Tris(4-methoxyphenyl)stibine

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The C_3-symmetrical molecule, tris(4-methoxyphenyl)stibine, $C_{21}H_{21}O_3Sb$, crystallizes with one third of the molecule in the asymmetric unit. Bond lengths and angles of the Sb—C bonds lie in between those of the isostructural homologues $C_{21}H_{21}O_3Bi$ and $C_{21}H_{21}O_3As$. The formation of dimers via six weak C—H···π interactions is considered.

3D view
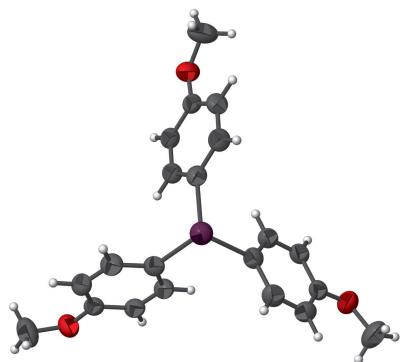
Chemical scheme
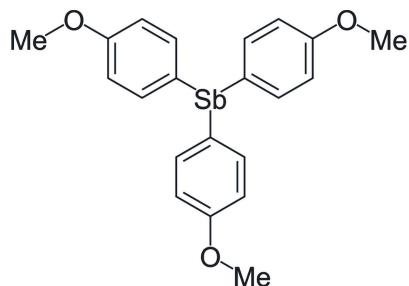
Structure description

The title compound, $C_{21}H_{21}O_3Sb$, exhibits perfect C_3-symmetry with one third of the molecule in the asymmetric unit. To our surprise, the structure of the title compound (Fig. 1) is not reported in the database (CSD; Groom et al., 2016), although we regularly observe it as a side product in our synthesis of asymmetric sulfides (Böhm et al., 2018). To fill the gap in the row of homologues of the type $C_{21}H_{21}O_3E$, with E being an element of group 14, the title compound is reported herein. It is isostructural with the homologues $C_{21}H_{21}O_3Bi$ (Hébert et al., 2016) and $C_{21}H_{21}O_3As$ (Sobolev & Belsky, 1981). The lighter homologue $C_{21}H_{21}O_3P$ (Allman et al., 1986; Bruckmann et al., 1995) crystallizes in the space group $P2_1/c$ while the lightest homologue $C_{21}H_{21}O_3N$ is, so far, not known in the CSD. The Sb—C bond distance and C—Sb—C angle observed here, 2.148 (2) Å and 95.8 (1)°, lie between those of the neighbouring isostructural As and Bi homologues. However, the Sb—C bond distance is closer to that of the Bi derivative with the Bi—C distances being 0.103 Å longer, and the As—C distance 0.175 Å shorter, than that observed for the title compound. No strong intermolecular interactions were observed, Fig. 2. The distances between the C1–C6 centroid and atoms C5 or C3 of the next molecules [3.814 (2) and 3.849 (2) Å, respectively] indicate weak C—H···π interactions, Table 1 and Fig. 3. It is noteworthy that two molecules are connected by six of these weak C—H···π interactions via C3, forming discrete dimeric units with the antimony atom facing outwards.
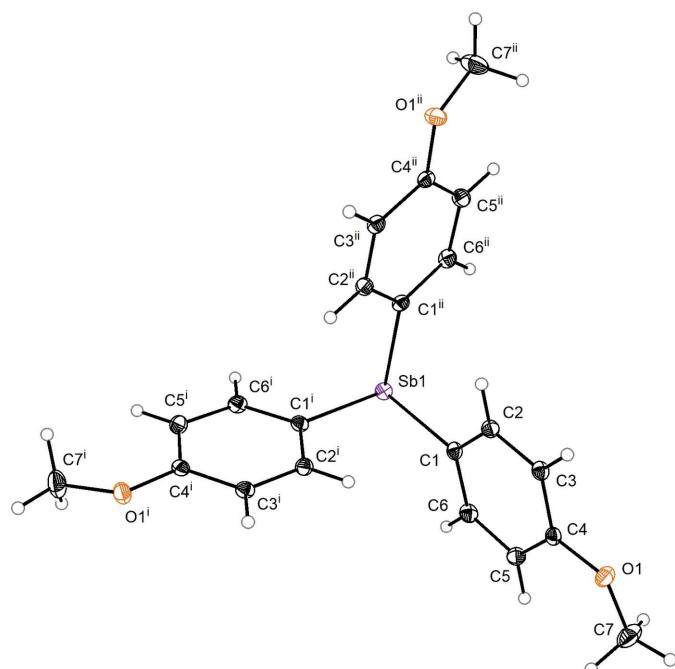
Figure 1
Displacement ellipsoid plot (50% probability) of the title compound. Symmetry codes used to generate the complete molecule: (i) $y - x$, $1 - x$, z; (ii) $1 - y$, $1 + x - y$, z.

