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2,2′-Bi-1,3-diselenole

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Key indicators

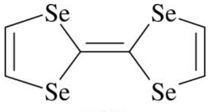
Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.004 Å
R factor = 0.020
wR factor = 0.051
Data-to-parameter ratio = 23.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title structure (commonly known as 2,2′,5,5′-tetraselenafulvalene or tetraselenafulvalene), $C_6H_4Se_4$, contains two independent molecules, one of which is planar and centrosymmetric. The other molecule has a pronounced boat conformation and no imposed crystallographic symmetry. Corresponding bond lengths in the two molecules are similar. A few short intermolecular Se⋯Se contacts are present.

Comment

2,2′-Bi-1,3-diselenole, commonly known as tetraselenafulvalene (TSF), and its sulfur analogue, tetrathiafulvalene (TTF), as well as derivatives of these molecules have been widely used as electron-donor molecules in charge-transfer compounds and cation-radical salts. A considerable number of these exhibit high electrical conductivity or even superconductivity (see, for example, Farges, 1994). A crystal structure study of TSF at room temperature has been reported in abstract form without atomic coordinates (Weidenborner *et al.*, 1977). TTF has been studied in a triclinic form (Ellern *et al.*, 1994) and in two closely related monoclinic forms (Cooper *et al.*, 1974; Batsanov, 2006). TTF is close to planar in crystals of pure TTF, as well as in most of its charge-transfer compounds. A gas-phase electron-diffraction study of TTF (Hargittai *et al.*, 1994) suggests a slight preference for a boat conformation.



TSF

The present study of TSF displays the rather unusual feature of having two independent molecules of very different conformation. One molecule (containing Se5 and Se6) is centrosymmetric and planar. The other molecule (containing Se1, Se2, Se3 and Se4) has no imposed crystallographic symmetry and has a pronounced boat shape. This feature is clearly demonstrated by the dihedral angles about the trans-annular Se⋯Se axes; these are 15.76 (7)° about Se1⋯Se2 and 28.54 (7)° about Se3⋯Se4 but only 2.3 (2)° about Se5⋯Se6. This observation suggests that TSF (in its neutral state) is a rather flexible molecule which can adapt its conformation to intermolecular forces.

In compounds of TSF and TTF, the bond lengths are often used as indicators of formal charge and bond delocalization [see an extensive comparison by Umland *et al.* (1988)]. In the present structure, however, the formal molecular charges are assumed to be zero, and corresponding distances in the two molecules do not differ significantly.

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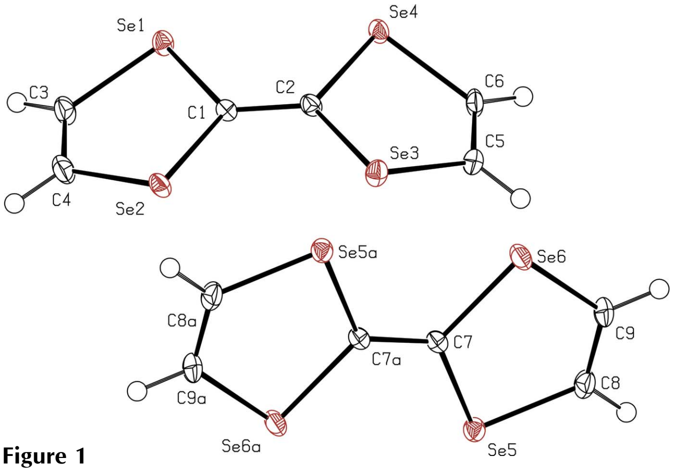

Figure 1
The structures of the boat-shaped (upper) and planar (lower) molecules of TSF with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radius. [Symmetry code: (a) $-x, 1-y, 1-z$].

As seen in Fig. 2, the two independent molecules are nearly orthogonal. The packing may be described as layers perpendicular to the [011] unit-cell direction. Within layers, back-to-back pairs of boat-shaped TSF's alternate with planar TSF's. Some short intermolecular Se$\cdots$Se contacts are observed: Se1$\cdots$Se5 = 3.5329 (1), Se3$\cdots$Se5 = 3.5829 (4) and Se4$\cdots$Se4 = 3.3797 (5) Å. As pointed out by several authors (*e.g.*, Ellern *et al.*, 1994), interactions may depend strongly on direction as well as distance.

Experimental

TSF was prepared as described earlier (Johannsen *et al.*, 1984) and purified by sublimation.

Crystal data

$C_6H_4Se_4$
$M_r = 391.93$
Triclinic, $P\overline{1}$
$a = 8.6303\ (3)$ Å
$b = 8.6454\ (3)$ Å
$c = 10.4231\ (3)$ Å
$\alpha = 105.245\ (1)^\circ$
$\beta = 106.382\ (1)^\circ$

$\gamma = 108.221\ (1)^\circ$
$V = 653.98\ (4)$ Å^3
$Z = 3$
Mo $K\alpha$ radiation
$\mu = 16.75$ mm^{-1}
$T = 120\ (2)$ K
$0.16 \times 0.15 \times 0.08$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.170$, $T_{\max} = 0.262$

7739 measured reflections
3143 independent reflections
2844 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.051$
$S = 1.04$
3143 reflections

136 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.69$ e Å^{-3}
$\Delta\rho_{\min} = -0.76$ e Å^{-3}

H atoms were placed in geometrically idealized positions and constrained to ride on their parent C atoms, with C—H = 0.95 Å and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C).

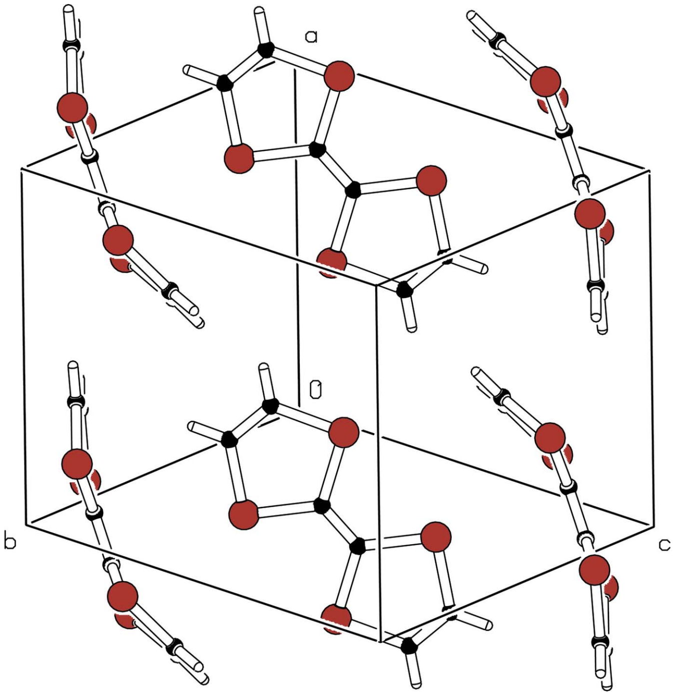

Figure 2
Packing of TSF molecules, demonstrating the orthogonal arrangement of boat-shaped and planar molecules.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *DIRDIF99* (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2001); molecular graphics: *SHELXTL* and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL* and *PLATON*.

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