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4-Bromoselenoanisole

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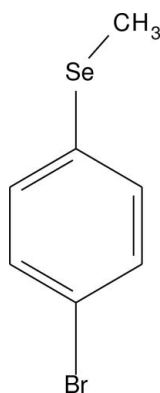
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 Key indicators: single-crystal X-ray study; $T = 122$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.027; wR factor = 0.075; data-to-parameter ratio = 19.2.

The title compound, 1-bromo-4-methylselenobenzene, $\text{C}_7\text{H}_7\text{BrSe}$, was prepared by methylation of 4-bromoselenophenolate with methyl iodide, and crystals suitable for structure determination were obtained by sublimation. The molecule is essentially planar; the Se—Me bond is rotated by only 2.59 (19)° out of the least-squares plane of the benzene ring. The most pronounced intermolecular interactions are two hydrogen bonds of the type $\text{C}-\text{H}\cdots\pi$, which determine a herring-bone pattern in the crystal packing.

Related literature

For related selenobenzene structures, see: Oddershede *et al.* (2003); Sørensen & Stuhr-Hansen (2009); Stuhr-Hansen *et al.* (2009). For the ^{77}Se -NMR spectrum, see: Eggert *et al.* (1986). For the melting point, see: Gilow *et al.* (1968).



Experimental

Crystal data

$\text{C}_7\text{H}_7\text{BrSe}$ $a = 5.8298$ (8) Å
 $M_r = 250.00$ $b = 7.0671$ (11) Å
 Orthorhombic, $Pna2_1$ $c = 18.776$ (6) Å

$V = 773.6$ (3) Å³
 $Z = 4$
 Cu $K\alpha$ radiation

$\mu = 11.86$ mm⁻¹
 $T = 122$ K
 $0.36 \times 0.09 \times 0.09$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 Absorption correction: numerical (DeTitta, 1985)
 $T_{\min} = 0.145$, $T_{\max} = 0.454$
 5823 measured reflections

1590 independent reflections
 1590 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$
 5 standard reflections
 frequency: 166.7 min
 intensity decay: 8.7%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.075$
 $S = 1.15$
 1590 reflections
 83 parameters
 1 restraint

H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.62$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.30$ e Å⁻³
 Absolute structure: Flack (1983)
 Flack parameter: -0.01 (4)

Table 1

Selected bond lengths (Å).

Se1—C1	1.916 (4)	Br1—C4	1.906 (4)
Se1—C7	1.930 (5)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C}2-\text{H}2\cdots\text{C}2^i$	0.95	2.84	3.747 (4)	159
$\text{C}5-\text{H}5\cdots\text{C}5^{ii}$	0.95	2.83	3.740 (5)	160

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *DREAR* (Blessing, 1987); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPII* (Johnson, 1976) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2225).

References

- Blessing, R. H. (1987). *Crystallogr. Rev.* **1**, 3–58.
 DeTitta, G. T. (1985). *J. Appl. Cryst.* **18**, 75–79.
 Eggert, H., Nielsen, O. & Henriksen, L. (1986). *J. Am. Chem. Soc.* **108**, 1725–1730.
 Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Gilow, H. M., Camp, R. B. & Clifton, E. C. (1968). *J. Org. Chem.* **33**, 230–233.
 Oddershede, J., Henriksen, L. & Larsen, S. (2003). *Org. Biomol. Chem.* **1**, 1053–1060.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

Sørensen, H. O. & Stuhr-Hansen, N. (2009). *Acta Cryst.* **E65**, o13.

Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.

Stuhr-Hansen, N., Götze, T. F., Henriksen, L., Sølling, T. I., Langkilde, A. & Sørensen, H. O. (2009). *Heteroat. Chem.* **20**, 101–108.

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4-Bromoselenoanisole

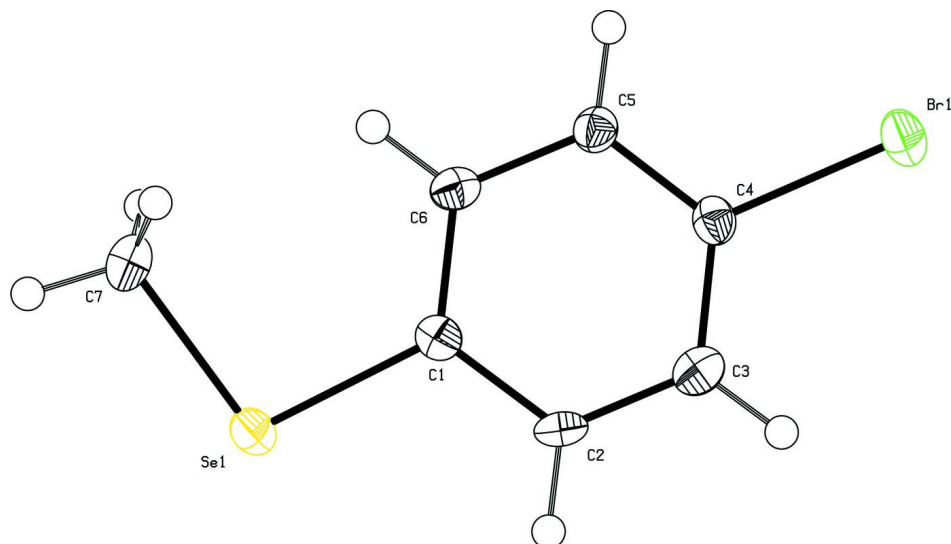
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S1. Experimental

