

Similarities and differences between bis[2-(bromomethyl)phenyl] diselenide, bis[2-(chloromethyl)phenyl] diselenide and bis[2-(hydroxymethyl)phenyl] diselenide

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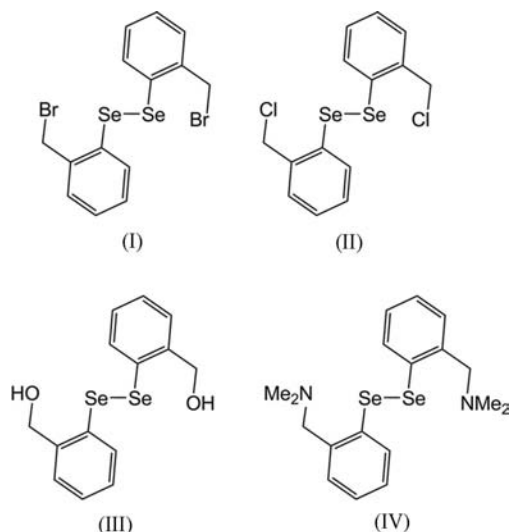
The title compounds, $C_{14}H_{12}Br_2Se_2$, (I), $C_{14}H_{12}Cl_2Se_2$, (II), and $C_{14}H_{14}O_2Se_2$, (III), feature a diselenide bridge between two *o*-benzyl bromide [in (I)], two *o*-benzyl chloride [in (II)] or two *o*-benzyl alcohol units [in (III)]. In the molecular structure of (I) and in both independent molecules of (II), close contacts are observed between the halogen centres and the diselenide unit. In the case of modification (IIIa), strong hydrogen bonds between the –OH groups dominate, whereas the molecular structures of modification (IIIb) and bis[2-[(dimethylamino)methyl]phenyl] diselenide, $C_{18}H_{24}N_2Se_2$, (IV), are comparable with those of (I) and (II). A correlation between the strength of the contacts and the angle between the benzene planes and the Se–Se units is found.

Comment

Organic selenides and diselenides tend to form close contacts with centres such as halogens (Iwaoka *et al.*, 2000, 2005; Iwaoka, Katsuda *et al.*, 2002; Iwaoka, Komatsu *et al.*, 2002; Nakanishi *et al.*, 1998) and chalcogens (Bleiholder *et al.*, 2006, 2007; Gleiter *et al.*, 2003, 2005; Mundt *et al.*, 2006; Schulte *et al.*, 2003; Werz *et al.*, 2002a,b, 2008; Lari *et al.*, 2009).

In bis[2-(bromomethyl)phenyl] diselenide, (I), and bis[2-(chloromethyl)phenyl] diselenide, (II), the halogen centres are properly situated to form contacts with the diselenide unit. Such an arrangement of an oxygen centre and a diselenide unit has also been reported for the structure of bis[2-(hydroxymethyl)phenyl] diselenide, (IIIb) (Tripathi *et al.*, 2005). Similarly, an almost linear arrangement of two dimethylamine units and a diselenide bridge was reported for bis[2-[(dimethylamino)methyl]phenyl] diselenide, (IV) (Kaur *et al.*, 1996). Common to all the conformations with contacts between the donor atoms and the diselenide unit is a rather small torsion angle between the benzene plane and the Se–Se

vector. In addition to the selenium contacts, the –OH groups of alcohol (III) may form intermolecular hydrogen bonds. Such hydrogen bonds were found in the new modification (IIIa).



The molecular structures of (I) and (II) (Figs. 1 and 2, and Tables 1 and 2) have in common a central Se1–Se2 unit which interacts with peripheral donor centres, *viz.* Br in (I) or Cl in (II). A new modification of (III), denoted (IIIa) (Fig. 3 and Table 3), was obtained when (III) was crystallized from a light petroleum/dichloromethane mixture, whereas the known modification (IIIb) ($P2_1/n$, $Z = 4$; Tripathi *et al.*, 2005) was crystallized from toluene.

For (IIIa) we found no significant interactions between selenium and oxygen. The intramolecular Se...O distances are 3.687 (2) and 4.586 (2) Å. These values are considerably longer than the sum of the van der Waals radii of 3.42 Å (Bondi, 1964). Interesting features of the solid-state structure of (IIIa) are not only O–H...O hydrogen bonds with O...O distances of 2.747 (3) Å, but also a short intermolecular Se...Se contact and an intermolecular Se...H contact involving a benzylic H atom (Table 3). These interactions cause a pairing of molecules (Fig. 3) and these pairs are linked into chains by a second pair of hydrogen bonds [O...O = 2.790 (3) Å].

