

## Tetraphenylarsonium iodide, a new determination

Philip A. W. Dean,<sup>a\*</sup> Donald C. Craig,<sup>b</sup> Marcia L. Scudder<sup>b</sup> and Ian G. Dance<sup>b</sup>

<sup>a</sup>Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7, and <sup>b</sup>School of Chemical Sciences, University of New South Wales, Sydney 2052, Australia

Correspondence e-mail: pawdean@uwo.ca

Received 12 August 2003

Accepted 9 October 2003

Online 31 October 2003

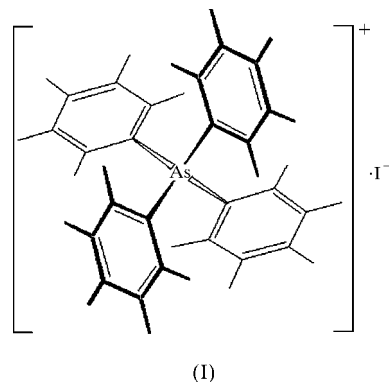
The reported crystal structures of  $\text{Ph}_4\text{P}^+\cdot\text{I}^-$  and  $\text{Ph}_4\text{As}^+\cdot\text{I}^-$  have been re-examined. An apparent instance of substitutional dimorphism could not be reproduced and, contrary to an earlier report, tetraphenylarsonium iodide,  $[\text{As}(\text{C}_6\text{H}_5)_4]\text{I}$  or  $\text{Ph}_4\text{As}^+\cdot\text{I}^-$ , was found to be isostructural with the phosphorus compound. The cation and anion are both located on  $\bar{4}$  symmetry sites. The crystal packing involves linear chains of cations in fourfold phenyl embraces.

### Comment

A search of the Cambridge Structural Database (CSD, Version 5.24; Allen, 2002) for  $\text{Ph}_4\text{E}^+\cdot\text{I}^-$  revealed three structure reports for  $\text{Ph}_4\text{P}^+\cdot\text{I}^-$  and  $\text{Ph}_4\text{As}^+\cdot\text{I}^-$ , all in space group  $\bar{4}$ , and with cell dimensions as follows: for  $\text{Ph}_4\text{P}^+\cdot\text{I}^-$  with CSD refcode SATSUB (crystallized from  $\text{CH}_2\text{Cl}_2$ -hexane; Schweizer *et al.*, 1989),  $a = b = 11.979$  and  $c = 6.981$  Å; for  $\text{Ph}_4\text{P}^+\cdot\text{I}^-$  with CSD refcode SATSUB01 (crystallized from  $\text{CH}_3\text{CN}$ ; Gorobinsky *et al.*, 2001),  $a = b = 11.967$  and  $c = 6.974$  Å; for  $\text{Ph}_4\text{As}^+\cdot\text{I}^-$  with CSD refcode TPHASI (crystallized from hot water; Mooney, 1940),  $a = b = 12.194$  and  $c = 7.085$  Å. The agreement factors for these structure determinations are 0.037, 0.046 and 0.280, respectively. The crystal forms of both  $\text{Ph}_4\text{P}^+\cdot\text{I}^-$  and  $\text{Ph}_4\text{As}^+\cdot\text{I}^-$ , obtained by us from various solvents and at a range of temperatures, are isostructural with that reported previously for  $\text{Ph}_4\text{P}^+\cdot\text{I}^-$ . Only our determination of the structure of the arsonium salt, (I), is described here.

The space group for (I) found in the present work is the same as that found by Mooney. The cell dimensions differ slightly, but significantly. In (I), the cation necessarily has  $S_4$  symmetry. The difference between the original structure and the present one lies in the (one) torsion angle of the phenyl groups in this cation, which is defined here as that described by the molecular  $S_4$  axis and the As—C—C orientation. This

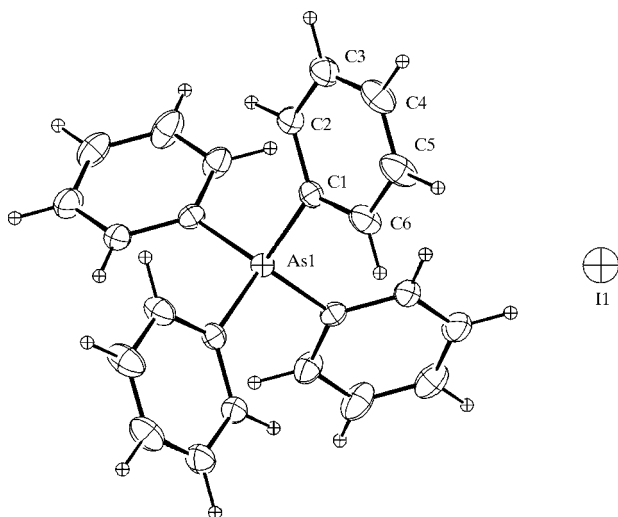
angle is  $88^\circ$  for the original structure determination but  $63.6(2)^\circ$  in our determination (Fig. 1). In  $\text{Ph}_4\text{As}^+\cdot\text{I}_3^-$  (Runsink *et al.*, 1972), the cation possesses twofold symmetry and the two independent torsion angles are  $51.8$  and  $58.5^\circ$  (relative to the molecular twofold axis).