The title compound was synthesized as described below. To a stirred solution containing di(4-bromophenyl) diselenide (2.35 g, 5 mmol) and hydrazine hydrate (2.75 mmol) in DMSO (8 ml) was added 25% methanolic sodium methanolate (approximately 2 g, the last 0.2 g added dropwise with intervals of 5 s until the yellow color of di(4-bromophenyl) diselenide disappeared). 4-Methyl iodide (1.70 g, 12 mmol) was added and the reaction mixture was further stirred for 10 minutes. The clear colourless reaction mixture was diluted with water (100 ml) and extracted with ether (3 x 25 ml). The combined organic phases were washed with water (15 ml), filtered through alumina (neutral, 6 g) by means of pentane and the solvent was evaporated *in vacuo*. Sublimation (200 °C, 5 m mHg) gave the title compound 4-bromoselenoanisole (2.24 g, 90%) as long white needles in a quality suitable for structure determination by single-crystal *x*-ray diffraction; mp 47–48 °C (lit. (Gilow *et al.*, 1968) mp 46–47 °C). C₇H₇BrSe: found C 33.69% H 2.57%; calc. C 33.63% H 2.82%. Mass spectrum (EI; *m/z*, relative intensity): 250 (*M*⁺, 100), 235 (67), 171 (7), 156 (56). ¹H-NMR (CDCl₃) δ: 2.33 (3H, s), 7.26 (2H, d, *J* = 8.6 Hz), 7.36 (2H, d, *J* = 8.6 Hz). ⁷⁷Se-NMR (Eggert *et al.*, 1986) (CDCl₃) δ: 211 p.p.m..

S2. Refinement

Hydrogen atoms were found in the difference Fourier map. All hydrogen atoms were treated as riding atoms with C—H distances of 0.95 for C_{ar} and 0.98 for the C_{Me}. Isotropic displacement parameters for all H atoms were constrained to 1.2 U_{eq} of the connected non-hydrogen atom (1.5 U_{eq} for Me groups).

**Figure 1**

Ortep drawing (Johnson, 1976) of the title compound including labelling of the atoms. The displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres with an arbitrary radii.

1-bromo-4-methylselenobenzene

Crystal data

C_7H_7BrSe

$M_r = 250.00$

Orthorhombic, $Pna2_1$

Hall symbol: P 2c -2n

$a = 5.8298$ (8) Å

$b = 7.0671$ (11) Å

$c = 18.776$ (6) Å

$V = 773.6$ (3) Å³

$Z = 4$

$F(000) = 472$

$D_x = 2.147$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å

Cell parameters from 20 reflections

$\theta = 39.2$ – 40.3°

$\mu = 11.86$ mm⁻¹

$T = 122$ K

Needle, white

$0.36 \times 0.09 \times 0.09$ mm

Data collection

Enraf–Nonius CAD-4
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω – 2θ scans

Absorption correction: numerical
(DeTitta, 1985)

$T_{\min} = 0.145$, $T_{\max} = 0.454$

5823 measured reflections

1590 independent reflections

1590 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\max} = 74.8^\circ$, $\theta_{\min} = 4.7^\circ$

$h = -7 \rightarrow 7$

$k = -8 \rightarrow 8$

$l = -23 \rightarrow 23$

5 standard reflections every 166.7 min

intensity decay: 8.7%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.075$

$S = 1.15$

1590 reflections

83 parameters

1 restraint

Primary atom site location: heavy-atom method

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2 + 0.4964P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.62 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -1.30 \text{ e } \text{\AA}^{-3}$$

Extinction correction: *SHELXL97* (Sheldrick, 2008), $F_c^* = kFc[1 + 0.001xFe^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0128 (5)

Absolute structure: Flack (1983)

Absolute structure parameter: -0.01 (4)

