Acta Crystallographica Section C
**Crystal Structure Communications**
ISSN 0108-2701

# Solvent-free synthesis and crystal structure of $(Ph_3PI)I_5$, the third member in the series $Ph_3P(I_2)_n$ ($n$ = 1, 2 and 3)

**Robin G. Pritchard* and Lee Moreland**

School of Chemistry, Faraday Building, University of Manchester, Sackville Street, Manchester M60 1QD, England
Correspondence e-mail: robin.pritchard@manchester.ac.uk

Received 29 August 2006
Accepted 27 September 2006
Online 19 October 2006

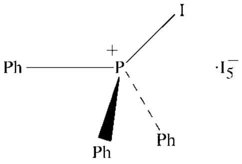
Red crystals of iodotriphenylphosphonium pentaiodide, $C_{18}H_{15}IP^+\cdot I_5^-$, appear on cooling the black melt formed by heating a mixture of the commonplace reagents triphenylphosphine and molecular iodine. The compound has the highest I:P ratio hitherto established for a crystalline iodophosphonium polyiodide and constitutes the third member of the series $Ph_3P(I_2)_n$ ($n$ = 1, 2 and 3). All atoms occupy general positions in the triclinic space group $P\bar{1}$. Comparison of the bond lengths within the above series reveals a pattern of primary and secondary bonding that is highly reminiscent of the much studied polyiodides, $I_{2n+1}^-$, where one of the $I_2$ moieties has been replaced by a P—I group.

## Comment

Classification of adducts formed by combining the common reagents $I_2$ and $Ph_3P$ has not been straightforward. The 1:1 adduct crystallizes from diethyl ether as the molecular compound $Ph_3PI_2$ (Godfrey *et al.*, 1991), (1), which remains un-ionized even when dissolved in dichloroethane (Deplano *et al.*, 1997). By contrast, the 2:1 adduct forms ionically diverse polymorphs, *viz*. $(Ph_3PI)I_3$, (2*a*), from toluene and $[(Ph_3PI)_2I_3]I_3$, (2*b*), from dichloroethane (Cotton & Kibala, 1987). This type of polymorphism, although not unknown (Katrusiak, 2003), is extremely rare and serves as a graphic illustration of the sensitivity of iodophosphonium polyiodides to solvent effects. In this case, the more polar solvent encourages auto-ionization and charge separation in what is already an extremely polarized species:

$$2(Ph_3PI)I_3 \rightarrow [(Ph_3PI)_2I_3]^+ + I_3^-$$

Indeed, (2*b*) is best described as an ion pair associating through a weak charge-transfer bond. The above structures represent the highest I:P ratio hitherto achieved in the $Ph_3P/I_2$ system and it is noteworthy that an iodophosphonium polyiodide structure with an I:P ratio of 6 or higher has yet to be reported. This is somewhat surprising given the ionic behavior outlined above and the fact that several molecular cations are known to form compounds with large polyiodide counter-ions, *e.g.* $Me_3S^+$ forms a series of crystalline polyiodides, including one in which the I:P ratio exceeds 8 (Svensson *et al.*, 2000), and $[Et_3S]I_x$ ($x > 4$) forms polyiodide melts in which non-polar $I_2$ is considered to be behaving as a solvent (Bengtsson *et al.*, 1991). The current investigation was therefore undertaken in order to discover how $Ph_3P$ would react with $I_2$ when freed from the influence of conventional solvents. Direct reaction of molten $Ph_3P$ with $I_2$ produced the title compound, $(Ph_3PI)I_5$, (3) (Fig. 1). Compound (3) is clearly related to (2*a*), the 2:1 polymorph grown in toluene, and forms the third member of the series $Ph_3P(I_2)_n$ ($n$ = 1, 2 and 3). This series, in turn, has strong similarities with the extensively studied polyiodides $I_{2n+1}^-$ ($n$ = 1, 2, 3 and 4), where $I^-$ replaces $Ph_3P$ as the base (Svensson & Kloo, 2003).



(3)

Polyiodides are classified according to their I—I bond lengths, *e.g.* $I_5^-$ can be described as V-shaped $[(I^-)\cdot 2I_2]$ or L-shaped $[(I_3^-)\cdot(I_2)]$, depending on the pattern of interatomic distances. Furthermore, below 3.3 Å (Coppens, 1982) or, arguably, 3.4 Å (Svensson & Kloo, 2003), the bonds are considered to be intramolecular or primary bonds. Above these values up to 3.7 Å, the bonds are defined as intermolecular or secondary and up to 3.9 Å as weak van der Waals interactions. The same rationale can be used to classify iodophosphonium polyiodide structures, with the proviso that P—I bonds are always primary. Alternatively, a more inclusive scheme based on bond order can easily be set up using empirical bond length *versus* bond order ($n$) relationships.

