Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0398$
$wR(F^2) = 0.0937$
$S = 1.057$
1897 reflections
127 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0479P)^2 + 0.7312P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.393$ e Å^{-3}
$\Delta\rho_{\min} = -0.241$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S(1)	0.00409 (12)	0.18199 (11)	0.36020 (2)	0.0374 (2)
S(2)	0.16891 (13)	0.46726 (11)	0.29436 (3)	0.0417 (2)
O(1)	−0.1942 (3)	0.2219 (3)	0.32289 (8)	0.0517 (6)
O(2)	0.3436 (4)	0.1360 (3)	0.43134 (7)	0.0544 (6)
O(3)	0.6294 (4)	0.3431 (3)	0.45711 (7)	0.0452 (5)
N(1)	0.6811 (5)	0.7037 (4)	0.38181 (10)	0.0564 (7)
C(1)	0.1667 (5)	−0.0146 (4)	0.33650 (11)	0.0434 (7)
C(2)	0.4489 (5)	0.5728 (5)	0.27759 (10)	0.0459 (7)
C(3)	0.2348 (4)	0.3636 (4)	0.34973 (9)	0.0307 (6)
C(4)	0.4138 (4)	0.4052 (4)	0.38386 (9)	0.0313 (6)
C(5)	0.5666 (5)	0.5693 (4)	0.38189 (9)	0.0383 (7)
C(6)	0.4553 (5)	0.2796 (4)	0.42614 (9)	0.0364 (6)
C(7)	0.6812 (6)	0.2176 (5)	0.49853 (11)	0.0604 (10)
C(8)	0.9026 (6)	0.2827 (6)	0.52545 (13)	0.0671 (11)

Table 2. *Selected geometric parameters* (Å, °)

S(1)—O(1)	1.482 (2)	O(3)—C(7)	1.461 (4)
S(1)—C(1)	1.794 (3)	N(1)—C(5)	1.137 (4)
S(1)—C(3)	1.837 (3)	C(3)—C(4)	1.354 (4)
S(2)—C(3)	1.716 (3)	C(4)—C(5)	1.431 (4)
S(2)—C(2)	1.797 (3)	C(4)—C(6)	1.473 (4)
O(2)—C(6)	1.196 (3)	C(7)—C(8)	1.462 (4)
O(3)—C(6)	1.323 (3)		
C(4)—C(3)—S(2)	129.5 (2)	C(3)—C(4)—C(5)	123.5 (2)
C(4)—C(3)—S(1)	121.3 (2)	C(3)—C(4)—C(6)	119.7 (2)
S(2)—C(3)—S(1)	109.10 (14)	C(5)—C(4)—C(6)	116.9 (2)

H atoms were added at calculated positions and refined using a riding model. The H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the atom to which the H atom is attached.

Data collection: Siemens *P*3*R*3 system. Cell refinement: Siemens *P*3*R*3 system. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*.

We wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1239). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Diphenylarsenic(III) Iodide

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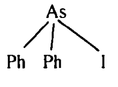
Abstract

$AsPh_2I$ (iododiphenylarsine) contains arsenic in trigonal pyramidal coordination with iodine and two phenyl groups, with effectively equal As—C distances [1.953 (6) and 1.942 (6) Å]. Bond angles at arsenic are 101.7 (2)° between the phenyl groups and a mean of 97.5° between iodine and phenyl. There are no intermolecular As···I interactions shorter than 4.4 Å.

Comment

Although there has been recent interest in the structures of a range of arylantimony(III) halides, including $SbPhX_2$, where X = Cl, Br or I (Mundt, Becker, Stadelmann & Thurn, 1992), $SbArX_2$, where Ar = 4-tolyl and X = Cl or Br, and $SbPh_2Br$ (Millington & Sowerby, 1994), structural information for related As compounds is limited to results from film data for the isostructural diphenylarsenic chloride (Trotter, 1962*a*), bromide (Trotter, 1962*b*) and iodide (Trotter, 1963). For the iodide, only the As—I distance (2.53 Å) was reported.

Features of interest in the antimony structures are (*a*) the formation of intermolecular halogen bridges, particularly for the monoaryl derivatives, and (*b*) the presence of weak asymmetric intermolecular interactions between antimony and the aryl group of a neighbouring molecule. The latter are reminiscent of the interations present in the well known Menshutkin complexes (Schmidbaur, Bublak, Huber & Müller, 1987). Similar features are possible with the arsenic analogues and, as we have recently obtained crystals of diphenylarsenic iodide, (I), its structure has been redetermined from three-dimensional X-ray data.



