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Dibromotriphenylantimony(V), a Second Polymorph

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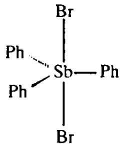
Abstract

The title compound, $[SbBr_2(C_6H_5)_3]$, contains discrete trigonal-bipyramidal molecules and is a polymorph of a previously reported structure. The relationship to the previous structure is presented, the main chemical difference being in the Br—Sb—C—C torsion angles. The preferred conformations of various Ph_3EX_2 (E = Group 15 element and X = halogen) molecules are displayed graphically.

Comment

Compounds of type Ph_3EX_2 (E = Group 15 element and X = halogen) have been extensively studied both in the solid state and in solution. The major structural type in the solid is trigonal bipyramidal (tbp) with axial X, although an alternative type with four-coordinate E and retaining an X—X bond Ph_3E—X—X is known for E = P, X = Br or I, and E = As, X = I (for a summary see Bricklebank *et al.*, 1994). Ph_3SbI_2 presents an interesting example with three polymorphs being reported: triclinic $P\bar{1}$ (Bricklebank *et al.*, 1994), orthorhombic $Fdd2$ and cubic $P4_332$ (Baker *et al.*, 1995), all containing the tbp form. In addition, the same molecule occurs in the species $[Ph_4Sb][FeCl_4]$.-Ph_3SbI_2 (Lane *et al.*, 1994). The structure of Ph_3SbBr_2, (I), has been reported (Begley & Sowerby, 1993) as being isomorphous with the orthorhombic form of the iodide. During attempts to grow crystals of $[Mo(CO)_3$-$(Ph_3Sb)_2Br_2]$, colourless crystals were obtained which subsequently turned out to be Ph_3SbBr_2. This has been prepared from Ph_3Sb and Br_2 (1:1) using chloroform (Begley & Sowerby, 1993) or diethyl ether (Baker *et al.*, 1995) solvents. The solid was subsequently prepared using chloroform as solvent and good quality crystals were obtained by layering EtOH onto a solution in CH_2Cl_2. These crystals were usually twinned, but the orthorhombic cell of Begley & Sowerby (1993) was obtained for one crystal, together with monoclinic forms for other crystals from the same batch.



(I)

The structure of Ph_3SbBr_2 in the monoclinic form consists of discrete tbp molecules with two independent molecules in the asymmetric unit (Fig. 1 and Table 1). Each molecule has no crystallographic symmetry and the major difference in geometry is the conformation of the phenyl rings (Table 1). With four molecules in the unit cell and space group Pa there is the suspicion of missed symmetry; however, a centre of symmetry could not be found and the form of some of the displacement ellipsoids suggests disorder may be present, although this has not been resolved. The transformation $\mathbf{a}' = \mathbf{a} - \mathbf{c}$, $\mathbf{b}' = \mathbf{b}$, $\mathbf{c}' = \mathbf{a} + \mathbf{c}$ gives $a' = 23.774$, $b' = 10.159$, $c' = 14.258$ Å and $\beta' = 91.37°$, and this illustrates the relationship to the F-orthorhombic cell and the structure

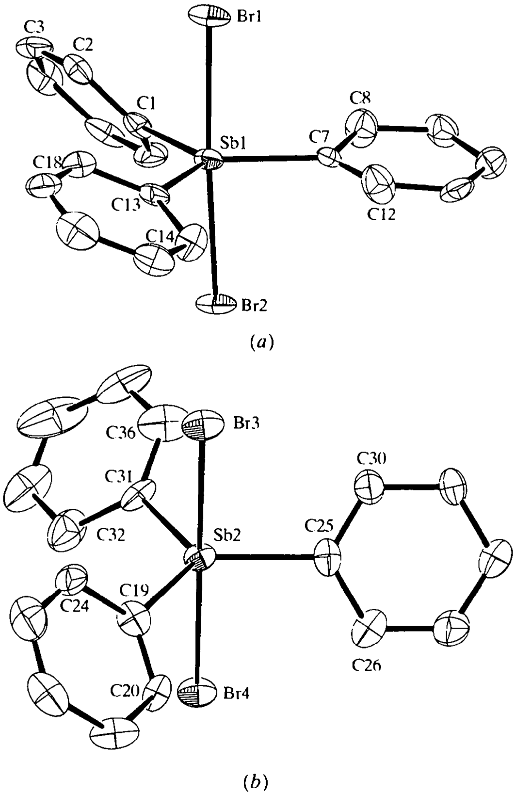


Fig. 1. The two independent molecules in the monoclinic form of Ph_3SbBr_2 showing the atom-labelling scheme (ring atoms numbered sequentially). Displacement ellipsoids are drawn at the 50% probability level.

previously reported (Begley & Sowerby, 1993). Small changes to the orientation and the phenyl-ring torsion angles would enable the transformation.