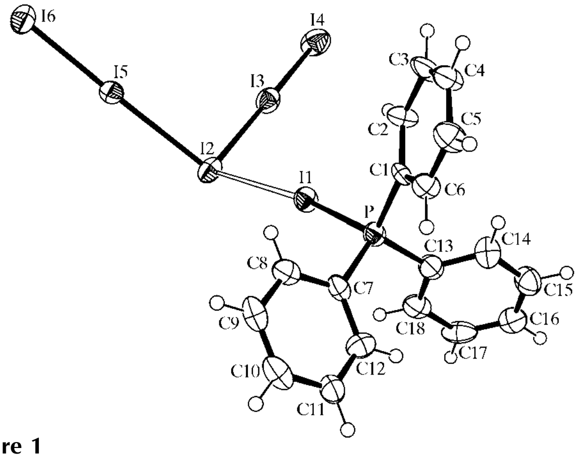


**Figure 1**
The molecular structure of $(Ph_3PI)I_5$, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

DOI: 10.1107/S0108270106039825

An existing equation, *viz*. I—I = 2.67 − 0.85log$_{10}$($n$) (Bürgi, 1975), allows the above bond-length ranges to be converted into bond orders, primary above 0.18 (or 0.14) and secondary down to 0.06. Also, as the crystal structures of several $R_3PI_2$ adducts are now known, a similar equation, P—I = 2.35 − 1.14log$_{10}$($n$), can be derived for P—I bonds by assuming $n_{I-P} = 1 - n_{I-I}$ (Fig. 2). The subsequent bond orders, calculated by applying these equations to crystallographically determined bond lengths from the $Ph_3P(I_2)_n$ series (Fig. 3), clearly justify the assignment of $Ph_3PI_2$ and $(Ph_3PI)I_3$ to compounds (1) and (2), respectively. Also, based on these values, $(Ph_3PI)I_5$ is the most appropriate description of (3).

Further support for these assignments comes from solution work carried out in dichloroethane, where $I_3^-$ and $I_5^-$ ions were detected but not $I^-$ (Deplano *et al.*, 1997). These iodophosphonium polyiodide structures are analogous to known polyiodide types: (1) corresponds to a typical asymmetric $I_3^-$, (2*a*) to an L-shaped $(I_3^-)\cdot I_2$ and (3) to pyramidal $(I_5^-)\cdot I_2$. In each case, the P—I moiety behaves like a low acidity, but by no means inert, $I_2$. More detailed examination of (3) shows that the $I_5^-$ part is nearly V-shaped, *i.e.* $(I^-)\cdot 2I_2$, and as the bond order of the intermolecular bond is close to an intramolecular value it is worth noting that (3) is bordering on $(Ph_3PI)(I_2)_2I$ *cf.* $(I^-)(I_2)_3$.

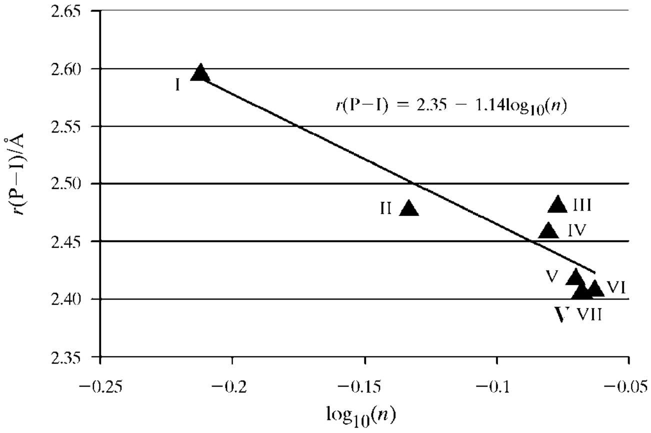


**Figure 2**
The variation of P—I bond length (Å) with bond order $n$. (I) is $(2\text{-Me-}1,2\text{-}C_2B_{10}H_{10})(^iPr)_2PI_2$ (Teixidor *et al.*, 2000), (II) is $Ph_3PI_2$ (Godfrey *et al.*, 1991), (III) is $[C_6H_2(OMe)_3]_3PI_2\cdot CH_2Cl_2$ (Godfrey *et al.*, 1998), (IV) is $(^tBu)_3PI_2$ (DuMont *et al.*, 1987), (V) is $(^iPr)_3PI_2\cdot CH_2Cl_2$ (Ruthe *et al.*, 2000) and (VI) is $PhMe_2PI_2$ (Bricklebank *et al.*, 1995).

