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1,3,5,7-Tetraselena-2,4,6,8(2,5)-tetrathiophenaoctaphane

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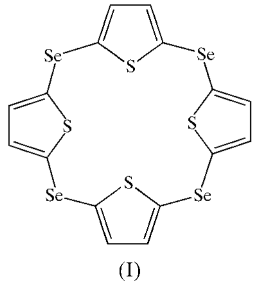
The novel title tetraselenacalix[4]arene, $C_{16}H_8S_4Se_4$ or $[(C_4H_2S)Se]_4$, has a centrosymmetric cyclic molecular structure with approximate C_{2h} molecular symmetry. The four thienyl rings are joined together by Se bridges and exhibit a *syn–syn–anti–anti* arrangement around the molecule. The lattice consists of skewed stacks of molecules, with chalcogen–chalcogen close contacts binding the stacks together, forming a two-dimensional network of molecules.

Comment

While the preparation, structural characterization and electrochemical properties of cyclic thiacalix[4]-, thiacalix[5]-, and thiacalix[6]arenes, and of some related species, have been reported (Nakayama *et al.*, 1997; Katano *et al.*, 1998; König *et al.*, 1997*a*,*b*; Nakabayashi *et al.*, 1999), no structural information on the analogous cyclic selenacalixarenes has been published to date. Tiecco *et al.* (2000) have recently demonstrated the formation of related open-chain oligomeric seleno-2,5-thienylenes by treatment of a large excess of thiophene or 2-methylthiophene with an electrophilic selenylating agent derived from dithienyl diselenide. With only a small excess of thiophene, an insoluble polymeric material was obtained.



(I)

Upon reinvestigation of this reaction by treating thiophene with a mixture of dithienyl diselenide and $PhI(OAc)_2$ (molar ratio 50:1:2) in acetonitrile, we also obtained, a yellow sparingly soluble precipitate that partially dissolves in tetrahydrofuran. Yellow crystals of the title compound, (I), $[(C_4H_2S)Se]_4$, were grown by slow evaporation of the solvent.

The lattice of (I) is composed of discrete centrosymmetric cyclic molecules, in which the four thienyl rings are joined together by four approximately coplanar Se bridges (Fig. 1). Selected bond distances and angles are given in Table 1. The asymmetric unit contains one half of the molecule, the other half being completed by symmetry. The C—Se bond lengths

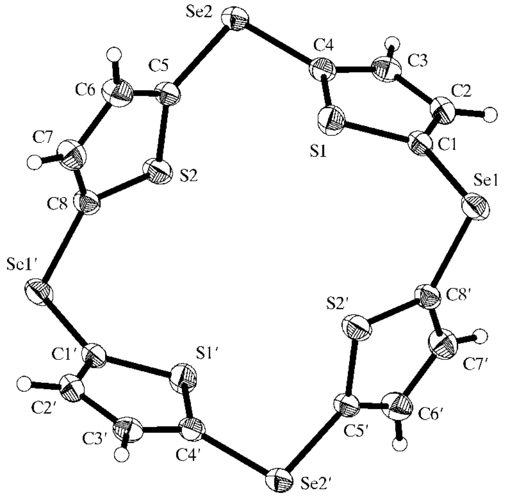


Figure 1
A view of the molecular structure of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Primed atoms are generated by the symmetry operation (1 − *x*, 1 − *y*, 2 − *z*).

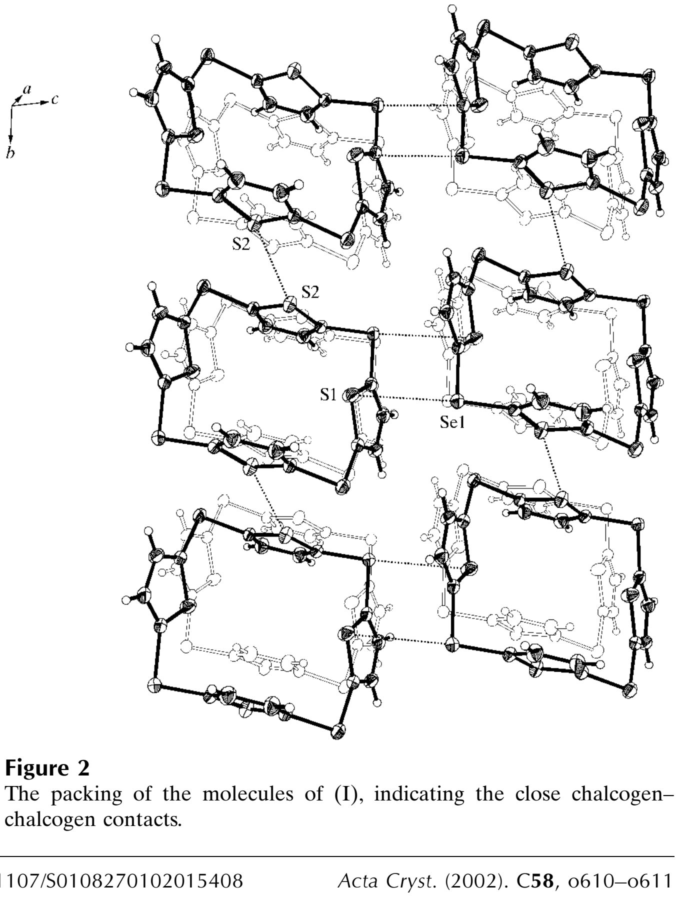


Figure 2
The packing of the molecules of (I), indicating the close chalcogen–chalcogen contacts.