(I)

The structure with the atom-numbering scheme is shown in Fig. 1. The As atom is connected to two phenyl groups at effectively equal distances (mean 1.948 Å) and an I atom at 2.600 (1) Å. This is a little longer than the sum of the covalent radii (2.54 Å) (Emsley, 1991), and should be compared with values of 2.58 Å in racemic *o*-phenylenebis(iodomethylarsine) (Henrick, Raston, White & Wild, 1977) and 2.522 (4) Å in the iodotetramethyldiarsenic cation, $[Me_2AsAsMe_2I]^+$ (Boardman, Small & Worrall, 1986). The only other As—I distance reported for an organoarsenic compound is that for the triphenylarsenic iodine complex $AsPh_3.I_2$ (2.64 Å) (McAuliffe, Beagley, Gott, Mackie, MacRory & Pritchard, 1987), but further comparisons may be made with the As—I distances in arsenic triiodide itself [2.59 (1) Å] (Enjalbert & Galy, 1980) and in an AsI_3 complex with (tetramethyl)(hexathia)adamantane (mean 2.58 Å) (Kniep & Reski, 1982). Distances and angles within the phenyl groups are normal.

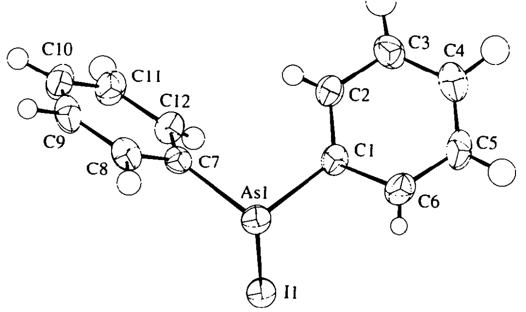


Fig. 1. Structure of $AsPh_2I$, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H-atom radii reflect the U_{iso} values.

As expected, the coordination about arsenic is trigonal pyramidal, as a consequence of the stereochemically active lone pair of electrons on arsenic, with a wider angle between the two phenyl groups [101.7 (2)°] than between iodine and phenyl (mean 97.5°). As there are no reports of accurate structure determinations for any diorganoarsenic halides, perhaps the most useful comparison is with diphenylantimony bromide (Millington & Sowerby, 1994), where the same order of bond angles is observed but, because of the greater size of antimony, the C—Sb—C angle is reduced to 98.5 (3)° and the C—Sb—Br angles to 93.5 (2) and 95.3 (2)°.

There are no intermolecular As···I interactions within 4.4 Å, the sum of the As and I van der Waals radii, probably as a consequence of the low Lewis acidity of the As-atom centre; in this respect $AsPh_2I$ is similar to $SbPh_2Br$.

There are, however, significant interactions (3.32–3.49 Å) in both phenyl and *p*-tolyl antimony dichlorides and dibromides; these occur between between the Group 15 element and three of the C atoms of a symmetry-related phenyl group. Corresponding interactions in diphenylantimony bromide are much reduced (contacts to two C atoms at *ca* 3.65 Å) while in the present case, it is doubtful if the related As···C contacts are significant as the closest are 3.73 (1) and 3.70 (1) Å to C(3) and C(4), respectively, of a phenyl group related by the symmetry operation $1-x$, $1-y$, $2-z$.

A further similarity between the structures of $AsPh_2I$ and $SbPh_2Br$ is seen in the equivalent phenyl group orientations in the two compounds, defined by the torsion angles (values for the $SbPh_2Br$ equivalents in parentheses): I(1)—As(1)—C(1)—C(2) 109.7 (6) (104.4), I(1)—As(1)—C(7)—C(8) 131.7 (4) (137.6), C(1)—As(1)—C(7)—C(8) −129.3 (5) (−128.0), C(7)—As(1)—C(1)—C(2) 9.9 (6) (8.5)°.