The difference in molecular conformations in the original and in the present determination of (I) is illustrated in Fig. 2. The almost orthogonal conformation of phenyl rings in the original structure is what we have previously described as the 'flipper' conformation (Dance & Scudder, 2000), *viz.* the planes of a pair of phenyl rings are not twisted relative to each other. In the present work, the phenyl rings are different from the original structure, by concerted torsion through  $24^\circ$ . The crystal packing in our structure of (I) contains infinite linear chains of fourfold phenyl embraces (LIT4PE) in the  $c$  direction. Along this chain, adjacent cations form the orthogonal fourfold phenyl embrace, O4PE, in which there is a concerted cycle of four edge-to-face (EF) phenyl-phenyl interactions (Dance & Scudder, 1996*a,b*). In addition, there are EF interactions which link the chains laterally. The I atom is located in a hydrogenous environment, taking part in a total of 24 C—H...I interactions in the range 3.7–4.2 Å, each substantially longer than the sum of the van der Waals radii (3.2 Å) and with linearity in the range  $103$ – $126^\circ$ , but sufficiently numerous to be considered a stabilizing influence.

We attempted to clarify whether our crystal of (I) was indeed a subtle dimorph of that produced by Mooney, in which case that crystal could be classified as an example of a 'disappearing polymorph' (Dunitz & Bernstein, 1995; Bombicz *et al.*, 2003). We have probed the existence of dimorphs for (I) from several points of view.

The original crystal structure, although carried out using photographic data, does not appear to be in error. The cell parameters were determined from powder diffraction data and are likely to be quite accurate. Mooney measured the crystal density and found it to be identical to that calculated (and significantly different from our measured and calculated density). There are no unexpectedly short bond lengths which might have resulted from misreading or misinterpreting coordinates. We analysed the crystal packing of both the original and the new crystal structures, looking for any unreasonably short intermolecular contacts which might suggest error; there was none. We took the original coordi-

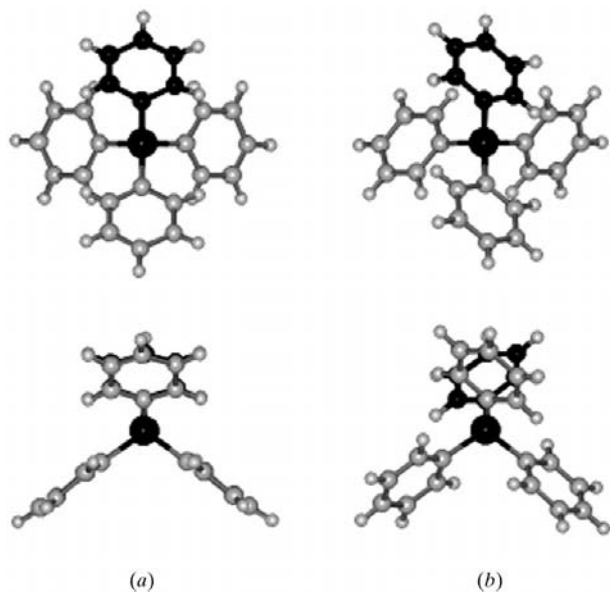


**Figure 1**

A view of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 30% probability level.

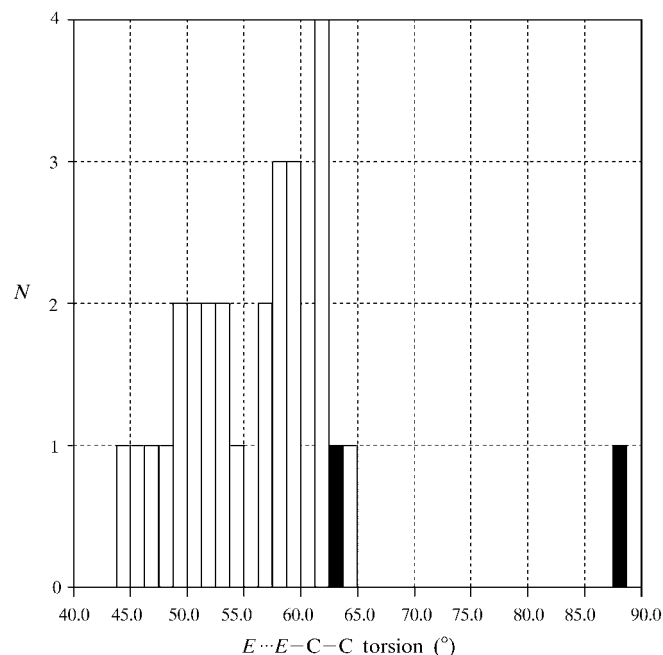
nates as a starting point for refinement using our diffraction data. Not surprisingly, the final result was identical to ours. There is no alternative solution for our data.

