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Two polymorphs of bis(2-bromophenyl) disulfide

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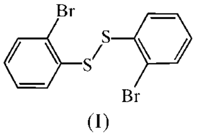
Colourless crystals of the title compound, bis(2-bromophenyl) disulfide, $C_{12}H_8Br_2S_2$, are obtained from the reaction of 2-bromophenylmercaptan with metallic sodium and either zinc chloride or cadmium chloride in methanol. In the presence of Zn^{II} ions, the crystals are orthorhombic (space group *Pbca*, with $Z' = 1$); with Cd^{II} ions present, the product is triclinic (space group $P\bar{1}$, with $Z' = 4$). Both polymorphs exhibit significant intramolecular C—H···S hydrogen bonds. In the orthorhombic form, molecules are linked by intermolecular C—H···Br hydrogen bonds, while in the triclinic form, molecules exhibit Br···Br contacts.

Comment



(I)

The electronic and structural properties of transition and main group metal complexes coordinated by S-donor atoms have attracted intense research interest over the past 30 years (Kasper & Interrante, 1976; Kobayashi *et al.*, 1982; Pullen *et al.*, 1998; Kie-Moon & Holm, 2001). Although some studies have appeared describing the behaviour of the disulfide group as a donor (Valde *et al.*, 1983; Matsubayashi & Yokozawa, 1990; Oshio, 1993; Kobayashi *et al.*, 1990), it has not been subjected to such detailed study as a number of other donor groups (Balch *et al.*, 1968; Gray, 1966; Schrauzer & Mayweg, 1966). This neglect is in part because the disulfide group tends to give bridged or polymeric metal complexes, which are extremely insoluble and are accordingly difficult to characterize or study. We report here the structures of two polymorphs of bis(2-bromophenyl) disulfide, isolated during attempts to synthesize zinc(II) or cadmium(II) complexes of the ligand. There are no significant differences in the bond lengths observed for the two polymorphs (Figs. 1 and 2, and Tables 1 and 3). The substituents are essentially coplanar with their respective rings, giving molecules in which all the atoms lie in two planes. The dihedral angle between the planes of the two phenyl rings in the orthorhombic form is 83.34 (9)°, while an average value of 84.90 (2)° is observed for the triclinic form. The values of the S11—S21—C21—C22, S11—S21—C21—C26, S21—S11—C11—C12 and S21—S11—C11—C16 torsion angles in the orthorhombic form [−174.69 (14), 7.46 (19), −172.68 (14) and 8.33 (18)°, respectively] are slightly different from the corresponding mean angles in the triclinic system [−169.9 (2), 11.1 (2), −169.2 (2) and 13.5 (2)°, respectively]. The orthorhombic form crystallizes with one

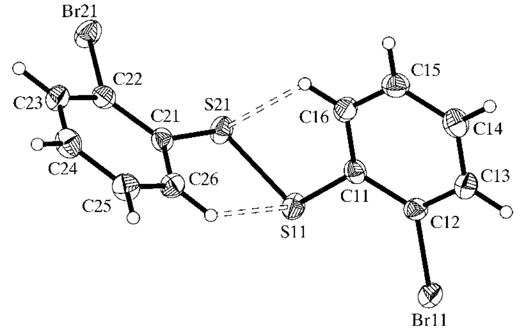
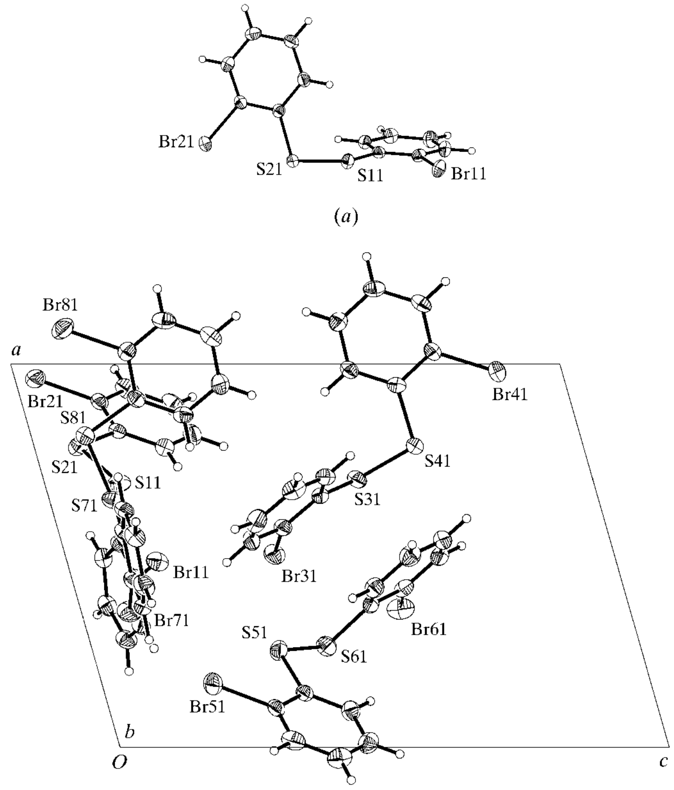