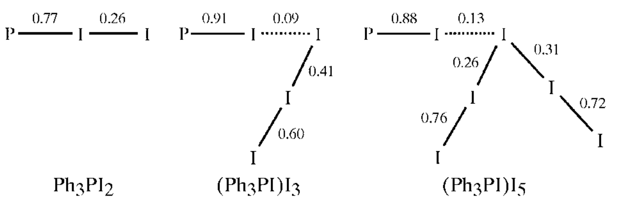


**Figure 3**
Empirically derived bond orders for $Ph_3P(I_2)_n$ ($n$ = 1, 2 and 3).

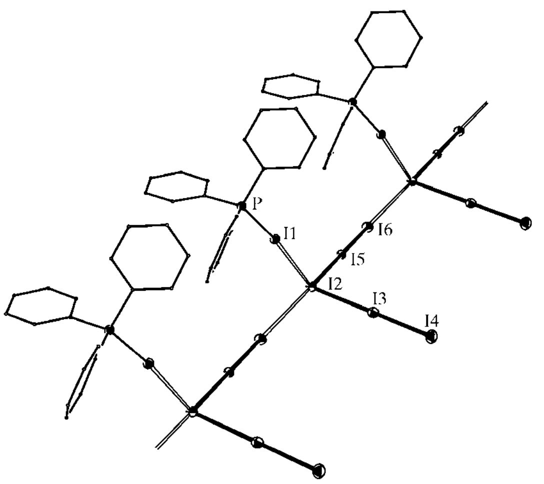


**Figure 4**
The sawhorse structure of (3), formed through association of pyramidal $Ph_3PI(I_5)$ units *via* secondary bonds.

The close parallels between the iodophosphonium polyiodides and polyiodides extend to their secondary interactions. Compound (2*a*) associates into a *trans*-chain, one of the common contact geometries for pentaiodides (Svensson & Kloo, 2003), by head-to-tail linking of adjacent $I_3^-$ groups *via* a 3.741 (1) Å ($n$ = 0.05) secondary bond. A stronger secondary bond of 3.601 (1) Å ($n$ = 0.08) links (3) into a *cis*-chain (Fig. 4), which can be pictured as evolving from the *trans*-chain by adding an extra $I_2$ side branch opposite the $IPPh_3$ moiety and then twisting the chain from *trans* to *cis*. This type of extended structure is also seen in the heptaiodide $[H_3O\cdot 18\text{-crown-}6]I_7$, where it has been described as a sawhorse (Abd El Khalik *et al.*, 1999; Junk *et al.*, 1995).

The current, solvent-free, work has broadened our understanding of iodophosphonium polyiodides and, perhaps more importantly, established clear parallels between the $Ph_3P(I_2)_n$ and $I_{2n+1}^-$ structures, suggesting that crystals with even higher iodine loadings may well be attainable. Despite the cursory nature of our observations on the melt associated with the formation of (3), there is sufficient evidence to suggest that research along the lines of that carried out on polyiodide melts (Bengtsson *et al.*, 1991) may well prove fruitful in this case too.

## Experimental

The title compound was prepared by placing powdered $Ph_3P$ in a 0.7 mm diameter special-glass X-ray sample tube to a depth of *ca* 10 mm, using a second tube as a funnel to prevent the glass becoming contaminated. Approximately the same quantity of fine $I_2$ crystals was added immediately prior to the tube being evacuated with a rotary pump and flame sealed. Although a narrow brown layer appeared instantaneously at the interface between the two materials, it did not develop further until the tube was heated to the melting point of $Ph_3P$. At this point, the $I_2$ crystals and their violet vapour disappeared to be replaced by a black melt which extended for several mm over the interface region. On cooling, red crystals of $Ph_3PI(I_5)$, (3), were recovered by breaking the glass tube under inert oil.

*Crystal data*

$C_{18}H_{15}IP^+\cdot I_5^-$
$M_r = 1023.67$
Triclinic, $P\bar{1}$
$a = 9.4288$ (3) Å
$b = 11.7262$ (4) Å
$c = 12.1270$ (5) Å
$\alpha = 86.196$ (1)°
$\beta = 77.290$ (1)°
$\gamma = 77.697$ (1)°
$V = 1277.66$ (8) Å$^3$
$Z = 2$
$D_x = 2.661$ Mg m$^{-3}$
Mo $K\alpha$ radiation
$\mu = 7.36$ mm$^{-1}$
$T = 150$ (2) K
Block, dark red
0.1 × 0.1 × 0.05 mm