The structures of a number of tbp Ph_3EX_2 molecules are available from the Cambridge Structural Database (Allen & Kennard, 1993). The highest point-group symmetry of the C_3EX_2 framework is D_{3h} ($\bar{6}m2$), but this is retained after the inclusion of phenyl groups only when the three rings are either parallel or perpendicular to the triad axis. Following the methods developed by Dunitz and co-workers for Ph_3PO (Bye *et al.*, 1982; Dunitz, 1979), it seemed appropriate to explore the torsion-angle parameter space adopted by this group of molecules. The symmetry of the three torsion angles is isomorphic with the trigonal space group $R\bar{3}m$ (No. 166). Transforming to hexagonal axes for ease of representation allows the three torsion angles of each example drawn from the database to be represented by a point (together with its symmetry-related points). A view of these points viewed down the hexagonal *c* axis is shown in Fig. 2 using 25 structures, including the present one, where points on the threefold axis have all three torsion angles the same ('propeller' arrangement) and lines joining threefold axes have two torsion angles the same (and different from the third). Certain areas of the map are not populated (by the rather small sample) and represent regions with unfavourable angles. A view perpendicular to the *c* axis did not show marked clustering of points.

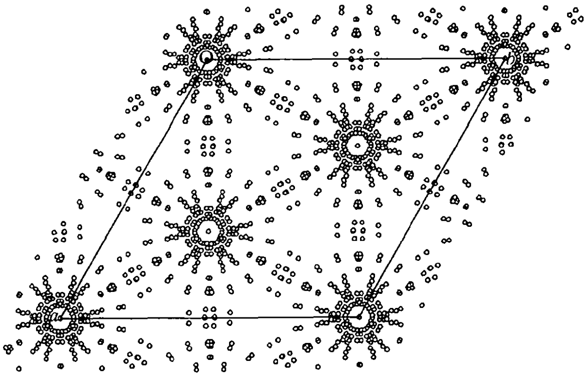


Fig. 2. The distribution of phenyl-group torsion angles (*X*—*E*—C—C) in trigonal-bipyramidal Ph_3EX_2 species (*X* = halogen) (see *Comment*).

Experimental

During attempts to grow crystals of $[Mo(CO)_3(Ph_3Sb)_2Br_2]$, colourless crystals of (I) were obtained which subsequently turned out to be Ph_3SbBr_2 (see *Comment*).

Crystal data

$[SbBr_2(C_6H_5)_3]$
$M_r = 512.87$
Monoclinic
Pa
$a = 13.714\ (4)$ Å
$b = 10.159\ (3)$ Å
$c = 14.006\ (2)$ Å
$\beta = 118.10\ (2)°$
$V = 1721.3\ (9)$ Å^3
$Z = 4$
$D_x = 1.979$ Mg m^{-3}
D_m not measured

Mo *Kα* radiation
$\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 18.9–21.1°$
$\mu = 6.236$ mm^{-1}
$T = 150\ (2)$ K
Plate
0.40 × 0.20 × 0.10 mm
Colourless

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical ψ scan (North *et al.*, 1968)
$T_{min} = 0.306$, $T_{max} = 0.535$
3359 measured reflections
3172 independent reflections

2310 reflections with $I > 2\sigma(I)$
$R_{int} = 0.042$
$\theta_{max} = 25.0°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 12$
$l = -16 \rightarrow 14$
3 standard reflections every 150 reflections intensity decay: 1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.148$
$S = 1.040$
3172 reflections
379 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.1008P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.100$

$\Delta\rho_{max} = 1.803$ e Å^{-3}
$\Delta\rho_{min} = -2.767$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.00 (2)

