

Refinement

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

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	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 ($\text{\AA}$, $^\circ$)

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 P3R3 system. Cell refinement: Siemens P3R3 system. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL93* (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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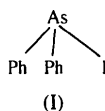
Abstract

AsPh₂I (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) $\text{\AA}$]. 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 $\text{\AA}$.

Comment

Although there has been recent interest in the structures of a range of arylantimony(III) halides, including SbPhX₂, where X = Cl, Br or I (Mundt, Becker, Stadelmann & Thurn, 1992), SbArX₂, where Ar = 4-tolyl and X = Cl or Br, and SbPh₂Br (Millington & Sowerby, 1994), structural information for related As compounds is limited to results from film data for the isostructural diphenylarsenic chloride (Trotter, 1962a), bromide (Trotter, 1962b) and iodide (Trotter, 1963). For the iodide, only the As—I distance (2.53 $\text{\AA}$) 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 interactions 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.



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, [Me₂AsAsMe₂I]⁺ (Boardman, Small & Worrall, 1986). The only other As—I distance reported for an organoarsenic compound is that for the triphenylarsenic iodine complex AsPh₃·I₂ (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 AsI₃ complex with (tetramethyl)(hexathia)adamantane (mean 2.58 Å) (Knief & Reski, 1982). Distances and angles within the phenyl groups are normal.

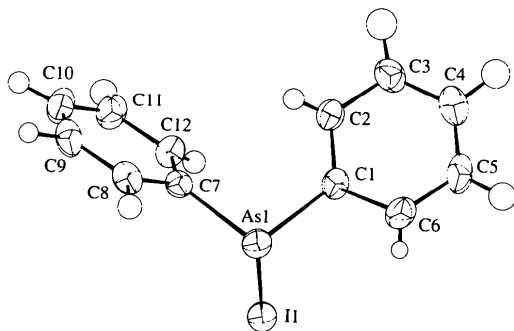


Fig. 1. Structure of AsPh₂I, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H-atom radii reflect the U_{iso} values.

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 AsPh₂I is similar to SbPh₂Br.

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 AsPh₂I and SbPh₂Br is seen in the equivalent phenyl group orientations in the two compounds, defined by the torsion angles (values for the SbPh₂Br 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

C₁₂H₁₀AsI
 $M_r = 356.1$
 Monoclinic
 $P2_1/a$
 $a = 11.002 (6) \text{ Å}$
 $b = 8.857 (4) \text{ Å}$
 $c = 12.246 (5) \text{ Å}$
 $\beta = 91.38 (3)^\circ$
 $V = 1193.0 (10) \text{ Å}^3$
 $Z = 4$
 $D_x = 1.982 \text{ Mg m}^{-3}$

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

Data collection

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

Refinement

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

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$)

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{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 ($\text{\AA}$, $^\circ$)

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 (C₁₈H₂₅BrO₂) 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—CO₂ group is 45.0 (2)°. The bond distances and angles of the molecule are in the normal ranges.