*Data collection*

Nonius KappaCCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (Blessing, 1995, 1997)
$T_{\min} = 0.478$, $T_{\max} = 0.683$
5574 measured reflections
5262 independent reflections
3809 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.067$
$\theta_{\max} = 26.5°$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.146$
$S = 1.07$
5262 reflections
226 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0677P)^2 + 14.7624P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 2.20$ e Å$^{-3}$
$\Delta\rho_{\min} = -1.42$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| C1—P | 1.784 (10) | I2—I3 | 3.1022 (11) |
| C7—P | 1.790 (10) | I3—I4 | 2.7906 (13) |
| C13—P | 1.797 (12) | I5—I6 | 2.7709 (10) |
| P—I1 | 2.412 (3) | | |
| C1—P—C7 | 109.9 (5) | C7—P—I1 | 107.8 (3) |
| C1—P—C13 | 110.6 (5) | C13—P—I1 | 109.2 (4) |
| C7—P—C13 | 109.9 (5) | I4—I3—I2 | 179.57 (4) |
| C1—P—I1 | 109.4 (3) | | |
| C2—C1—P—I1 | −28.2 (10) | C14—C13—P—I1 | 129.7 (9) |
| C8—C7—P—I1 | −54.7 (9) | | |

As the melt-grown crystals formed as a fused mass, it proved difficult to select an ideal crystal. Despite this, a reasonable quality data set was obtained, enabling the structure to be solved and subsequently refined in the space group $P\bar{1}$ (No. 2). Some peaks as high as 2.2 e Å$^{-3}$ remained in the difference Fourier map. These peaks shared $y$ and $z$ coordiates with I atoms but were shifted in the $x$ direction. Since a twinned refinement did not affect the size of the extra peaks or improve the $R$ factors, a twinned model was rejected. It is suggested that stacking faults may occur along the $a$ axis, which coincides with the backbone of the sawhorse. H atoms were constrained to chemically reasonable positions, with C—H = 0.95 Å and $U_{\rm iso}(H) = 1.2U_{\rm eq}(C)$.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors acknowledge the use of the EPSRC Chemical Database Service at Daresbury (Fletcher *et al.*, 1996; Allen *et al.*, 1983) and EPSRC support for the purchase of equipment.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC3017). Services for accessing these data are described at the back of the journal.

## References

Abd El Khalik, S., El Essawi, M., Dombrowski, I. & Tebbe, K. F. (1999). *Z. Naturforsch. Teil B*, **54**, 136–139.
Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–153.
Bengtsson, L. A., Stegemann, H., Holmberg, B. & Fullbier, H. (1991). *Mol. Phys.* **73**, 283–296.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
Bricklebank, N., Godfrey, S. M., Lane, H. P., McAuliffe, C. A., Pritchard, R. G. & Moreno, J. M. (1995). *J. Chem. Soc. Dalton Trans.* pp. 2421–2424.
Bürgi, H.-B. (1975). *Angew. Chem. Int. Ed. Engl.* **14**, 460–473.
Coppens, P. (1982). *Extended Linear Chain Compounds*, edited by J. S. Miller, Vol. 1, ch. 7, pp. 333–356. New York: Plenum Press.
Cotton, F. A. & Kibala, P. A. (1987). *J. Am. Chem. Soc.* **109**, 3308–3312.
Deplano, P., Godfrey, S. M., Isaia, F., McAuliffe, C. A., Mercuri, M. L. & Trogu, E. F. (1997). *Chem. Ber.* **130**, 299–305.
DuMont, W. W., Batcher, M., Pohl, S. & Saak, W. (1987). *Angew. Chem. Int. Ed. Engl.* **26**, 912–913.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Fletcher, D. A., McMeeking, R. F. & Parkin, D. (1996). *J. Chem. Inf. Comput. Sci.* **36**, 746–749.
Godfrey, S. M., Kelly, D. G., McAuliffe, C. A., Mackie, A. G., Pritchard, R. G. & Watson, S. M. (1991). *J. Chem. Soc. Chem. Commun.* pp. 1163–1164.
Godfrey, S. M., McAuliffe, C. A., Pritchard, R. G. & Sheffield, J. M. (1998). *J. Chem. Soc. Dalton Trans.* pp. 1919–1923.
Junk, P. C., Macgillivray, L. R., May, M. T., Robinson, K. D. & Atwood, J. L. (1995). *Inorg. Chem.* **34**, 5395–5396.
Katrusiak, A. (2003). *Org. Lett.* **5**, 1903–1905.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Ruthe, F., Jones, P. G., du Mont, W. W., Deplano, P. & Mercuri, M. L. (2000). *Z. Anorg. Allg. Chem.* **626**, 1105–1111.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Svensson, P. H. & Kloo, L. (2003). *Chem. Rev.* **103**, 1649–1684.
Svensson, P. H., Raud, G. & Kloo, L. (2000). *Eur. J. Inorg. Chem.* pp. 1275–1282.
Teixidor, F., Núñez, R., Viñas, C., Sillanpää, R. & Kivekäs, R. (2000). *Angew. Chem. Int. Ed.* **39**, 4290–4292.