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

Sb1—Br1	2.634 (3)	Sb2—Br3	2.638 (3)
Sb1—Br2	2.629 (2)	Sb2—Br4	2.652 (2)
Sb1—C1	2.135 (16)	Sb2—C19	2.134 (18)
Sb1—C7	2.082 (17)	Sb2—C25	2.110 (17)
Sb1—C13	2.111 (17)	Sb2—C31	2.102 (18)
C7—Sb1—C13	121.1 (7)	C31—Sb2—C25	118.1 (8)
C7—Sb1—C1	119.6 (7)	C31—Sb2—C19	120.4 (7)
C13—Sb1—C1	119.4 (7)	C25—Sb2—C19	121.6 (7)
C7—Sb1—Br2	86.4 (5)	C31—Sb2—Br3	90.0 (5)
C13—Sb1—Br2	91.5 (5)	C25—Sb2—Br3	89.9 (5)
C1—Sb1—Br2	91.8 (5)	C19—Sb2—Br3	90.5 (5)
C7—Sb1—Br1	90.7 (5)	C31—Sb2—Br4	91.0 (5)
C13—Sb1—Br1	87.3 (5)	C25—Sb2—Br4	89.9 (5)
C1—Sb1—Br1	92.4 (5)	C19—Sb2—Br4	88.7 (5)
Br2—Sb1—Br1	175.74 (9)	Br3—Sb2—Br4	178.91 (9)
Br1—Sb1—C1—C2	−37.6 (14)	Br3—Sb2—C19—C20	−133.9 (15)
Br1—Sb1—C7—C8	−89.2 (16)	Br3—Sb2—C25—C26	135.8 (15)
Br1—Sb1—C13—C14	−113.2 (16)	Br3—Sb2—C31—C32	−130.5 (16)

The crystal was mounted in oil on a glass fibre for low-temperature X-ray examination. The largest peaks in the final difference map were *ca* 1 Å from Sb1. A rigid bond restraint (*DELU*) was applied to the phenyl groups.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*II (Johnson, 1976).

I thank EPSRC for funds to purchase the diffractometer and access to the Chemical Database Service at Daresbury Laboratory.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1211). Services for accessing these data are described at the back of the journal.

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(1,2-Benzenedicarbonitrile-κN)diiodo(phthalocyaninato-$\kappa^4 N$)zirconium(IV)

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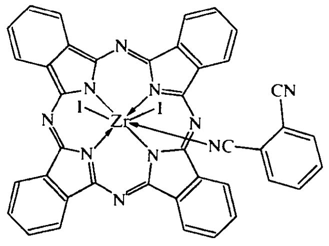
Abstract

A new zirconium phthalocyanine complex [$ZrI_2(Pc)\{C_6H_4(CN)_2\}$] (Pc = $C_{32}H_{16}N_8$) was obtained in crystalline form by the reaction of zirconium with 1,2-dicyanobenzene (*o*-DCB) under a stream of iodine. The molecule is a reaction product of zirconium, I atoms and *o*-DCB molecules, four of which form the Pc macrocycle. The crystal structure of this compound consists of discrete molecules in which seven-coordinate Zr^{IV} is surrounded by four N atoms of the phthalocyaninato ligand, two *cis*-I atoms and an N atom from one of the cyano groups of the fifth *o*-DCB molecule. A set of hydrogen-bonded interactions links the molecules in the crystal lattice.

Comment

The iodination of metallophthalocyanines provides a large class of materials with potentially useful properties (Kasuga & Tsutsui, 1980). We present here a portion of our work in this area which is related to the synthesis and structures of iodometallophthalocyanines (Ejsmont & Kubiak, 1997; Kubiak & Janczak, 1997).

The chemical composition of the title compound $I_2Zr(C_8H_4N_2)_5$, (1), is analogous to $O_2U(C_8H_4N_2)_5$, (2) (Day *et al.*, 1975). However, in (2), all five *o*-DCB units are part of the macrocycle and a super-phthalocyanine (SPc = $C_{40}H_{20}N_{10}$) is formed so that the conjugated π-electron ring system comprises all C and N atoms. In (1), a normal phthalocyanine ring involving four $C_8H_4N_2$ subunits does exist, but the fifth *o*-DCB molecule is ligated to the central Zr atom through the N atom of one of its two cyano groups. Thus (1) could also be written in the form $(PcZrI_2)(NC)C_6H_4(CN)$. There are also five *o*-DCB molecules in the compound $[(PcNb)_2O_2Br]^+.Br_3^-$. However, in this case, the fifth *o*-DCB residue is a discrete molecule of crystallization (Gingl & Strähle, 1989).



(1)

The seven-coordinate Zr^{IV} atom in (1) is surrounded by the four isoindole N atoms (N_4) of the Pc ring, two *cis*-I atoms and an N atom from one of the cyano groups of the fifth *o*-DCB molecule. The Zr atom lies 1.067 (2) Å above the N_4 plane. This value is slightly smaller than that observed in $ZrPc_2$ (1.10 Å; Silver *et al.*, 1991). The average interatomic distances in the phthalocyanine ring are 1.388 (3) for C—N_4, 1.315 (3) for C—N_{azam} (N_{azam} is an azamethine N atom) and 1.399 (6) Å for C—C. These distances are in agreement with other phthalocyanine macrocycles and, in particular, those for $ZrPc_2$ (Silver *et al.*, 1991).

The ligated fifth *o*-DCB unit evidently differs in structure from free *o*-DCB (Janczak & Kubiak, 1995)