Figure 1
The asymmetric unit of the orthorhombic form ($Z' = 1$), (I). Displacement ellipsoids are shown at the 50% probability level.



(*a*)

(*b*)

Figure 2
Views of (*a*) the molecule and (*b*) the unit-cell packing of the triclinic form ($Z' = 4$), (II). Displacement ellipsoids are shown at the 50% probability level.

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independent molecule in each asymmetric unit (Fig. 1), while in the triclinic form there are four (Fig. 2). In both polymorphs, the phenyl rings participate in significant intramolecular C—H···S interactions, with average H···S distances of 2.69 and 2.72 Å (for the orthorhombic and triclinic forms, respectively). The crystal packing for the orthorhombic form shows repulsion between Br atoms, leading to a staggered arrangement of Br atoms in adjacent molecules. This staggered conformation involves intermolecular C—H···S and C—H···Br hydrogen bonds that are not present in the triclinic form (Fig. 3 and Table 2). The orthorhombic form exhibits mean H···S and H···Br distances of 2.98 and 3.04 Å, respectively. In contrast, the triclinic form shows eclipsed dispositions for the Br atoms in different molecules (Fig. 4), which minimizes the intermolecular hydrogen bonding predominant in the orthorhombic form (Table 4). As a result of this eclipsed conformation between adjacent Br atoms and the large covalent radius of these atoms (1.14 Å), an accumulation of charge exists around each Br atom. The higher electron density around the Br atoms produces closer [3.770 (9) Å] repulsive contacts between them (Table 5), giving rise to less efficient packing, which can be seen by comparing the cell volumes [2480.4 (6) and 2531.4 (8) $Å^3$] and crystal densities (2.014 and 1.974 Mg m^{-3}) for the orthorhombic and triclinic forms.

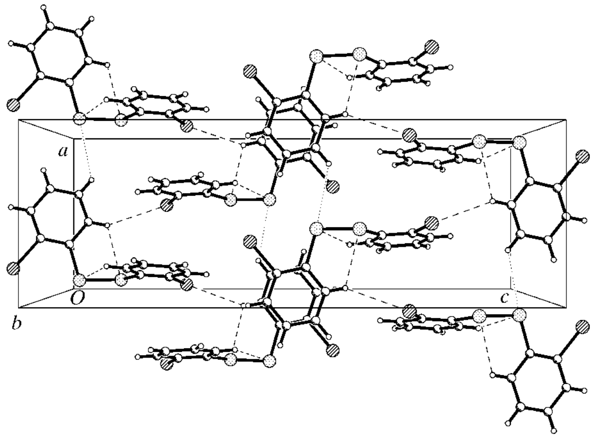

Figure 3
The packing arrangement in the orthorhombic form, (I), viewed along *b*. Hydrogen bonds are indicated by dashed lines.

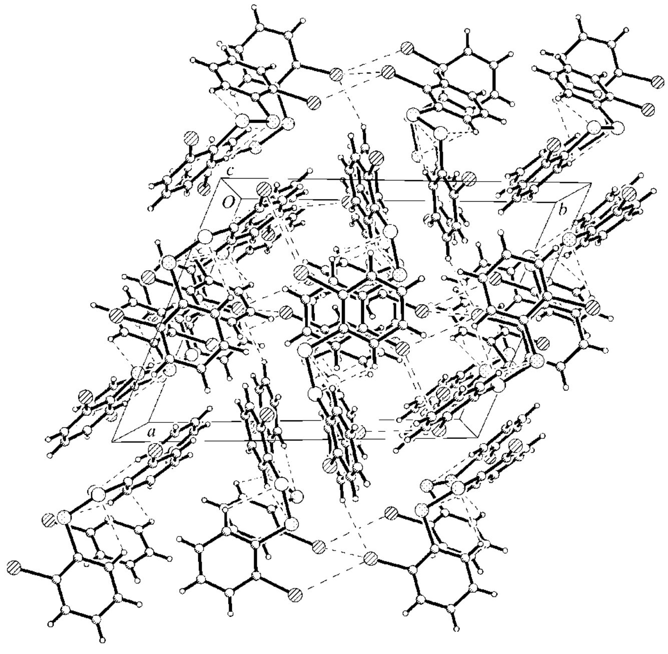

Figure 4
The packing arrangement in the triclinic form, (II), viewed along *c*. Hydrogen bonds and Br···Br contacts are indicated by dashed lines.

