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Tris[2-(morpholin-4-ylmethyl)phenyl-κ^2C^1,N]antimony(III)

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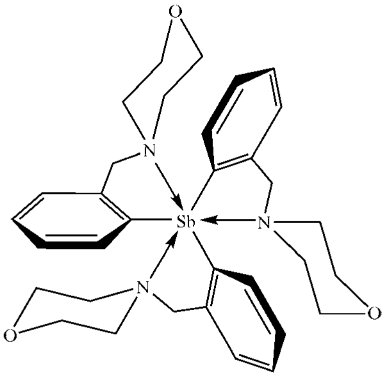
The title compound, [Sb($C_{11}H_{14}NO$)$_3$], is monomeric with the Sb atom located on a threefold axis. The complex exhibits distorted trigonal–antiprismatic geometry around the Sb atom, owing to the presence of intramolecular N→Sb interactions. H···phenyl intermolecular interactions lead to the formation of dimers stacked along the *c* axis. The morpholine rings exhibit almost ideal chair conformations. No intermolecular interactions between the morpholine rings of neighbouring molecules were observed.

Comment

Triorganoantimony compounds have attracted increased interest in recent years as ligands in transition metal chemistry, owing to the different electronic properties of stibines compared with their lighter analogues (Levason & Reid, 2006). Trialkylantimony derivatives are air sensitive and strong reducing agents, in contrast to the aryl derivatives (Breunig & Wagner, 2007). Optically active 2,2′-bis(diarylstibano)-1,1′-binaphthyl compounds [aryl is *p*-tolyl (*p*-tol) or phenyl] are effective chiral ligands for rhodium-catalysed asymmetric reduction of prochiral ketones to secondary alcohols (Yasuike *et al.*, 2000, 2003). Recently, an asymmetric stibine, phenyl(1-phenylethynyl)mesitylstibine, was successfully used as a ligand in order to modify the $Co_2(CO)_8$ catalytic system for alkene amidocarbonylation (Wakamatsu reaction) under mild conditions (Gomez *et al.*, 2007).

Symmetric triorganoantimony(III) compounds containing aromatic groups bearing one pendant arm able to establish N→Sb intramolecular coordination {*e.g.* 2-(Me_2NCH_2)C_6H_4, (II) (Kamepalli *et al.*, 1996; Sharma *et al.*, 2004), 2-(Me_2NCHMe)C_6H_4Me, (III) (Sharma *et al.*, 2004), 2-[(*p*-tol)-CH(CH_3)NCH]C_6H_4, (IV), and 2-[($HOCH_2$)CH(CH_2CH_3)-NCH]C_6H_4, (V) (Sharma *et al.*, 2007)} have been reported.

In order to investigate the influence of the pendant arm attached to an aromatic ring on the antimony centre, we performed the synthesis and structural characterization of the title compound, (I). Compound (I) is monomeric (Fig. 1). The molecule contains three 2-[O(CH_2CH_2)$_2NCH_2$]C_6H_4 units bonded to an Sb atom, which lies on a threefold axis of the space group $R\overline{3}$, so the primary monomeric unit is generated by symmetry.



(I)

The primary coordination polyhedron consists of a trigonal–pyramidal SbC_3 skeleton. Including the three intramolecular N→Sb interactions, the Sb atom can be described as six-coordinate. The geometry around antimony is a distorted trigonal antiprism; three C atoms describe one triangular base of the antiprism, parallel to the triangular base described by the three N atoms from the pendant arms of the morpholine groups (the distance between the C_3 and N_3 planes is 1.7877 Å). The distortion is the result of the opening on the N_3Sb face as evidenced by the large N—Sb—N angles [115.65 (6)°] compared with the C—Sb—C angles [95.54 (11)°]. The bond distances between the Sb and C atoms [2.167 (3) Å] are similar to those in other triorganoantimony derivatives [2.18 (1) Å in (II), 2.17 (1) Å in (III), 2.20 (3) Å in (IV) and 2.18 (1) Å in (V)]. The Sb—N distances in (I) [3.15 (1) Å] lie between the sums of the respective covalent [$\Sigma r_{\rm cov}$(Sb,N) = 2.11 Å] and van der Waals radii [$\Sigma r_{\rm vdW}$(Sb,N) =