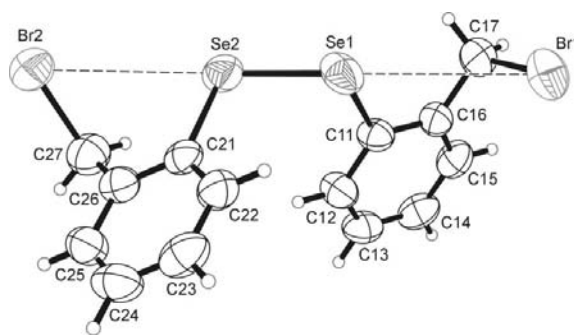
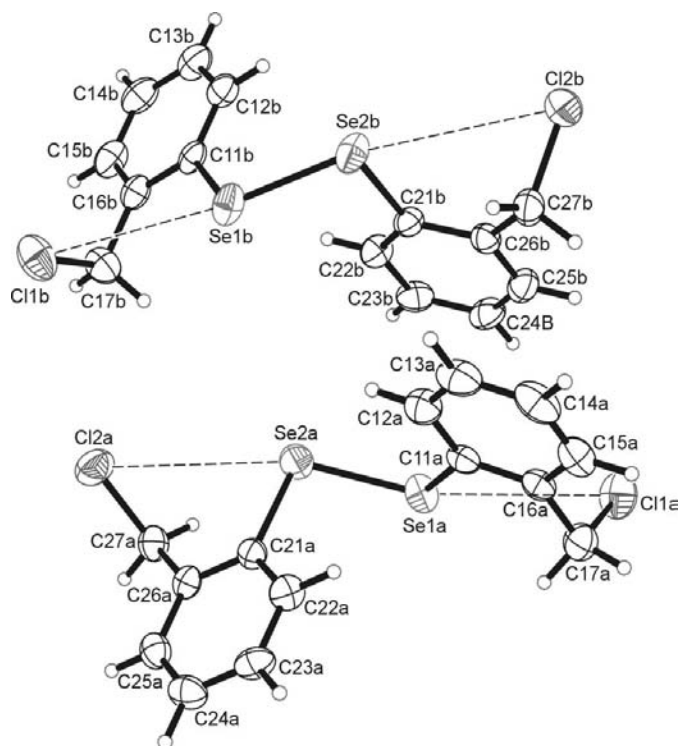
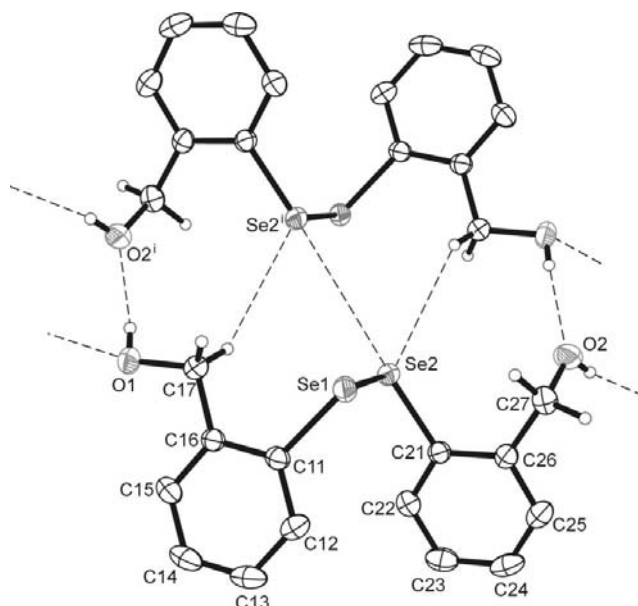


Figure 1
The molecular structure of (I). The Br...Se contacts are indicated by dashed lines and displacement ellipsoids are drawn at the 50% probability level.

**Figure 2**

The two independent molecules of (II). The Cl \cdots Se contacts are indicated by dashed lines and displacement ellipsoids are drawn at the 50% probability level.

