Diiodophosphoranes. Synthesis and Structure in the Solid State and in Solution

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Nineteen diiodophosphoranes, R_3PI_2 (R_3 = Ph_3, substituted triaryl, mixed arylalkyl, or trialkyl), the vast majority of which have previously not been reported, are described. Their $^{31}P\{H\}$ NMR data indicate an ionic $[R_3PI]I$ structure in $CDCl_3$ solution, in keeping with results of other solution studies of a limited number of dihalogenophosphoranes, but solid-state ^{31}P-{H} magic angle spinning NMR data for R_3PI_2 (R_3 = Ph_3, $PhMe_2$ or Me_3) indicate a molecular four-co-ordinate R_3P–I–I structure, strongly suggesting that this is the common structure for diiodophosphoranes, and not the five-co-ordinate trigonal-bipyramidal structure of conventional wisdom.

Iodophosphoranes have found significant use as reagents in synthetic organic chemistry. Diiodotriphenylphosphorane in particular is useful for the conversion of alcohols and phenols into iodides,[1,2] in the synthesis of halohydrins,[3] conversion of vicinal diols into olefins,[4] and the transformation of aliphatic sulfonic acids, sulfinic acids, thiols, sulfinates, thiosulfonates and disulfides into the corresponding alkyl iodides.[5]

Thus, the nature of triorganophosphorus dihalogen compounds is of interest to both organic and inorganic chemists, and studies into their chemistry dates over a hundred years to the work of Michaelis.[6] However, even now the precise structural nature of the compounds formed between triorganophosphorus species and dihalogens is not known with certainty. Consequently, interest in this area remains considerable. Recent work in our laboratory,[7,8] together with reports by Dillon and co-workers,[9,10] as well as others[11–14] has revealed the interesting structural diversity exhibited by triorganophosphorus dihalides. In particular, the very delicate balance between ionic and covalent forms for these compounds is now well established. Our own interest in these compounds is in the novel synthesis of tertiary phosphine complexes of transition metals by the reaction of course-grain unactivated metal powders with triorganophosphorus dihalides [equation (1)].[15–17]

$$M + nR_3PX_2 \longrightarrow M(PR_2)_nX_y + zX_2 \qquad (1)$$

For dihalogenophosphoranes there are essentially three types of structure to be considered, *viz.* the predominant solution species which is ionic, $R_3PX^+X^-$, the traditionally accepted five-co-ordinated molecular solid-state R_3PX_2 structure, and, largely due to our investigations, the molecular solid-state 'spoke' structure R_3P–X–X.[7,8]

Solution studies have mainly been the conductometric measurements of Harris and co-workers,[14,18] which have led to the conclusion that phosphoranes of stoichiometry R_3PI_2 ionise to form $R_3PI^+I^-$, although information of this type for iodophosphoranes is much less than that available for the analogous dichlorophosphoranes, R_3PCl_2.[11,19] Quite remarkably, prior to the work reported here, there has only been one report of ^{31}P-{H} NMR solution data for a compound of stoichiometry R_3PI_2, $Bu^t_3PI_2$, which gave a shift of δ 112.

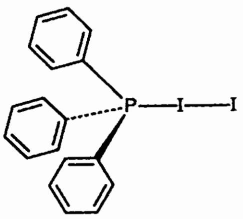

Fig. 1 The molecular structure of Ph_3PI_2[7]

As for solid-state structures, reports are limited to vibrational spectroscopic studies of Me_3PI_2[20] and Ph_3PI_2[21,22] and a solid-state ^{31}P NMR study of Ph_3PI_2,[23] plus single-crystal X-ray studies of Ph_3PI_2[7] and $Bu^t_3PI_2$.[12]

The solid-state structure of Ph_3PI_2 is shown schematically in Fig. 1. This compound, which had been crystallised from diethyl ether, exists as a solid molecular four-co-ordinate compound, isostructural with Ph_3P–Br–Br[8] and Ph_3As–I–I,[24,25] all of which have the linear 'spoke' structure R_3E–X–X. The X–X bond in these structures is considerably lengthened with respect to that in molecular X_2 (*e.g.* 3.16 Å in Ph_3PI_2, 2.67 Å in I_2), but is still well within bonding distance when compared to the van der Waals radius of, *e.g.*, diiodine (4.3 Å).

