_2N)_3PI]^+$ cation and the I_3^- anion, d(I–I) = 3.944(2) Å, the weakest I–I interaction for any R_3PI_4 compound reported so far, lying just within the van der Waals radius for two iodine atoms. Again this compound illustrates the change in solid state structure for R_3PI_4 compounds upon changing the nature of R since the connectivity observed in this species is different to that seen for $Pr^i_3PI_4$ which exists as $[(Pr^i_3PI)_2I_3]I_3$, Fig. 1 and the two isomers[9] of Ph_3PI_4 $[(Ph_3PI)_2I_3]I_3$ (two Ph_3PI^+ cations sharing the same iodine atom of an I_3^- anion) and $[Ph_3PI]I_3$ (interaction between Ph_3PI^+ and the terminal iodine atom of an I_3^- anion, this atom also interacting with the terminal iodine atom of an adjacent I_3^- anion in another $[Ph_3PI]I_3$ molecule, thus forming a weakly linked polymer). In fact, $(Pr^n_2N)_3PI_4$ is best described as fully ionic, this certainly being the case for one molecule in the asymmetric unit (no I–I interaction observed) and the second molecule only shows a very weak I–I interaction. The reasons for this change in structure is almost certainly due to the high basicity and large steric bulk (large cone angle) of the parent tertiary phosphine, $(Pr^n_2N)_3P$.

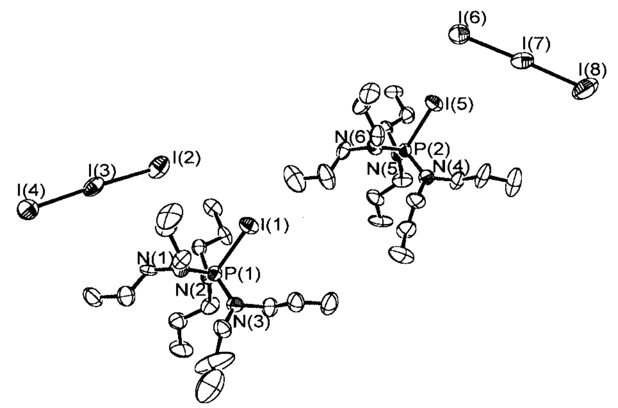


Fig. 2 The crystal structure of $[(Pr^n_2N)_3PI]I_3$; two molecules are present in the asymmetric unit. For clarity, carbon atoms are unlabelled and hydrogen atoms omitted.

Conclusion

Subtle solid-state structural changes for compounds of formula R_3PI_4 are observed upon changing R. Where R = Pr^i a single $Pr^i_3PI^+$ cation interacts with both the terminal iodine atoms of an I_3^- anion to produce the cation $[(Pr^i_3PI)_2I_3]^+$, the charge being balanced by a discrete I_3^- anion. In contrast, $(Pr^n_2N)_3PI_4$ is essentially ionic, $[(Pr^n_2N)_3PI]I_3$. Both of these structures, in turn, show different connectivities in the solid state compared to the two polymorphs of Ph_3PI_4,[9] previously reported, thus illustrating the variety of solid state structure observed for compounds of nominal formula R_3PI_4.

Experimental

All of the compounds reported here are moisture sensitive, consequently strictly anaerobic and anhydrous conditions were employed for their synthesis. Any subsequent manipulations were carried out inside a Vacuum Atmospheres HE-493 glovebox. Diethyl ether (BDH) was dried by standing over sodium wire for *ca.* 1 d, subsequently refluxed over CaH_2 in an inert atmosphere and distilled directly into the reaction vessel. Tertiary phosphines were obtained commercially and used as received, as was diiodine.

All the R_3PI_4 compounds were synthesized in a similar way, that of $Pr^i_3PI_4$ being typical. Triisopropylphosphine (1.00 g, 6.25 mmol) was dissolved in Et_2O (*ca.* 50 cm^3) and subsequently diiodine (3.175g, 12.5 mmol) added. After *ca.* 2 d the resultant dark purple solid was isolated using standard Schlenk techniques. The solids were then transferred to predried argon-filled ampoules which were flame sealed.

Elemental analyses were performed by the analytical laboratory of this department and the results are presented in Table 1. 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, visible spectra on a Shimadzu UV-2101 spectrophotometer.

Crystallography

Crystals of R_3PI_4 (R = Pr^i or Pr^n_2N) 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,

Table 4 Crystal data and details of refinement for R_3PI_4 (R = Pr^i or Pr^n_2N)

	$Pr^i_3PI_4$	$(Pr^n_2N)_3PI_4$
Formula	$C_9H_{21}I_4P$	$C_{36}H_{84}I_8N_6P_2$
M	667.83	1678.23
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a/Å	15.072(5)	16.913(3)
b/Å	11.309(7)	9.744(1)
c/Å	31.99(1)	35.602(8)
β/°	92.88(3)	94.02(2)
U/Å^3	5446(4)	5853(1)
Z	12	4
D_c/Mg m^{-3}	2.443	1.905
μ/cm^{-1}	69.29	43.22
F(000)	3624	3184
Crystal size/mm	0.30 × 0.25 × 0.17	0.28 × 0.20 × 0.15
No. reflections	9830	10630
No. observations	9438	10630
Maximum, minimum transmission	0.3379, 0.2303	
No. parameters	382	481
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0739, 0.1896	0.0695, 0.1230
(all data)	0.1068, 0.2198	0.1768, 0.1631
Maximum, minimum residual electron density	1.873, −1.924	0.936, −0.972

transferred to the diffractometer and cooled to *ca.* 203(2) K in the cold gas stream derived from liquid nitrogen. All measurements were performed on a Nonius MAC3 CAD4 diffractometer employing graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) and ω–2θ scans. Both structures were solved by direct methods. Unit-cell dimensions were derived from the setting angles of 25 accurately centred reflections. Lorentz-polymerisation corrections were applied. Details of the X-ray measurements and subsequent structure determinations are presented in Table 4. Hydrogen atoms were confined to chemically reasonable positions. Neutral atom scattering factors were taken from ref. 13, anomalous dispersion effects from ref. 14. All calculations were performed using SHELXS 86 and SHELXL 93 crystallographic software packages.[15,16]

CCDC reference number 186/1554.

See http://www.rsc.org/suppdata/dt/1999/2795/ for crystallographic files in .cif format.

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