We tested the possibility that alternative crystal forms with different torsions of the phenyl rings might occur, or transform, as a result of temperature variation, by making powder diffraction measurements in the temperature range 299–373 K. The reflections 132, 310, 330 and 112 were identified and monitored. The  $2\theta$  variations over the temperature range studied were as follows: for reflection 132, 34.98 (at 299 K) to 34.71° (at 373 K); for reflection 310, 23.08–22.99°; for reflection



**Figure 2**

The conformations of the phenyl rings in  $\text{Ph}_4\text{As}^+$  as found in (a) the original (Mooney, 1940) and (b) the present determination of the crystal structure of (I). One ring is coloured black to emphasize the difference in the ring orientations.



**Figure 3**

Histogram of phenyl-ring torsion angles (°) for species  $\text{Ph}_4\text{E}$  with  $S_4$  symmetry in tetragonal space groups in the CSD. The black outlier is from the original determination (Mooney, 1940) of (I), and the other black entry is for the present determination of (I).

tion 330, 31.17–31.08°; for reflection 112, 27.86–27.64°, consistent with thermal expansion but not indicating a phase change over the temperature range studied. The calculated  $2\theta$  values from our (and Mooney's) crystal structures are: 132 34.99° (34.38°); 310 23.13° (23.06°); 330 31.20° (31.12°); 112 27.93° (27.21°). Our powder results are consistent with our crystal structure but significantly different from those computed from Mooney's structure.

We analysed all other (cationic, anionic and neutral)  $\text{Ph}_4\text{E}$  structures in the CSD which crystallize in tetragonal space groups with  $E$  located on a  $\bar{4}$  site and contiguous  $\text{Ph}_4\text{E}$  along  $c$  separated by 6.8–7.2 Å. These structures all have the molecular packing type which incorporates LIT4PE chains with an  $E \cdots E$  (the tetragonal axial length  $c$ ) distance of about 7 Å. The distribution of phenyl-ring torsion angles is shown in Fig. 3. The black bars correspond to our determination of the structure of (I) and that of Mooney, with the latter being the outlier at 88°. This unusual result is the only one that might lead to some suspicion about the accuracy of the earlier determination.

Despite considering evidence of various types, we leave open to question the existence or otherwise of dimorphs of (I).

## Experimental

Commercial  $\text{Ph}_4\text{P}^+\text{I}^-$  was recrystallized by slow cooling of a hot aqueous solution, giving colourless needles which were shown (by X-ray diffraction) to have unit-cell parameters and atomic coordinates identical to those published for  $\text{Ph}_4\text{P}^+\text{I}^-$  crystallized from  $\text{CH}_2\text{Cl}_2$ -hexane. Commercial  $\text{Ph}_4\text{As}^+\text{Cl}^- \cdot \text{H}_2\text{O}$  was converted into  $\text{Ph}_4\text{As}^+\text{I}^-$  by dissolving equimolar amounts of NaI and  $\text{Ph}_4\text{As}^+$

$\text{Cl}^- \cdot \text{H}_2\text{O}$  in MeOH, and then precipitating NaCl by the addition of acetone. The mixture was filtered and the mixed solvent was removed on a rotary evaporator. Dichloromethane was added to the crude solid product, the mixture was filtered and the solvent was removed from the filtrate on a rotary evaporator. The final solid product, (I), was crystallized from both hot water (as colourless needles; analysis found: C 56.28, H 3.99%; calculated: C 56.49, H 3.95%) and  $\text{CH}_2\text{Cl}_2$ -hexane (as colourless prisms). These crystals had identical unit-cell parameters and preliminary structure determinations indicated that they had the same atomic coordinates. The full X-ray analysis was carried out on the crystals of (I) obtained from  $\text{CH}_2\text{Cl}_2$ -hexane. A site population analysis during the data analysis confirmed that the material was at least 99% pure on a molar basis; no evidence was found for the presence of  $\text{Cl}^-$ . The powder diffraction data for (I) were measured using Cu  $K\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) on a Bruker D5005 X-ray powder diffractometer at 16 temperatures in the range 299–373 K.