Synthesis and crystallization

Tris(4-methoxyphenyl)stibine is obtained regularly as a side product of a reaction of the corresponding Grignard reagent with SbF_6 salts (Böhm *et al.*, 2018). Intentional synthesis of the title product: $SbCl_3$ (69.1 mg, 303 µmol) was dissolved in dry THF (2 ml) and the obtained clear solution was cooled to $-77°C$. *para*-Methoxyphenyl magnesium bromide (0.5 M in THF, 2.0 ml, 211 mg, 1.00 mmol, 3.30 equiv.) was added dropwise to the white suspension and the mixture was allowed to slowly warm up to r.t. overnight. The grey suspension was quenched with sat. aq. NH_4Cl solution (3.0 ml). The aqueous phase was extracted with DCM (20 ml). The organic phase was dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (hexane: DCM; 90: 10→100: 0) and the title compound was obtained as a white solid (38.9 mg, 87.8 µmol, 29%). Colour-
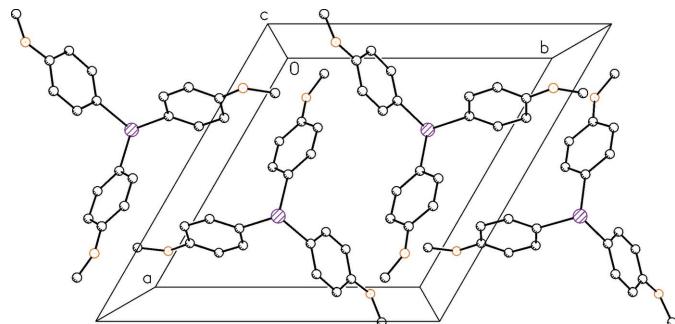

Figure 2
Packing diagram excluding hydrogen atoms.

Table 1
C—H···π interactions (Å, °).

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

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···$Cg1^i$	0.93	3.11	3.849 (2)	138
C5—H5···$Cg1^{ii}$	0.93	2.91	3.814 (2)	165

Symmetry codes: (i) $-x + y + \frac{2}{3}$, $-x + \frac{1}{3}$, $z + \frac{4}{3}$; (ii) $x - y + \frac{1}{3}$, $x + \frac{2}{3}$, $-z + \frac{5}{3}$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{21}H_{21}O_3Sb$
M_r	443.13
Crystal system, space group	Trigonal, $R\bar{3}$
Temperature (K)	298
a, c (Å)	13.1612 (5), 19.0063 (7)
V (Å^3)	2851.1 (2)
Z	6.0
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.47
Crystal size (mm)	$0.25 \times 0.23 \times 0.23$
Data collection	
Diffractometer	Bruker D8 Venture PHOTON-II
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.686, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18268, 2098, 1975
R_{int}	0.027
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.736
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.025, 0.062, 1.09
No. of reflections	2098
No. of parameters	77
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.78, −0.91

Computer programs: *APEX3* (Bruker, 2017), *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

less block-like crystals of the title compound were obtained by the diffusion method (DCM/pentane) at 4°C over a duration of two days.
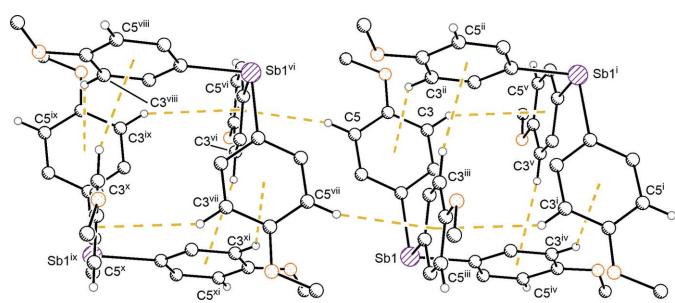