In our opinion the interpretation of the single-crystal X-ray structure of $Bu^t_3PI_2$ by du Mont *et al.*[12] as ionic $Bu^t_3PI^+I^-$ is erroneous. In this structure *d*(I–I) is 3.32 Å, which, although longer than *d*(I–I) of Ph_3P–I–I (3.12 Å),[7] is, nonetheless, better described as representing another example of the molecular four-co-ordinate 'spoke' structure exemplified by Ph_3PX_2 (X = Br[8] or I[7]) and Ph_3AsI_2.[24,25]

In addition to these studies there are a number of other reports[26–32] of the formation of charge-transfer complexes between diiodine and solvents or molecules containing a lone pair of electrons. Crystallographic studies on such complexes clearly show a lengthening of the I–I bond upon adduct formation.[33,34] This phenomenon is expected, since electron density is sent into the σ* orbitals of the diiodine by the electron donor. Although no charge-transfer complex between a tertiary phosphine and diiodine had been crystallographically characterised prior to our study of Ph_3P–I–I,[7] electronic spectroscopic studies had been reported.[35]

We now report studies of a large number of diiodophosphoranes, R_3PI_2, almost all of which have been synthesised,

Table 1 Analytical and spectroscopic data for the compounds R_3PI_2

		Analysis (%)			$\delta(^{31}P\text{-}\{H\})$		
Compound	Colour	C	H	I	*a*	*b*	ν(P–I)/cm^{-1}
$(p\text{-}FC_6H_4)_3PI_2$	Dark green	38.2 (37.9)	2.1 (2.1)	43.8 (44.5)	41.6		132
$(p\text{-}ClC_6H_4)_3PI_2$	Yellow	39.5 (41.0)	2.2 (1.9)	35.0 (34.9)	41.8		145
$(o\text{-}MeSC_6H_4)_3PI_2$	Red-brown	37.8 (38.5)	3.1 (3.2)	39.7 (38.8)	44.8		162
$(m\text{-}MeOC_6H_4)_2PhPI_2$	Yellow	41.9 (41.7)	3.6 (3.3)	43.9 (44.1)	43.1		145
$(p\text{-}MeSC_6H_4)_2PhPI_2$	Yellow	39.7 (39.5)	3.1 (3.1)	41.3 (41.8)	47.1		147
$(p\text{-}MeSC_6H_4)Ph_2PI_2$	Yellow	40.3 (40.6)	3.2 (3.0)	44.9 (45.2)	45.4		157
$(m\text{-}MeC_6H_4)_3PI_2$	Yellow	44.9 (45.2)	3.7 (3.8)	45.3 (45.5)	46.6		149
$(p\text{-}MeC_6H_4)Ph_2PI_2$	Orange	43.8 (43.0)	3.1 (3.2)	47.4 (47.9)	45.3		170
$(m\text{-}MeC_6H_4)Ph_2PI_2$	Mustard	43.7 (43.0)	3.3 (3.2)	47.5 (47.9)	46.3		164
$(o\text{-}MeC_6H_4)Ph_2PI_2$	Mustard	43.2 (43.0)	3.1 (3.2)	47.7 (47.9)	47.1		172
Ph_3PI_2	Yellow	41.8 (41.9)	2.9 (2.9)	49.2 (49.2)	44.8	−17.8	160
$Ph_2Pr^nPI_2$	Pale yellow	37.5 (37.3)	3.6 (3.5)	52.6 (52.7)	50.1		182
Ph_2MePI_2	Yellow	34.1 (34.4)	3.2 (2.9)	54.9 (55.9)	52.6		185
$PhMe_2PI_2$	Buff	24.6 (24.5)	3.1 (2.8)	64.6 (64.8)	61.9	−7.6	204
$Bu^n{}_3PI_2$	Buff	31.6 (31.6)	6.2 (5.9)	55.7 (55.7)	102.3		200
$Pr^n{}_3PI_2$	White	26.9 (26.1)	5.6 (5.1)	60.2 (61.3)	102.4		209
Et_3PI_2	White	19.3 (19.4)	4.3 (4.0)	68.7 (68.3)	89.0		235
Et_2MePI_2	White	17.1 (16.8)	3.9 (3.6)	69.9 (70.9)	103.0		208
Me_3PI_2	White	10.6 (10.9)	2.5 (2.8)	77.1 (77.0)	80.0	−5.3	208
PI_3	Black	—	—	—	—		169

[a] In $CDCl_3$ solution, shifts relative to 85% phosphoric acid standard. [b] Solid-state $^{31}P\text{-}\{H\}$ MAS NMR shifts, compounds prepared from diethyl ether, shifts relative to 85% phosphoric acid as standard.

characterised and are reported for the first time; their solid and solution structures are discussed. As expected, they are all ionic in $CDCl_3$. However, their solid-state NMR spectra clearly indicate a molecular four-co-ordinate 'spoke' structure.