Table 4 presents a comparison of the geometric parameters related to the Se \cdots X contacts of the three structures plus data for the previously published structures of (III*b*) (Tripathi *et al.*, 2005) and (IV) (Kaur *et al.*, 1996). For (I) and (II), one notices rather short Se \cdots halogen contacts and an almost linear arrangement of this interaction with the Se1–Se2 bond direction. In the case of (III*b*), only one of the oxygen centres forms a short contact with the Se1–Se2 unit, with an almost linear Se1–Se2 \cdots O2 array. The other oxygen is situated at a distance of 4.637 (3) Å, which is much further than the van der Waals distance of 3.42 Å (Bondi, 1964). In the case of (IV), one finds short Se \cdots N contacts and an almost linear arrangement of the N \cdots Se–Se \cdots N centres again. We notice a close relationship of the angles between the benzene planes and the Se–Se units and the strength of the contacts. In cases where these angles are near 90°, there are no contacts; for angles around 40°, the contacts are in the range of the van der Waals distances; whereas smaller angles (10–20°) result in even shorter contacts. We ascribe this to the fact that only a small torsion angle allows the donor atoms to approach the diselenide unit in the direction opposite to the Se–Se bond. We assume an attractive Se \cdots X interaction composed of dispersion forces and directed forces between the lone pairs of the donor atoms and the σ^* -acceptor orbital of the Se–Se bond (Bleholder *et al.*, 2006, 2007). However, the Se–Se distances do not seem to be affected by the interaction. If there is an effect on the Se–Se bond length it is compensated for by other influences.

**Figure 3**

The molecular structure of a pair of (III*a*) molecules. The upper molecule is generated by inversion [symmetry code: (i) $-x, 2-y, 1-z$]. Inter-molecular Se \cdots Se and Se \cdots H contacts and O–H \cdots O hydrogen-bond bridges are indicated by dashed lines. The outwardly directed hydrogen-bond bridges produce a chain of pairs. Displacement ellipsoids are drawn at the 50% probability level. Only selected H atoms are displayed.

The torsion angles between Se–C bonds along the Se–Se axis (C11–Se1–Se2–C21) are close to 90° in all cases. This conformation of the diselenide units is preferred due to the repulsion of the 4*p* lone pairs at the Se centres.

Experimental

Compounds (I) and (II) were synthesized according to Iwaoka *et al.* (2005). Single crystals of (I) and (II) were obtained from a mixture of light petroleum and dichloromethane. The synthesis of (III) was carried out following the procedure described by Tripathi *et al.* (2005).

Compound (I)

Crystal data

$C_{14}H_{12}Br_2Se_2$	$V = 3066.2$ (5) Å ³
$M_r = 497.98$	$Z = 8$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 11.4093$ (11) Å	$\mu = 10.02$ mm ^{−1}
$b = 11.3589$ (11) Å	$T = 296$ K
$c = 24.176$ (2) Å	$0.13 \times 0.11 \times 0.04$ mm
$\beta = 101.861$ (2)°	

Data collection

Bruker APEX CCD diffractometer	12556 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2008 <i>b</i>)	2811 independent reflections
$T_{min} = 0.346$, $T_{max} = 0.670$	1907 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.048$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$	163 parameters
$wR(F^2) = 0.082$	H-atom parameters constrained
$S = 1.02$	$\Delta\rho_{max} = 0.58$ e Å ^{−3}
2811 reflections	$\Delta\rho_{min} = -0.46$ e Å ^{−3}

Table 1

Selected geometric parameters (Å, °) for (I).

Se1—C11	1.935 (5)	Se2—C21	1.941 (5)
Se1—Se2	2.3090 (9)		
C11—Se1—Se2	101.69 (15)	C21—Se2—Se1	103.12 (16)
C11—Se1—Se2—C21	87.6 (2)		

Table 2

Selected geometric parameters (Å, °) for (II).

Se1A—C11A	1.937 (4)	Se1B—C11B	1.935 (4)
Se1A—Se2A	2.3124 (8)	Se1B—Se2B	2.3140 (8)
Se2A—C21A	1.944 (4)	Se2B—C21B	1.928 (4)
C11A—Se1A—Se2A	103.20 (14)	C11B—Se1B—Se2B	103.60 (14)
C21A—Se2A—Se1A	100.96 (14)	C21B—Se2B—Se1B	102.10 (14)
C11A—Se1A—Se2A—C21A	90.15 (19)	C11B—Se1B—Se2B—C21B	85.08 (19)

Compound (II)

Crystal data

C ₁₄ H ₁₂ Cl ₂ Se ₂	$\gamma = 90.610 (1)^\circ$
$M_r = 409.06$	$V = 1467.58 (5) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 4$
$a = 7.9160 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 8.0215 (1) \text{ \AA}$	$\mu = 5.38 \text{ mm}^{-1}$
$c = 23.4689 (4) \text{ \AA}$	$T = 200 \text{ K}$
$\alpha = 98.388 (1)^\circ$	$0.21 \times 0.20 \times 0.06 \text{ mm}$
$\beta = 95.287 (1)^\circ$	