Experimental

The title compound was prepared by refluxing a methanol solution (15 ml) of 2-bromophenylmercaptan (2 mmol) in the presence of metallic sodium (1 g) and either $ZnCl_2$ or $CdCl_2$ (1 mmol). After refluxing for 4 h at 338 K, the volume of the solution was concentrated to 5 ml and maintained at 278 K for a week, leading to the formation of colourless columns ($ZnCl_2$) or plates ($CdCl_2$). IR and NMR spectra for both crystals correspond to the title compound. Analysis found for the orthorhomic form: C 38.15, H 2.38, S 17.22%; found for the triclinic form: C 38.15, H 2.30, S 16.98%; calculated for $C_{12}H_8Br_2S_2$: C 38.30, H 2.13, S 17.02%.

Compound (I)

Crystal data

$C_{12}H_8Br_2S_2$
$M_r = 376.12$
Orthorhombic, *Pbca*
$a = 7.6844\ (10)$ Å
$b = 14.4240\ (18)$ Å
$c = 22.378\ (3)$ Å
$V = 2480.4\ (6)$ $Å^3$
$Z = 8$
$D_x = 2.014$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 2137 reflections
$\theta = 1.8$–$26.4°$
$\mu = 6.84$ mm^{-1}
$T = 150\ (2)$ K
Column, colourless
0.38 × 0.20 × 0.16 mm

Data collection

Bruker SMART APEX CCD diffractometer with an Oxford Cryosystems low-temperature device
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.211$, $T_{max} = 0.335$

18 462 measured reflections
2537 independent reflections
2224 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 26.4°$
$h = -9 \rightarrow 9$
$k = -18 \rightarrow 18$
$l = -27 \rightarrow 27$

Table 1
Selected geometric parameters (Å, °) for (I).

Br11—C12	1.897 (2)	S11—S21	2.0270 (7)
Br21—C22	1.897 (2)	S21—C21	1.780 (2)
S11—C11	1.785 (2)		
C11—S11—S21	104.78 (7)	C11—C12—Br11	119.41 (15)
C21—S21—S11	105.64 (7)	C22—C21—S21	117.61 (15)
C12—C11—S11	118.20 (15)	C26—C21—S21	124.15 (15)
C16—C11—S11	123.71 (15)	C23—C22—Br21	118.86 (15)
C13—C12—Br11	119.02 (15)	C21—C22—Br21	119.56 (15)
C11—S11—S21—C21	−83.34 (9)	S11—S21—C21—C22	−174.69 (14)
S21—S11—C11—C12	−172.68 (14)	S11—S21—C21—C26	7.46 (19)
S21—S11—C11—C16	8.33 (18)		

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
C16—H16···S21	0.93	2.67	3.185 (2)	115
C26—H26···S11	0.93	2.71	3.215 (2)	115
C25—H25···S21^{i}	0.93	2.96	3.607 (2)	128
C24—H24···S21^{i}	0.93	2.99	3.620 (2)	126
C26—H26···Br11^{ii}	0.93	3.04	3.882 (2)	151

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.049$
$S = 1.02$
2537 reflections
145 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0317P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.42$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}

Compound (II)

Crystal data

$C_{12}H_8Br_2S_2$
$M_r = 376.12$
Triclinic, $P\overline{1}$
$a = 11.8186$ (19) Å
$b = 15.489$ (3) Å
$c = 15.653$ (3) Å
$\alpha = 102.122$ (5)°
$\beta = 100.393$ (5)°
$\gamma = 110.001$ (5)°
$V = 2531.4$ (8) Å^3

$Z = 8$
$D_x = 1.974$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3180 reflections
$\theta = 1.4$–28.8°
$\mu = 6.70$ mm^{-1}
$T = 150$ (2) K
Plate, colourless
0.13 × 0.11 × 0.06 mm

Table 3
Selected geometric parameters (Å, °) for (II).