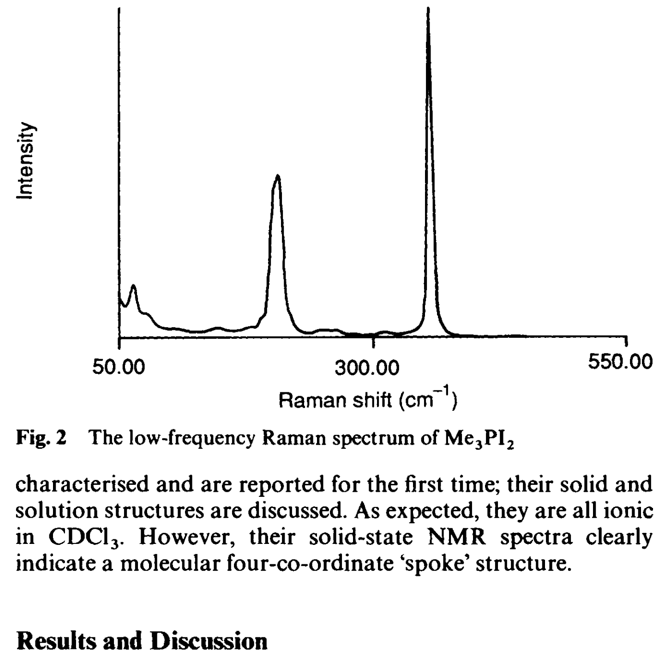

Fig. 2 The low-frequency Raman spectrum of Me_3PI_2

Results and Discussion

Table 1 contains the iodophosphoranes synthesised in this study. The compounds are readily prepared by the reaction of equimolar amounts of molecular iodine with the tertiary phosphine in dry diethyl ether under argon for 3 d.

Table 1 also contains the Raman band for each compound assigned to ν(P–I). Since no other band appears in this region of the spectrum, the assignment can be made with some confidence. The value of 160 cm^{-1} for ν(P–I) of Ph_3PI_2 is in good agreement with previous reports by Parrett[21] and by Tornieporth-Oetting and Klapötke.[22] However, for Me_3PI_2 our assignment of ν(P–I) to an intense band at 208 cm^{-1}, Fig. 2, differs from that of Goubeau and Baumgartner[20] who assigned a band at 358 cm^{-1} to this vibration. Whilst we do observe a band at 358 cm^{-1}, we feel that this is unlikely to arise from ν(P–I), and that the lower-energy band fits in well with the values we report for other diiodophosphoranes in Table 1, and with those reported by other workers.[21,22] However, it must be remarked that Table 1 does indicate a fair spread of values for this band, with the more basic phosphines exhibiting the highest ν(P–I) band energy, and the phosphines containing electron-withdrawing groups exhibiting the lowest energy. This is to be expected.

The delicate forces which dictate the solid-state structure of these compounds is well illustrated by Ph_3PI_2. We synthesised this compound in diethyl ether and by X-ray single-crystal studies showed it to have a four-co-ordinate 'spoke' structure, Fig. 1. However, Dillon and Waddington[23] obtained this compound from the much more polar nitrobenzene solvent. Their solid-state $^{31}P\text{-}\{H\}$ NMR spectrum exhibited a single peak at δ 42.5, from which they concluded that their Ph_3PI_2 was ionic in the solid state. Their conclusion fits well with our ^{31}P NMR spectra recorded in $CDCl_3$, Table 1, and we therefore conclude Ph_3PI_2 adopts an ionic $[Ph_3PI]I$ structure in $CDCl_3$ solution.

Indeed, all the R_3PI_2 compounds in this study exhibit $^{31}P\text{-}\{H\}$ NMR values in $CDCl_3$ indicating complete ionisation of R_3PI_2 to $[R_3PI]I$ in this solvent, Table 1. Addition of a further 1 equivalent of diiodine to these diiodophosphoranes, which is known[18] to produce the ionic tetraiodophosphorane, $[R_3PI]I_3$, resulted in a pronounced darkening of the solution (due to I_3^- formation), but no change in the position of the $^{31}P\text{-}\{H\}$ NMR resonance. The formation of the I_3^- ion was confirmed by UV/VIS spectra; for all of the compounds studied bands at 294 and 366 nm immediately appeared on addition of diiodine to a solution of the phosphorane in chloroform; such bands are diagnostic for I_3^-.[36] The identical $^{31}P\text{-}\{H\}$ NMR shifts for both the diiodophosphoranes and the corresponding tetraiodophosphoranes illustrates that complete ionisation of the former occurs in $CDCl_3$ solution.