Data collection

Bruker SMART CCD diffractometer	14837 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2008b)	6651 independent reflections
$T_{\min} = 0.390$, $T_{\max} = 0.724$	4403 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.056$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$	325 parameters
$wR(F^2) = 0.100$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{\max} = 0.49 \text{ e \AA}^{-3}$
6651 reflections	$\Delta\rho_{\min} = -0.51 \text{ e \AA}^{-3}$

Compound (IIIa)

Crystal data

C ₁₄ H ₁₄ O ₂ Se ₂	$\gamma = 76.978 (1)^\circ$
$M_r = 372.17$	$V = 675.81 (4) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 8.4461 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 8.9003 (3) \text{ \AA}$	$\mu = 5.46 \text{ mm}^{-1}$
$c = 9.7427 (3) \text{ \AA}$	$T = 200 \text{ K}$
$\alpha = 72.904 (1)^\circ$	$0.24 \times 0.16 \times 0.10 \text{ mm}$
$\beta = 78.950 (1)^\circ$	

Data collection

Bruker SMART CCD diffractometer	6951 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2008b)	3051 independent reflections
$T_{\min} = 0.336$, $T_{\max} = 0.581$	2667 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.071$	$\Delta\rho_{\max} = 0.60 \text{ e \AA}^{-3}$
$S = 1.09$	$\Delta\rho_{\min} = -0.52 \text{ e \AA}^{-3}$
3051 reflections	
171 parameters	

Table 3

Selected geometric parameters (Å, °) for (IIIa).

Se1—C11	1.924 (2)	Se2···H17B ⁱ	3.09
Se1—Se2	2.3441 (3)	O1···O2 ⁱⁱ	2.747 (3)
Se2—C21	1.929 (2)	O1···O2 ⁱⁱ	2.790 (3)
Se2···Se2 ⁱ	3.7646 (5)		
C11—Se1—Se2	98.92 (7)	C21—Se2···Se2 ⁱ	174.82 (7)
C21—Se2—Se1	99.06 (7)		
C11—Se1—Se2—C21	−74.30 (10)		

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

Table 4

Geometric parameters (Å, °) related to the Se—Se···X contacts of (I) ($X = \text{Br}$), (II) ($X = \text{Cl}$), (IIIa) and (IIIb) ($X = \text{O}$; Tripathi *et al.*, 2005), and (IV) ($X = \text{N}$; Kaur *et al.*, 1996); also given in each case is the sum of the van der Waals radii r_w (Bondi, 1964).

	(I)	(II)	(IIIa)	(IIIb)	(IV)
Contacts					
Se1···X1	3.828 (1)	3.537 (2)/3.471 (2)			2.856 (3)
Se2···X2	3.673 (1)	3.681 (2)/3.679 (2)		3.008 (3)	2.863 (4)
$r_w(\text{Se}) + r_w(X)$	3.75	3.65	3.42	3.42	3.45
Angles					
Se2—Se1···X1	167.97 (3)	166.39 (4)/173.35 (4)			174.0 (1)
Se1—Se2···X2	170.02 (3)	162.51 (3)/169.83 (3)		166.1 (1)	172.7 (1)
Interplanar angles					
Ph—C11/Se1/Se2	37.8 (2)	14.3 (1)/21.7 (1)	85.06 (6)	77.1 (1)	17.3
Ph—C21/Se2/Se1	19.7 (3)	43.2 (1)/34.1 (1)	88.32 (6)	11.1 (1)	26.0

The H atoms of the hydroxy groups of (IIIa) were refined isotropically; both O—H distances refined to 0.74 (3) Å. All other H atoms were treated using appropriate riding models [idealized geometry with C—H distances of 0.97 Å for methylene and 0.93 Å for aromatic H atoms in (I), and 0.99 Å for methylene and 0.95 Å for aromatic H atoms in (II) and (IIIa), and with isotropic displacement parameters of 1.2 times U_{eq} of the parent C atom for all H atoms]. Three reflections with very low values of F_{obs} relative to F_{calc} , that were probably caught by the beam stop, were omitted for (I), and one such reflection was omitted for (II).

Data collection: SMART (Bruker, 2001) for (I); SMART (Bruker, 1995) for (II) and (IIIa). Cell refinement: SAINT (Bruker, 2001) for (I); SAINT (Bruker, 1995) for (II) and (IIIa). Data reduction: SAINT (Bruker, 2001) for (I); SAINT (Bruker, 1995) for (II) and (IIIa). For all compounds, program(s) used to solve structure: SHELXTL (Sheldrick, 2008a); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3293). Services for accessing these data are described at the back of the journal.

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