## Crystal data

$[\text{As}(\text{C}_6\text{H}_5)_4]\text{I}$	Mo $K\alpha$ radiation
$M_r = 510.3$	Cell parameters from 10 reflections
Tetragonal, $I\bar{4}$	$\theta = 13\text{--}15^\circ$
$a = 12.174 (2) \text{ \AA}$	$\mu = 3.16 \text{ mm}^{-1}$
$c = 6.885 (2) \text{ \AA}$	$T = 294 \text{ K}$
$V = 1020.4 (4) \text{ \AA}^3$	Prism, colourless
$Z = 2$	$0.24 \times 0.12 \times 0.08 \text{ mm}$
$D_x = 1.66 \text{ Mg m}^{-3}$	
$D_m = 1.66 \text{ Mg m}^{-3}$	
$D_m$ measured by flotation in $\text{CCl}_4/\text{CHBr}_3$	

## Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.008$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 25^\circ$
Absorption correction: analytical (de Meulenaer & Tompa, 1965)	$h = 0 \rightarrow 14$
$T_{\text{min}} = 0.70$ , $T_{\text{max}} = 0.77$	$k = 0 \rightarrow 14$
539 measured reflections	$l = 0 \rightarrow 8$
532 independent reflections	1 standard reflection
499 reflections with $I > 2\sigma(I)$	frequency: 30 min
	intensity decay: none

## Refinement

Refinement on $F$	$w = 1/[\sigma^2(F) + 0.0004F^2]$
$R = 0.022$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$wR = 0.030$	$\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$
$S = 1.13$	$\Delta\rho_{\text{min}} = -0.54 \text{ e \AA}^{-3}$
499 reflections	Absolute structure: anomalous scattering (Flack, 1983)
28 parameters	Flack parameter = 0.13 (3)
H-atom parameters constrained	

As and I atoms were refined anisotropically, while the phenyl group was refined with thermal motion described by a 15-parameter TLX group (where **T** is the translation tensor, **L** is the libration tensor

and **X** is the origin of libration, set at the As atom). The phenyl ring was modelled as a planar group with refineable  $mm2$  symmetry. The H atoms of the cation were included in calculated positions and were included in the group thermal for the phenyl ring. The enantiomer was confirmed, the alternative giving  $R = 0.039$  and  $wR = 0.054$ .

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: local program; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *RAELS* (Rae, 2000); molecular graphics: *ORTEPII* (Johnson, 1976) and *CrystalMaker* (Palmer, 2003); software used to prepare material for publication: local programs.

This research was supported by the Australian Research Council and the University of New South Wales. PAWD is grateful to the University of Western Ontario for a sabbatical leave which enabled this work to be carried out. We thank Dr T. C. Deivaraj, Chemistry Department, National University of Singapore, for carrying out the variable-temperature powder XRD measurements.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1032). Services for accessing these data are described at the back of the journal.

## References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Bombicz, P., Czugler, M., Tellgren, R. & Kalman, A. (2003). *Angew. Chem. Int. Ed.* **42**, 1957–1960.
- Dance, I. & Scudder, M. (1996a). *Chem. Eur. J.* **2**, 481–486.
- Dance, I. & Scudder, M. (1996b). *J. Chem. Soc. Dalton Trans.* pp. 3755–3769.
- Dance, I. G. & Scudder, M. L. (2000). *J. Chem. Soc. Dalton Trans.* pp. 1579–1586.
- Dunitz, J. D. & Bernstein, J. (1995). *Acc. Chem. Res.* **28**, 193–200.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Gorobinsky, L. V., Antsyshkina, A. S., Sadikov, G. G., Chernyavsky, A. S., Solntsev, K. A., Sergienko, V. S. & Kuznetsov, N. T. (2001). *Zh. Neorg. Khim.* **46**, 784–790. (In Russian.)
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.
- Mooney, R. C. L. (1940). *J. Am. Chem. Soc.* **62**, 2955–2959.
- Palmer, D. C. (2003). *CrystalMaker*. URL: <http://www.crystallmaker.co.uk>.
- Rae, A. D. (2000). *RAELS*. Australian National University, Canberra, Australia.
- Runsink, J., Swen-Walstra, S. C. & Migchelsen, T. (1972). *Acta Cryst.* **B28**, 1331–1335.
- Schweizer, E. E., Baldacchini, C. J. & Rheingold, A. L. (1989). *Acta Cryst.* **C45**, 1236–1239.