We have been able to obtain solid-state magic angle spinning (MAS) $^{31}P\text{-}\{H\}$ NMR spectra for some of the diiodophosphoranes reported, Table 1. The organic substituents in R_3PI_2 were varied widely for this study, from triaryl to trialkyl (R_3 = Ph_3, $PhMe_2$, Me_3), but the results (δ −7.6 to −17.8) suggest that the molecular four-co-ordinate R_3P–I–I structure[11] exemplified by Ph_3PI_2 is also exhibited by $PhMe_2PI_2$ and Me_3PI_2. These values differ markedly from the solid-state value, δ 42.5, recorded by Dillon and Waddington[23] for the ionic $Ph_3PI^+I^-$ prepared in nitrobenzene. These results suggest that the 'spoke' structures found crystallographically for Ph_3P–X–X (X = Br[8] or I[7]) may well be ubiquitous to diiodotriorganophosphoranes.

Conclusion

The results reported clearly show that a large number of iodophosphoranes of stoichiometry R_3PI_2 completely ionise in solution to form $[R_3PI]I$. The solid-state ^{31}P-{H} MAS NMR results and a crystallographic study of Ph_3PI_2 suggest that these diiodophosphoranes exist as molecular species in which the phosphorus adopts a tetrahedral geometry onto which the dihalogen is bound as a linear 'spoke'. Clearly this novel structure may be common to compounds of stoichiometry R_3PI_2 when prepared in diethyl ether; however, the subtle nature of the compounds prevents a firm conclusion being made for all compounds of formula R_3PI_2. The differing structure of Ph_3PI_2 when prepared in diethyl ether (molecular) and nitrobenzene (ionic) gives further evidence for the very delicate balance between molecular and ionic forms of dihalogenoorganophosphorus compounds.

Experimental

All of the compounds reported are moisture sensitive, some intensely so; therefore, strictly anaerobic and anhydrous conditions were employed for their synthesis. Any subsequent manipulations were carried out inside a Vacuum Atmosphere 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. Tertiary phosphines were either synthesised by standard Grignard techniques or obtained commercially from Aldrich (PPh_3, PEt_3, PMe_3). The purity of all the tertiary phosphines used was confirmed by elemental analysis and ^{31}P-{H} NMR spectroscopy prior to use. Iodine was obtained commercially (Aldrich) and used as received.

All the iodophosphoranes were synthesised in a similar way, the synthesis of Ph_3PI_2 being typical. Triphenylphosphine (3.00 g, 11.45 mmol) was dissolved in diethyl ether (*ca.* 100 cm^3) and subsequently diiodine (2.91 g, 11.45 mmol) was added. After *ca.* 3 d the resultant bright yellow solid was isolated using standard Schlenk techniques and dried *in vacuo*. It was then transferred to pre-dried 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. Raman spectra were recorded by the University of Manchester Raman service using a Coherent Innova 90 5 W argon-ion laser and a SPEX 1403 double monochromator (focal length 0.85 m) fitted with a BGCS microscope sampling attachment. The radiation was detected using a Hamamatsu R928 photomultiplier tube which was cooled to −30 °C in a Products for Research Inc. TE 177 RF-005 cooler housing. The data were processed on a SPEX DM1B data station. Solution ^{31}P-{H} NMR spectra were recorded as $CDCl_3$ solutions on a Brucker AC200 high-resolution multiprobe spectrometer relative to concentrated phosphoric acid as standard. Solid-state ^{31}P-{H} NMR spectra were recorded on a Bruker ASL 500 MHz high-resolution multiprobe MAS solid-state spectrometer. Shifts were recorded relative to concentrated phosphoric acid as standard.