Figure 3
All C—H···π interactions, shown as dashed lines, in two adjacent dimeric units. Hydrogen atoms not involved in interactions are omitted for clarity. Symmetry codes: (i) $-x$, $-y$, $1 - z$; (ii) y, $y - x$, $1 - z$; (iii) $y - x$, $-x$, z; (iv) $-y$, $x - y$, z; (v) $x - y$, x, $1 - z$; (vi) $\frac{2}{3} - y$, $\frac{1}{3} + x$, $\frac{1}{3} + x$, $\frac{4}{3} - z$; (vii) $\frac{2}{3} - x$, $\frac{1}{3} - y$, $\frac{4}{3} - z$; (viii) $\frac{2}{3} + y$, $\frac{1}{3} - x + y$, $\frac{4}{3} - z$; (ix) $\frac{2}{3} + x$, $\frac{1}{3} + y$, $\frac{1}{3} + z$; (x) $\frac{2}{3} + y - x$, $\frac{1}{3} - x$, $\frac{1}{3} + z$; (xi) $\frac{2}{3} - y$, $\frac{1}{3} + x - y$, $\frac{1}{3} + z$.

^{1}H NMR (300 MHz, CD$_2$Cl$_2$ p.p.m.) δ = 3.79 (*s*, 9H), 6.89 (*d*, *J* = 8.7 Hz, 6H), 7.34 (*d*, *J* = 8.7 Hz, 6H). ^{13}C NMR (126 MHz, CD$_2$Cl$_2$ p.p.m.) δ = 55.6, 115.1, 129.6, 137.7, 160.6. IR (ATR, cm^{-1}): 3008.4, 2962.1, 2922.6, 2834.8, 1580.4, 1561.1, 1487.8, 1459.8, 1450.2, 1435.7, 1393.3, 1373.1, 1306.5, 1277.6, 1235.2, 1175.4, 1118.5, 1100.2, 1062.6, 1044.3, 1025.0, 1002.8, 965.2, 941.1, 829.2, 816.7, 785.9, 739.6, 710.6, 584.3, 518.8. M.p. 356 K. HRMS: (ESI-pos.) calculated for C$_{21}$H$_{21}$Sb [M + Na]$^+$ = 465.0421; found = 465.0401.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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full crystallographic data

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Tris(4-methoxyphenyl)stibine

Crystal data

$C_{21}H_{21}O_3Sb$	$D_x = 1.548$ Mg m^{-3}
$M_r = 443.13$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Trigonal, $R\overline{3}$	Cell parameters from 3409 reflections
$a = 13.1612$ (5) Å	$\theta = 3.7–27.4°$
$c = 19.0063$ (7) Å	$\mu = 1.47$ mm^{-1}
$V = 2851.1$ (2) Å^3	$T = 298$ K
$Z = 6.0$	Block, colourless
$F(000) = 1332$	$0.25 \times 0.23 \times 0.23$ mm

