4-Bromoselenoanisole

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4-Bromoselenoanisole

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The title compound, 1-bromo-4-methylselenobenzene, C7H7BrSe, was prepared by methylation of 4-bromoselenoanisole 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 C—H···π, 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 77Se-NMR spectrum, see: Eggert et al. (1986). For the melting point, see: Gilow et al. (1968).

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

References


**Experimental**

Crystal data

C7H7BrSe

Orthorhombic, Pna21

V = 773.6 (3) Å³

Z = 4

Cu Kα radiation

μ = 11.86 mm⁻¹

T = 293 K

0.36 × 0.09 × 0.09 mm

Data collection

Enraf–Nonius CAD-4 diffractometer

Absorption correction: numerical

DeTitta (1985)

Tmin = 0.145, Tmax = 0.454

5233 measured reflections

5190 independent reflections

5 standard reflections

frequency: 166.7 min

intensity decay: 8.7%

Refinement

H-atom parameters constrained

Absorption correction: numerical

DeTitta (1985)

R(δI)/R(int) = 0.062 e Å⁻³

Δρmax = 1.30 e Å⁻³

Absolute structure: Flack (1983)

Flack parameter: −0.01 (4)

Table 1

Selected bond lengths (Å).

Table 2

Hydrogen-bond geometry (Å, °).

Symmetry codes: (i) x, y−1, z; (ii) x, y+1, z.

Another alternative for the crystal structure is hydrogen bonding. This is indicated by the presence of intermolecular hydrogen bonds, as noted in the crystal packing section.

supplementary materials
4-Bromoselenoanisole

H. O. Sørensen and N. Stuhr-Hansen

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-Methyliodide (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 mh g) gave the title compound 4-bromoselenoanisol (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). C\textsubscript{7}H\textsubscript{7}BrSe: found C 33.69% H 2.57%; calc. C 33.63% H 2.82%. Mass spectrum (EI; m/\textsubscript{z}, relative intensity): 250 (M\textsuperscript{+}, 100), 235 (67), 171 (7), 156 (56). \textsuperscript{1}H-NMR (CDCl\textsubscript{3}) 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) (CDCl\textsubscript{3}) δ: 211 p.p.m..

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\textsubscript{ar} and 0.98 for the C\textsubscript{Me}. Isotropic displacement parameters for all H atoms were constrained to 1.2U\textsubscript{eq} of the connected non-hydrogen atom (1.5U\textsubscript{eq} for Me groups).

Figures

Fig. 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

\( F_{000} = 472 \)

\( D_x = 2.147 \) Mg m\textsuperscript{-3} 

\( \lambda = 1.54184 \) Å

Cell parameters from 20 reflections

\( \theta = 39.2–40.3^\circ \)

\( \mu = 11.86 \) mm\textsuperscript{-1}
supplementary materials

c = 18.776 (6) Å  
\( V = 773.6 \) (3) Å³  
Z = 4  
0.36 × 0.09 × 0.09 mm

\( T = 122 \) K  
Needle, white

Data collection

Enraf–Nonius CAD-4  
diffractometer  
\( R_{\text{int}} = 0.031 \)

Radiation source: fine-focus sealed tube  
0\( _{\text{max}} = 74.8^\circ \)

Monochromator: graphite  
0\( _{\text{min}} = 4.7^\circ \)

\( T = 122 \) K  
\( h = -7 \rightarrow 7 \)

\( \omega \)–2\( \theta \) scans  
\( k = -8 \rightarrow 8 \)

Absorption correction: numerical  
(DeTitta, 1985)  
\( l = -23 \rightarrow 23 \)

\( T_{\text{min}} = 0.145, T_{\text{max}} = 0.454 \)

5823 measured reflections  
ev\( \text{ery 166.7 min} \)

1590 independent reflections  
intensity decay: 8.7%

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

Refinement

Refinement on \( F^2 \)  
Hydrogen site location: inferred from neighbouring sites

Least-squares matrix: full  
H-atom parameters constrained

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

\( wR(F^2) = 0.075 \)

S = 1.15  
\( \Delta \rho_{\text{max}} = 0.62 \) e Å\(^{-3} \)

1590 reflections  
\( \Delta \rho_{\text{min}} = -1.29 \) e Å\(^{-3} \)

83 parameters  
Extinction correction: SHELXL97 (Sheldrick, 2008),  
\( F^c = kF^{-1}[1+0.001xF^{-2}/\sin(2\theta)]^{1/4} \)

1 restraint  
Extinction coefficient: 0.0128 (5)

Primary atom site location: heavy-atom method  
Absolute structure: Flack (1983)

Secondary atom site location: difference Fourier map  
Flack 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 (Å\(^2\))**

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<th>(y)</th>
<th>(z)</th>
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**Atomic displacement parameters (Å\(^2\))**

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**Geometric parameters (Å, °)**

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supplementary materials

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, °)

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