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References

1 G. A. Wiley, R. L. Hershkowitz, B. M. Rein and B. C. Chang, *J. Am. Chem. Soc.*, 1964, **86**, 964.
2 G. A. Wiley, B. M. Rein and R. L. Hershkowitz, *Tetrahedron Lett.*, 1964, 2509.
3 G. Palumbo, C. Ferreri and R. Caputo, *Tetrahedron Lett.*, 1983, 1307.
4 P. G. Garegg and B. Samuelsson, *Synthesis*, 1979, 469.
5 S. Oae and H. Togo, *Synthesis*, 1981, 371.
6 A. Michaelis, *Justus Liebigs Ann. Chem.*, 1886, **233**, 39.
7 S. M. Godfrey, D. G. Kelly, C. A. McAuliffe, A. G. Mackie, R. G. Pritchard and S. M. Watson, *J. Chem. Soc., Chem. Commun.*, 1991, 1163.
8 N. Bricklebank, S. M. Godfrey, C. A. McAuliffe, A. G. Mackie and R. G. Pritchard, *J. Chem. Soc., Chem. Commun.*, 1992, 355.
9 K. B. Dillon and T. A. Straw, *J. Chem. Soc., Chem. Commun.*, 1991, 234.
10 K. B. Dillon and J. Lincoln, *Polyhedron*, 1985, **4**, 1333; 1989, **8**, 1445.
11 M. A. H. A. Al-Juboori, P. N. Gates and A. S. Muir, *J. Chem. Soc., Chem. Commun.*, 1991, 1270.
12 W. W. du Mont, M. Batcher, S. Pohl and W. Saak, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 912.
13 F. A. Cotton and P. A. Kibala, *J. Am. Chem. Soc.*, 1987, **109**, 3308.
14 G. S. Harris and J. S. McKechnie, *Polyhedron*, 1985, **4**, 115.
15 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, 1447.
16 C. A. McAuliffe, S. M. Godfrey, A. G. Mackie and R. G. Pritchard, *J. Chem. Soc., Chem. Commun.*, 1992, 483.
17 C. A. McAuliffe, S. M. Godfrey, A. G. Mackie ad R. G. Pritchard, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 919.
18 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.
19 G. A. Wiley and W. R. Stine, *Tetrahedron Lett.*, 1967, **24**, 2321; D. B. Denney, D. Z. Denney and B. C. Chang, *J. Am. Chem. Soc.*, 1968, **90**, 6332; G. G. Arzoumandis, *Chem. Commun.*, 1969, 217; K. B. Dillon, R. N. Reeve and T. C. Waddington, *J. Inorg. Nucl. Chem.*, 1976, **38**, 1439; K. B. Dillon, R. J. Lynch, R. N. Reeve and T. C. Waddington, *J. Chem. Soc., Dalton Trans.*, 1976, 1243; B. V. Tumokhin, V. P. Feshin, V. I. Dmitriev, V. I. Glukhikh, G. V. Dolgushin and M. G. Voronkov, *Dokl. Akad. Nauk SSSR*, 1977, **236**, 938; K. B. Dillon, R. N. Reeve and T. C. Waddington, *J. Chem. Soc., Dalton Trans.*, 1978, 1318; R. Appel and H. Scholer, *Chem. Ber.*, 1977, **110**, 2382.
20 J. Goubeau and R. Baumgartner, *Z. Electrochem.*, 1960, **64**, 598.
21 F. W. Parrett, *Spectrochim. Acta, Part A*, 1969, **26**, 1271.
22 I. Tornieporth-Oetting and T. Klapötke, *J. Organomet. Chem.*, 1989, **379**, 251.
23 K. B. Dillon and T. C. Waddington, *Nature (London), Phys. Sci.*, 1971, **230**, 158.
24 C. A. McAuliffe, B. Beagley, G. A. Gott, A. G. Mackie, P. P MacRory and R. G. Pritchard, *Angew. Chem., Int. Ed. Eng.*, 1987, 26, 264.
25 B. Beagley, C. B. Colburn, O. El-Sayrafi, G. A. Gott, D. G. Kelly, A. G. Mackie, C. A. McAuliffe, P. P. MacRory and R. G. Pritchard, *Acta. Crystallogr., Sect. C*, 1988, **44**, 38.
26 H. Tsumbomura and S. Nagakura, *J. Chem. Phys.*, 1957, 819.
27 E. K. Plyler and R. S. Mulliken, *J. Am. Chem. Soc.*, 1959, **81**, 823.
28 S. G. W. Ginn and J. L. Wood, *Trans. Faraday Soc.*, 1966, **62**, 777.
29 K. Toyoda and W. B. Person, *J. Am. Chem. Soc.*, 1965, **88**, 1629.
30 S. Kobinata and S. Nagakura, *J. Am. Chem. Soc.*, 1966, **89**, 3905.
31 P. Klaboe, *J. Am. Chem. Soc.*, 1966, **89**, 3667.
32 E. Augdahl, J. Grundnes and P. Klaboe, *Inorg. Chem.*, 1965, **4**, 1475.
33 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn., Wiley-Interscience, New York, 1988, p. 530.
34 O. Hassel and H. Hope, *Acta Chem. Scand.*, 1961, **15**, 407.
35 K. R. Bhasker, S. N. Bhat, S. S. Singh and C. N. R. Rao, *J. Inorg. Nucl. Chem.*, 1966, **28**, 1915.
36 A. I. Popov and R. F. Svensen, *J. Am. Chem. Soc.*, 1955, **77**, 3724.

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