Experimental

Diphenylarsenic iodide was obtained as a by-product in a reaction between iodine and oxobis[diphenylarsenic(III)]. Although the compound can be obtained *via* metathesis between the corresponding chloride and sodium iodide in acetone solution (Steinkopf & Schwen, 1921), it can also be obtained by treating oxobis[diphenylarsenic(III)] with HI (Pope & Turner, 1920). In the present case, the iodide clearly results from hydrolysis during the reaction with iodine. Crystals suitable for X-ray investigation were grown from ethanol and mounted on a glass fibre.

Crystal data

$C_{12}H_{10}AsI$
$M_r = 356.1$
Monoclinic
$P2_1/a$
$a = 11.002\ (6)$ Å
$b = 8.857\ (4)$ Å
$c = 12.246\ (5)$ Å
$\beta = 91.38\ (3)°$
$V = 1193.0\ (10)$ Å^3
$Z = 4$
$D_x = 1.982$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 12 reflections
$\theta = 12–16°$
$\mu = 5.4$ mm^{-1}
$T = 293$ K
Prism
0.50 × 0.35 × 0.30 mm
Pale yellow

Data collection

Hilger Y290 diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.14$, $T_{\max} = 0.23$
2259 measured reflections
2259 independent reflections
1755 observed reflections [$I > 3\sigma(I)$]
$\theta_{\max} = 25°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 9$
$l = -15 \rightarrow 15$
3 standard reflections monitored every 100 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.039$
$wR = 0.045$
1755 reflections
167 parameters
All H-atom parameters refined
Weights: four-parameter Chebyshev polynomial
$(\Delta/\sigma)_{\max} = 0.02$
$\Delta\rho_{\max} = 0.53$ e Å^{-3}
$\Delta\rho_{\min} = -0.62$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
I(1)	0.58009 (5)	0.08604 (5)	0.69855 (4)	0.0586
As(1)	0.48010 (5)	0.33026 (8)	0.77258 (5)	0.0488
C(1)	0.5679 (5)	0.3360 (7)	0.9120 (5)	0.0449
C(2)	0.6551 (6)	0.4398 (9)	0.9395 (6)	0.0522
C(3)	0.7107 (7)	0.438 (1)	1.0436 (6)	0.0633
C(4)	0.6767 (8)	0.334 (1)	1.1183 (6)	0.0659
C(5)	0.5892 (9)	0.231 (1)	1.0928 (6)	0.0662
C(6)	0.5331 (8)	0.233 (1)	0.9904 (6)	0.0622
C(7)	0.5708 (5)	0.4767 (7)	0.6875 (4)	0.0441
C(8)	0.5007 (6)	0.5866 (8)	0.6349 (5)	0.0545
C(9)	0.5559 (8)	0.6942 (8)	0.5709 (5)	0.0601
C(10)	0.6795 (9)	0.6902 (9)	0.5564 (6)	0.0649
C(11)	0.7496 (8)	0.5800 (9)	0.6073 (6)	0.0650
C(12)	0.6946 (6)	0.4731 (8)	0.6724 (5)	0.0515

Table 2. *Selected geometric parameters* (Å, °)

I(1)—As(1)	2.600 (1)	As(1)—C(7)	1.953 (6)
As(1)—C(1)	1.942 (6)		
C(1)—As(1)—I(1)	97.0 (2)	C(6)—C(1)—As(1)	116.9 (6)
C(7)—As(1)—I(1)	98.1 (2)	C(8)—C(7)—As(1)	115.3 (5)
C(7)—As(1)—C(1)	101.7 (2)	C(12)—C(7)—As(1)	125.1 (5)
C(2)—C(1)—As(1)	124.5 (5)		

The structure was solved using *MULTAN* (Main *et al.*, 1980) and refined using the *CRYSTALS* program package (Watkin, Carruthers & Betteridge, 1985).

This work was supported by the British Council through the ROMLISS program.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, and a packing diagram of the title compound have been deposited with the IUCr (Reference: MU1163). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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L-(+)-α-Bromobenzeneacetic Acid (−)-Menthyl Ester

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Abstract

The crystal structure of L-(+)-α-bromobenzeneacetic acid (−)-menthyl ester ($C_{18}H_{25}BrO_2$) is reported. The Br atom and the O(carbonyl) atom are in *trans* positions. The 1-methyl-4-isopropylcyclohexane ring has a chair conformation. The dihedral angle between the least-squares plane through the phenyl ring and the least-squares plane of the C—CO_2 group is 45.0 (2)°. The bond distances and angles of the molecule are in the normal ranges.

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