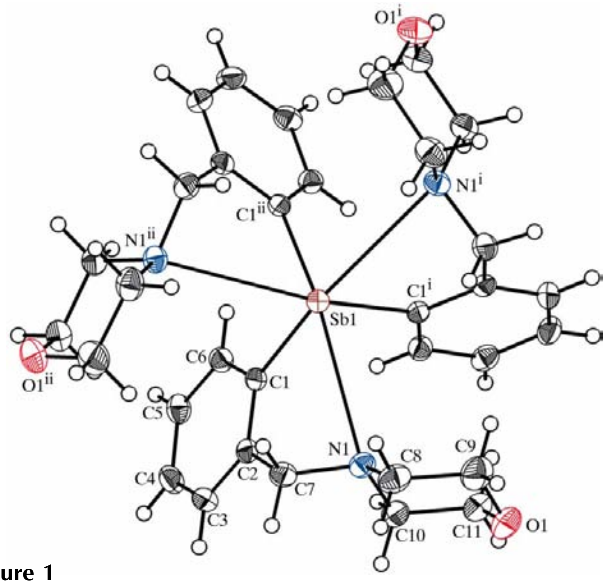


Figure 1
A view of (I), showing the atom-numbering scheme (30% probability displacement ellipsoids) for the $R_{\rm N}$,$R_{\rm N}{}^{\rm i}$,$R_{\rm N}{}^{\rm ii}$ isomer. [Symmetry codes: (i) $1 - y, 1 + x - y, z$; (ii) $-x + y, 1 - x, z$.]

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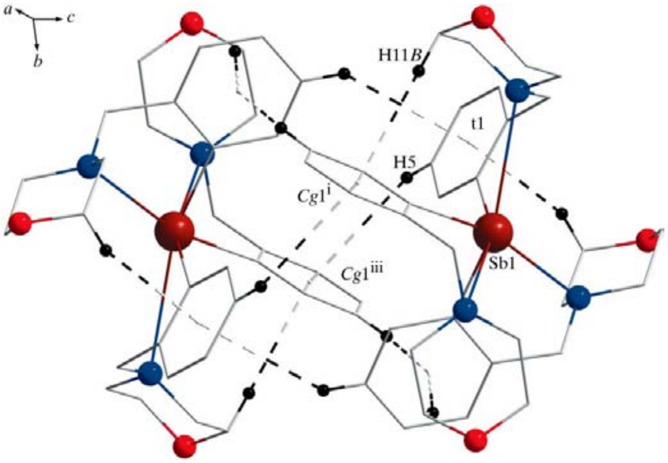

Figure 2
The dimer of the title compound. H$\cdots$Ph interactions are shown as dashed lines. Only H atoms involved in these interactions are shown. [Symmetry codes: (i) $1 - y, 1 + x - y, z$; (iii) $-\frac{1}{3} + y, \frac{1}{3} - x + y, \frac{1}{3} - z$.]

3.74 Å] (Emsley, 1994), and are longer than those in related compounds [3.05 (5) Å in (II), 2.95 (5) Å in (III), 2.92 (4) Å in (IV) and 2.87 (2) Å in (V)] owing to the bulkiness of the morpholine rings of the pendant arms. The Sb atom deviates from the N_3 plane by 0.6639 (3) Å and from the C_3 plane by 1.1238 (3) Å. An almost ideal chair conformation was observed for the morpholine groups, with torsion angles [C8—N1—C10—C11 = 54.0 (4)° and C11—O1—C9—C8 = −60.3 (4)°] similar to those found in 4-benzylmorpholin-4-ium chloride (Copolovici *et al.*, 2007).

As a result of the intramolecular N→Sb interactions, nonplanar five-membered rings are formed, with the N atoms lying out of the Sb1/C1/C2/C7 mean plane. The chelate ring exhibits a dihedral angle of 57.67 (1)° between the Sb/N/C and Sb/C/C/C planes. This induces planar chirality (with the aromatic ring and the N atom as chiral plane and pilot atom, respectively; IUPAC, 1979). The compound crystallizes as a racemate, *i.e.* a mixture of $R_N,R_N{}^{i},R_N{}^{ii}$ and $S_N{}^{iii},S_N{}^{iv},S_N{}^{v}$ isomers [symmetry codes: (i) $1 - y, 1 + x - y, z$; (ii) $-x + y, 1 - x, z$; (iii) $-\frac{1}{3} + y, \frac{1}{3} - x + y, \frac{1}{3} - z$; (iv) $\frac{2}{3} + x - y, \frac{1}{3} + x, \frac{1}{3} - z$; (v) $\frac{2}{3} - x, \frac{4}{3} - y, \frac{1}{3} - z$].

One H atom from the morpholine ring is involved in an intramolecular H$\cdots$Ph interaction (H5$\cdots$$Cg1^{i}$; Table 1), while one aromatic H atom forms a weaker intermolecular H$\cdots$Ph interaction (H11*B*$\cdots$$Cg2^{iii}$), thus resulting in a dimeric unit that contains the two $R_N,R_N{}^{i},R_N{}^{ii}$ and $S_N{}^{iii},S_N{}^{iv},S_N{}^{v}$ isomers (Fig. 2).

In the crystal structure, the two isomers are arranged alternately and stacked along the *c* axis, with staggered positions of the different isomers and intercalated positions for the same isomers, with no intermolecular interactions between the dimeric units.