Data collection

Bruker D8 Venture PHOTON-II diffractometer	2098 independent reflections
	1975 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.027$
Absorption correction: multi-scan (SADABS; Bruker, 2016)	$\theta_{max} = 31.5°$, $\theta_{min} = 3.7°$
$T_{min} = 0.686$, $T_{max} = 1.000$	$h = -19 \rightarrow 19$
18268 measured reflections	$k = -15 \rightarrow 19$
	$l = -27 \rightarrow 27$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.025$	$w = 1/[\sigma^2(F_o^2) + (0.0229P)^2 + 3.1602P]$
$wR(F^2) = 0.062$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} = 0.001$
2098 reflections	$\Delta\rho_{max} = 0.78$ e Å^{-3}
77 parameters	$\Delta\rho_{min} = -0.91$ e Å^{-3}
0 restraints	
Primary atom site location: dual	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. 1. Fixed Uiso At 1.2 times of: All C(H) groups At 1.5 times of: All C(H,H,H) groups 2.a Aromatic/amide H refined with riding coordinates: C2(H2), C3(H3), C5(H5), C6(H6) 2.b Idealized Me refined as rotating group: C7(H7A,H7B,H7C)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
Sb1	0.000000	0.000000	0.70199 (2)	0.05031 (8)
O1	0.31482 (13)	0.46412 (12)	0.52928 (8)	0.0612 (3)
C1	0.10752 (15)	0.15805 (14)	0.64366 (8)	0.0455 (3)
C2	0.06716 (15)	0.18896 (15)	0.58391 (9)	0.0467 (3)
H2	−0.009131	0.139453	0.568436	0.056*
C3	0.13748 (15)	0.29087 (15)	0.54735 (9)	0.0467 (3)
H3	0.108327	0.309508	0.507860	0.056*
C4	0.25205 (15)	0.36600 (14)	0.56940 (9)	0.0454 (3)
C5	0.29484 (16)	0.33758 (16)	0.62858 (10)	0.0527 (4)
H5	0.371393	0.386981	0.643654	0.063*
C6	0.22236 (16)	0.23488 (17)	0.66499 (10)	0.0530 (4)
H6	0.251288	0.216775	0.704800	0.064*
C7	0.4225 (2)	0.5548 (2)	0.55660 (17)	0.0869 (8)
H7A	0.451384	0.622751	0.527008	0.130*
H7B	0.478675	0.528568	0.557995	0.130*
H7C	0.410236	0.574304	0.603309	0.130*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sb1	0.05679 (10)	0.05679 (10)	0.03736 (10)	0.02839 (5)	0.000	0.000
O1	0.0573 (7)	0.0504 (7)	0.0669 (8)	0.0201 (6)	−0.0086 (6)	0.0045 (6)
C1	0.0500 (8)	0.0458 (7)	0.0422 (7)	0.0252 (7)	−0.0075 (6)	−0.0062 (6)
C2	0.0463 (8)	0.0479 (8)	0.0461 (8)	0.0237 (7)	−0.0118 (6)	−0.0077 (6)
C3	0.0506 (8)	0.0488 (8)	0.0452 (8)	0.0282 (7)	−0.0117 (6)	−0.0061 (6)
C4	0.0481 (8)	0.0430 (7)	0.0486 (8)	0.0254 (6)	−0.0059 (6)	−0.0069 (6)
C5	0.0467 (8)	0.0524 (9)	0.0563 (9)	0.0227 (7)	−0.0152 (7)	−0.0080 (7)
C6	0.0557 (9)	0.0572 (9)	0.0482 (8)	0.0296 (8)	−0.0165 (7)	−0.0053 (7)
C7	0.0690 (14)	0.0602 (12)	0.0997 (19)	0.0084 (11)	−0.0174 (13)	0.0076 (12)

Geometric parameters (Å, º)

Sb1—C1^i	2.1483 (17)	C3—H3	0.9300
Sb1—C1	2.1483 (17)	C3—C4	1.391 (2)
Sb1—C1^{ii}	2.1483 (17)	C4—C5	1.390 (2)
O1—C4	1.366 (2)	C5—H5	0.9300
O1—C7	1.418 (3)	C5—C6	1.388 (3)
C1—C2	1.398 (2)	C6—H6	0.9300
C1—C6	1.394 (2)	C7—H7A	0.9600
C2—H2	0.9300	C7—H7B	0.9600
C2—C3	1.377 (3)	C7—H7C	0.9600
C1^i—Sb1—C1^{ii}	95.77 (6)	O1—C4—C5	124.84 (16)
C1^{ii}—Sb1—C1	95.77 (6)	C5—C4—C3	119.55 (16)
C1^i—Sb1—C1	95.77 (6)	C4—C5—H5	120.3

C4—O1—C7	117.95 (17)	C6—C5—C4	119.46 (16)
C2—C1—Sb1	122.61 (12)	C6—C5—H5	120.3
C6—C1—Sb1	120.18 (12)	C1—C6—H6	119.0
C6—C1—C2	117.21 (16)	C5—C6—C1	121.96 (16)
C1—C2—H2	119.2	C5—C6—H6	119.0
C3—C2—C1	121.68 (15)	O1—C7—H7A	109.5
C3—C2—H2	119.2	O1—C7—H7B	109.5
C2—C3—H3	119.9	O1—C7—H7C	109.5
C2—C3—C4	120.13 (15)	H7A—C7—H7B	109.5
C4—C3—H3	119.9	H7A—C7—H7C	109.5
O1—C4—C3	115.60 (15)	H7B—C7—H7C	109.5

Symmetry codes: (i) $-y, x-y, z$; (ii) $-x+y, -x, z$.

Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the C1–C6 benzene ring

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C3—H3⋯$Cg1^{iii}$	0.93	3.11	3.849 (2)	138
C5—H5⋯$Cg1^{iv}$	0.93	2.91	3.814 (2)	165

Symmetry codes: (iii) $-x+y+2/3, -x+1/3, z+4/3$; (iv) $x-y+1/3, x+2/3, -z+5/3$.