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Se1	-0.08215 (7)	0.05711 (4)	0.00008 (2)	0.02110 (15)
Br1	0.38155 (8)	-0.04502 (5)	0.317143 (19)	0.02756 (16)
C1	0.0636 (7)	0.0211 (5)	0.0905 (2)	0.0176 (7)
C2	-0.0585 (6)	0.0834 (5)	0.1507 (2)	0.0185 (7)
H2	-0.2055	0.1395	0.1450	0.022*
C3	0.0336 (8)	0.0636 (4)	0.2178 (2)	0.0219 (8)
H3	-0.0478	0.1066	0.2586	0.026*
C4	0.2483 (6)	-0.0207 (5)	0.22490 (18)	0.0184 (7)
C5	0.3691 (6)	-0.0843 (5)	0.1666 (2)	0.0184 (7)
H5	0.5149	-0.1420	0.1727	0.022*
C6	0.2759 (7)	-0.0633 (4)	0.0982 (2)	0.0193 (8)
H6	0.3579	-0.1067	0.0577	0.023*
C7	0.1556 (9)	-0.0397 (6)	-0.0615 (3)	0.0300 (9)
H7A	0.2997	0.0268	-0.0517	0.045*
H7B	0.1117	-0.0195	-0.1113	0.045*
H7C	0.1759	-0.1753	-0.0528	0.045*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Se1	0.0191 (2)	0.0252 (2)	0.0190 (2)	0.00090 (10)	-0.00294 (17)	0.00115 (15)
Br1	0.0276 (2)	0.0363 (3)	0.0188 (2)	0.00065 (13)	-0.00506 (19)	0.00065 (16)
C1	0.0174 (18)	0.0161 (14)	0.0193 (18)	-0.0014 (12)	-0.0005 (13)	0.0019 (13)
C2	0.0120 (15)	0.0178 (15)	0.026 (2)	0.0030 (12)	0.0026 (13)	-0.0003 (13)
C3	0.022 (2)	0.0201 (16)	0.024 (2)	0.0001 (11)	0.0034 (17)	-0.0019 (12)
C4	0.0186 (19)	0.0202 (16)	0.0166 (17)	-0.0032 (12)	-0.0007 (15)	0.0015 (12)
C5	0.0168 (15)	0.0206 (14)	0.0177 (18)	-0.0018 (12)	0.0009 (13)	-0.0014 (13)
C6	0.0170 (19)	0.0178 (16)	0.0230 (19)	0.0009 (10)	0.0012 (16)	-0.0022 (11)
C7	0.032 (2)	0.039 (2)	0.019 (2)	0.0061 (15)	0.0035 (18)	-0.0038 (14)

Geometric parameters (Å, °)

Se1—C1	1.916 (4)	C3—H3	0.9500
Se1—C7	1.930 (5)	C4—C5	1.377 (5)
Br1—C4	1.906 (4)	C5—C6	1.401 (6)
C1—C6	1.382 (5)	C5—H5	0.9500
C1—C2	1.406 (5)	C6—H6	0.9500
C2—C3	1.377 (6)	C7—H7A	0.9800
C2—H2	0.9500	C7—H7B	0.9800
C3—C4	1.392 (6)	C7—H7C	0.9800
C1—Se1—C7	99.5 (2)	C4—C5—C6	119.7 (3)
C6—C1—C2	120.3 (4)	C4—C5—H5	120.2
C6—C1—Se1	123.2 (3)	C6—C5—H5	120.2
C2—C1—Se1	116.5 (3)	C1—C6—C5	119.3 (4)
C3—C2—C1	120.4 (4)	C1—C6—H6	120.4
C3—C2—H2	119.8	C5—C6—H6	120.4
C1—C2—H2	119.8	Se1—C7—H7A	109.5
C2—C3—C4	118.8 (4)	Se1—C7—H7B	109.5
C2—C3—H3	120.6	H7A—C7—H7B	109.5
C4—C3—H3	120.6	Se1—C7—H7C	109.5
C5—C4—C3	121.6 (3)	H7A—C7—H7C	109.5
C5—C4—Br1	119.0 (3)	H7B—C7—H7C	109.5
C3—C4—Br1	119.5 (3)		
C7—Se1—C1—C6	-3.0 (3)	C2—C3—C4—Br1	178.8 (3)
C7—Se1—C1—C2	177.8 (3)	C3—C4—C5—C6	0.4 (6)
C6—C1—C2—C3	1.0 (5)	Br1—C4—C5—C6	-178.5 (3)
Se1—C1—C2—C3	-179.8 (3)	C2—C1—C6—C5	-0.7 (5)
C1—C2—C3—C4	-0.6 (5)	Se1—C1—C6—C5	-179.8 (3)
C2—C3—C4—C5	-0.1 (5)	C4—C5—C6—C1	0.0 (5)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C2—H2...C2 ⁱ	0.95	2.84	3.747 (4)	159
C5—H5...C5 ⁱⁱ	0.95	2.83	3.740 (5)	160

Symmetry codes: (i) $x-1/2, -y+1/2, z$; (ii) $x+1/2, -y-1/2, z$.