Experimental

A solution of BuLi in hexane (51 ml, 1.6 *M*, 81.89 mmol) was added dropwise to a stirred solution of {2-[O(CH$_2$CH$_2$)$_2$NCH$_2$]C$_6$H$_4$}Br (20.976 g, 81.89 mmol) in hexane (125 ml). The reaction mixture was stirred overnight at room temperature, the solvent removed with a syringe and the resulting white solid, {2-[O(CH$_2$CH$_2$)$_2$NCH$_2$]-C$_6$H$_4$}Li, washed with hexane and dried under vacuum. Freshly sublimed $SbCl_3$ (4.53 g, 19.85 mmol) dissolved in Et_2O (100 ml) was added dropwise to a cooled (195 K) suspension of {2-[O(CH$_2$CH$_2$)$_2$-NCH$_2$]C$_6$H$_4$}Li (12.50 g, 68.23 mmol, excess) in Et_2O (300 ml). The reaction mixture was stirred at 195 K for 1 h and then overnight while warming to room temperature. The solvent was removed under vacuum and extraction with CH_2Cl_2 was performed to obtain a yellow solution. Colourless crystals suitable for X-ray diffraction studies were obtained from the concentrated CH_2Cl_2 solution, maintained at 245 K (yield 8.76 g, 68%; m.p. 523 K). Analysis found: C 60.60, H 6.79, N 6.48%; calculated for $C_{33}H_{42}N_3O_3Sb$: C 60.94, H 6.51, N 6.46%. ^{1}H NMR (300 MHz, CDCl$_3$, 291 K): δ 2.21 (4H, *s*, *br*, N—CH$_2$—CH$_2$—O), 3.06 (4H, *s*, *br*, N—CH$_2$—CH$_2$—O), 4.06 (2H, *s*, *br*, C$_6$H$_4$—CH$_2$—N), 7.05 (1H, *m*, C$_6$H$_4$), 7.19 (3H, *m*, C$_6$H$_4$). ^{13}C NMR (75.4 MHz, CDCl$_3$, 291 K): δ 52.94 (*s*, N—CH$_2$—CH$_2$—O), 65.91, 66.28 (*s*, N—CH$_2$—CH$_2$—O, C$_6$H$_4$—CH$_2$—N), 127.29, 127.33, 129.55 (*s*, C-3–5), 137.48 (*s*, C-6), 142.67, 144.58 (*s*, C-1,2). MS [CI$_{pos}$, NH$_3$, *m/z* (%)]: 650 (2) [*M* + H]$^+$, 473 (100) [*M*-{2-O(CH$_2$CH$_2$)$_2$N-CH$_2$}C$_6$H$_4$]$^+$, 178 (89) [{2-O(CH$_2$CH$_2$)$_2$NCH$_2$}C$_6$H$_4$ + 2H]$^+$, 88 (34) [2-{O(CH$_2$CH$_2$)$_2$NCH$_2$}C$_6$H$_4$]$^+$.

Crystal data

$[Sb(C_{11}H_{14}NO)_3]$
$M_r = 650.45$
Rhombohedral, $R\bar{3}$
$a = 19.026\ (3)$ Å
$c = 14.521\ (5)$ Å
$\gamma = 120°$
$V = 4552.4\ (17)$ Å^3
$Z = 6$
Mo $K\alpha$ radiation
$\mu = 0.95$ mm^{-1}
$T = 297\ (2)$ K
0.20 × 0.13 × 0.10 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SAINT-Plus*; Bruker, 2000)
$T_{min} = 0.833$, $T_{max} = 0.911$
12299 measured reflections
2050 independent reflections
1872 reflections with $I > 2\sigma(I)$
$R_{int} = 0.062$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.081$
$S = 1.12$
1878 reflections
121 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 1.23$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}

Table 1
Y—H$\cdots\pi$-ring interactions (Å, °).

*Cg*1 is the centroid of the C1–C6 benzene ring.

Y—H$\cdots$*Cg*	Y—H	H$\cdots$*Cg*	$Y\cdots$*Cg*	Y—H$\cdots$*Cg*
C5—H5$\cdots$$Cg1^{i}$	0.97	2.76	3.68 (1)	160
C11—H11*B*$\cdots$$Cg1^{iii}$	0.93	3.14	3.91 (1)	142

Symmetry codes: (i) $1 - y, 1 + x - y, z$; (iii) $-\frac{1}{3} + y, \frac{1}{3} - x + y, \frac{1}{3} - z$.

All H atoms were placed in calculated positions (C—H = 0.93–0.97 Å) and treated using a riding model [$U_{iso}(H) = 1.2U_{eq}(C)$].

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 2000); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2007).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3067). Services for accessing these data are described at the back of the journal.

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