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are in the range 1.900 (4)–1.910 (5) Å and show typical single-bond values. The C—C and C—S bond lengths within the thienyl rings also show expected values. The C—Se—C angles span the range 97.9 (2)–98.8 (2)° and are in agreement with the value found in Me_2Se (96.18°; Beecher, 1966). The respective C—S bond lengths and C—S—C angles in cyclic $[(C_4H_2S)S]_n$ (n = 4–6) of 1.736–1.768 Å and 100.82–105.15° (Nakayama *et al.*, 1997; Katano *et al.*, 1998) are consistent with the geometric parameters found in (I).

The molecule of (I) exhibits approximate C_{2h} molecular symmetry, with the two thienyl rings bound to Se1 exhibiting a *syn* arrangement and those bound to Se2 exhibiting an *anti* arrangement. This *syn–syn–anti–anti* arrangement is also observed in $[(C_4H_2S)S]_4$ (Katano *et al.*, 1998).

While the molecular structures of $[(C_4H_2S)S]_4$ (Katano *et al.*, 1998) and (I) are similar, their packing in the lattice is different. The molecules of both (I) and $[(C_4H_2S)S]_4$ form skewed stacks, but the geometry of the close chalcogen–chalcogen contacts is different. In the case of (I), the S2···S2 and Se1···S1 contacts [3.649 (2) and 3.472 (2) Å, respectively] form a two-dimensional network (Fig. 2), whereas in $[(C_4H_2S)S]_4$, the corresponding S···S contacts of 3.396 (9)–3.657 (5) Å assemble the molecules into a three-dimensional lattice (Katano *et al.*, 1998).

Experimental

Thiophene (4 ml, 50.63 mmol) was added to a mixture of dithienyl diselenide (0.3252 g, 1.00 mmol) and $PhI(OAc)_2$ (0.6451 g, 2.00 mmol) in acetonitrile (6 ml). The reaction mixture was stirred overnight, during which time a sparingly soluble yellow precipitate was obtained. Analysis found: C 31.74, H 1.51, S 19.49%; calculated for $C_{16}H_8S_4Se_4$: C 29.82, H 1.25, S 19.91%. The precipitate was partially dissolved in tetrahydrofuran. Yellow crystals of (I) were obtained upon slow evaporation of the solvent.

Crystal data

$C_{16}H_8S_4Se_4$
$M_r = 644.34$
Triclinic, $P\overline{1}$
$a = 6.3186$ (13) Å
$b = 8.0176$ (16) Å
$c = 9.7493$ (19) Å
$\alpha = 97.96$ (3)°
$\beta = 92.49$ (3)°
$\gamma = 92.68$ (3)°
$V = 487.99$ (17) Å^3
$Z = 1$
$D_x = 2.192$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1636 reflections
$\theta = 3.1$–26.0°
$\mu = 7.94$ mm^{-1}
$T = 293$ (2) K
Block, yellow
0.20 × 0.15 × 0.15 mm

Table 1
Selected geometric parameters (Å, °).

Se1—C1	1.906 (4)	Se2—C5	1.900 (4)
Se1—C8^{i}	1.910 (4)	Se2—C4	1.901 (4)
C1—Se1—C8^{i}	98.75 (18)	S1—C4—Se2	122.4 (3)
C5—Se2—C4	97.86 (18)	C6—C5—Se2	126.7 (3)
C2—C1—Se1	127.5 (4)	S2—C5—Se2	121.9 (3)
S1—C1—Se1	120.8 (2)	C7—C8—Se1^{i}	128.6 (3)
C3—C4—Se2	126.8 (3)	S2—C8—Se1^{i}	119.8 (3)

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

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: ψ scan (*XPREP* in *SHELXTL*; Bruker, 2001)
$T_{\min} = 0.238$, $T_{\max} = 0.304$
6496 measured reflections
1908 independent reflections
1636 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.046$
$\theta_{\max} = 26°$
$h = -7 \rightarrow 7$
$k = -9 \rightarrow 9$
$l = -12 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.091$
$S = 1.16$
1908 reflections
110 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0291P)^2 + 0.7694P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.66$ e Å^{-3}
$\Delta\rho_{\min} = -0.48$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0063 (17)

H atoms were treated as riding, with C—H = 0.93 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

Data collection: *KappaCCD Server Software* (Bruker–Nonius, 2001); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1580). Services for accessing these data are described at the back of the journal.

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