Br11—C12	1.898 (3)	Br51—C52	1.894 (3)
Br21—C22	1.896 (3)	Br61—C62	1.901 (3)
S11—C11	1.789 (3)	S51—C51	1.787 (3)
S11—S21	2.0326 (12)	S51—S61	2.0317 (13)
S21—C21	1.782 (3)	S61—C61	1.783 (3)
Br31—C32	1.900 (3)	Br71—C72	1.906 (3)
Br41—C42	1.895 (3)	Br81—C82	1.898 (3)
S31—C31	1.782 (3)	S71—C71	1.783 (3)
S31—S41	2.0291 (14)	S71—S81	2.0279 (13)
S41—C41	1.785 (3)	S81—C81	1.787 (3)
C11—S11—S21	105.42 (11)	C51—S51—S61	104.42 (12)
C21—S21—S11	105.55 (12)	C61—S61—S51	105.17 (12)
C16—C11—S11	124.2 (2)	C56—C51—S51	124.7 (3)
C12—C11—S11	117.0 (2)	C52—C51—S51	117.0 (2)
C22—C21—S21	117.3 (3)	C62—C61—S61	118.3 (3)
C26—C21—S21	124.1 (2)	C66—C61—S61	123.8 (3)
C31—S31—S41	105.39 (12)	C71—S71—S81	104.62 (11)
C41—S41—S31	104.64 (12)	C81—S81—S71	105.05 (12)
C32—C31—S31	117.8 (2)	C76—C71—S71	124.1 (2)
C36—C31—S31	124.0 (3)	C72—C71—S71	117.5 (2)
C46—C41—S41	124.0 (3)	C86—C81—S81	124.6 (3)
C42—C41—S41	117.1 (3)	C82—C81—S81	116.7 (3)
C11—S11—S21—C21	−84.88 (16)	C51—S51—S61—C61	−83.35 (16)
S21—S11—C11—C16	14.1 (3)	S61—S51—C51—C56	10.2 (3)
S21—S11—C11—C12	−168.4 (2)	S61—S51—C51—C52	−171.7 (2)
S11—S21—C21—C22	−174.3 (2)	S51—S61—C61—C62	−169.2 (2)
S11—S21—C21—C26	6.8 (3)	S51—S61—C61—C66	10.9 (3)
C31—S31—S41—C41	−85.78 (15)	C71—S71—S81—C81	85.61 (15)
S41—S31—C31—C32	−167.6 (2)	S81—S71—C71—C76	−16.9 (3)
S41—S31—C31—C36	16.2 (3)	S81—S71—C71—C72	166.6 (2)
S31—S41—C41—C46	15.6 (3)	S71—S81—C81—C86	−6.1 (3)
S31—S41—C41—C42	−166.1 (2)	S71—S81—C81—C82	176.5 (2)

Data collection

Bruker SMART APEX CCD diffractometer with an Oxford Cryosystems low-temperature device
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.408$, $T_{\max} = 0.669$

22 934 measured reflections
13 188 independent reflections
8387 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.031$
$\theta_{\max} = 28.8°$
$h = -15 \rightarrow 16$
$k = -20 \rightarrow 20$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.060$
$S = 1.00$
11 915 reflections
577 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0121P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.98$ e Å^{-3}
$\Delta\rho_{\min} = -1.03$ e Å^{-3}

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
C16—H16···S21	0.93	2.73	3.232 (3)	114
C26—H26···S11	0.93	2.71	3.216 (4)	115
C36—H36···S41	0.93	2.74	3.230 (4)	114
C46—H46···S31	0.93	2.71	3.205 (3)	114
C56—H56···S61	0.93	2.70	3.202 (3)	115
C66—H66···S51	0.93	2.70	3.206 (4)	115
C76—H76···S81	0.93	2.71	3.207 (3)	114
C86—H86···S71	0.93	2.70	3.208 (4)	115
C44—H44···Br11^{iii}	0.93	2.99	3.743 (3)	139

Symmetry code: (iii) $2 - x, 1 - y, 1 - z$.

Table 5
Br···Br contacts (Å) in (II).

Br11···Br71	3.8681 (9)	Br21···Br51^{iv}	3.7056 (10)
Br11···Br31	3.6755 (9)	Br31···Br61^{vi}	3.6926 (9)
Br21···Br71^{iv}	3.7499 (9)	Br51···Br71	3.8931 (10)
Br21···Br41^{v}	3.8056 (9)		

Symmetry codes: (iv) $1 - x, -y, -z$; (v) $x, y - 1, z - 1$; (vi) $1 - x, -y, 1 - z$.

All H atoms were initially located from difference Fourier maps and thereafter placed at idealized positions and refined using a riding model, with a C—H distance of 0.93 Å and $U_{\rm iso}$(H) values equal to $1.2U_{\rm eq}$(C).

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1522). Services for accessing these data are described at the back of the journal.

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