TTF d'équation $-0,9122y - 0,4097z = 0$. Les angles d'inclinaison de ces plans par rapport au plan (010) sont respectivement 33,6 et 24,2°; les modes de recouvrement sont les mêmes que ceux rencontrés dans la structure du TTF–TCNQ (Kistenmacher, Phillips & Cowan, 1974).

Greene *et al.* (1976) ont trouvé un résidu moléculaire de 8% dans une position plan symétrique par rapport au plan (010). Nous avons calculé une série différence en fin d'affinement et nous avons confirmé l'existence de densité électronique résiduelle. Nous avons pu l'évaluer à un taux de 5% en introduisant dans l'affinement des facteurs d'occupation. Le facteur R final reste inchangé et les modifications apportées aux paramètres atomiques sont insignifiantes. L'existence d'une macle rend compte du résidu.

Les piles de TCNQ et de HMTTF sont strictement ordonnées et enchaînées par liaisons $S \cdots N$ fortes (quatre par molécule, $S \cdots N = 3,25$ Å); leur succession dans la direction cristallographique **a** est rigoureuse. Elles forment des feuillets (001) ne se reproduisant pas de façon régulière créant donc de légères traînées.

Selon Weger & Friedel (1977) dans le cas du TTF–TCNQ les approches $S \cdots N$ doivent favoriser les échanges électroniques entre les piles de TCNQ et de TTF. Dans le cas présent le calcul des tenseurs de translation et de rotation autour des axes d'inertie des molécules indique que le TCNQ vibre comme un corps rigide. Dans la direction $S \cdots N$ l'amplitude de la translation est 0,13 Å, celle de la rotation 1,5°, soit 0,12 Å. L'amplitude de la translation dans la direction normale au plan moléculaire est de 0,13 Å.

Le mouvement de la molécule HMTTF dans la direction $S \cdots N$ s'exprime uniquement en terme de translation: son amplitude est 0,14 Å. L'amplitude de la translation dans la direction normale au plan moléculaire est 0,17 Å.

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2,5-Dimethyl-1,2-diselenolo[1,5-*b*][1,2]oxaselenole

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Abstract. $C_7H_8OSe_2$, $M_r = 266 \cdot 1$, monoclinic, $P2_1/c$, $a = 4 \cdot 45$ (1), $b = 10 \cdot 89$ (1), $c = 17 \cdot 58$ (2) Å, $\beta = 95 \cdot 93$ (5)°, $U = 848 \cdot 1$ Å^3, $Z = 4$, $D_o = 2 \cdot 0$ (by flotation), $D_c = 2 \cdot 08$ g cm^{-3}, μ(Cu $K\alpha$) = 110 cm^{-1}. The molecule is nearly planar and bond lengths indicate that the electronic distribution is not simply described by a ketonic formula.

Introduction. Crystals were prepared by Traverso (1958). Data were collected with Ni-filtered Cu $K\alpha$ radiation by the multiple-film equi-inclination Weissenberg method for layers 0*kl* to 4*kl*, and 1395 reflections were observed. For interlayer scaling, *hnl* reflections (recorded on precession photographs with Zr-filtered Mo $K\alpha$ radiation) were used. The structure was solved by Patterson and Fourier methods and refined anisotropically by a full-matrix least-squares program to $R = 0 \cdot 10$. The *ORFLS* program (Busing, Martin & Levy, 1962), as adapted in the XRAY 70 system (1970), on an IBM 7094/7040 DCS computer, was applied; the weighting scheme was $w = \{1 + [(k|F_o| - b)/a]^2\}^{-1}$ with $a = 8|F_{min}| = 32$, $b = 5|F_{min}| = 20$ and $k = 0 \cdot 8$. The atomic scattering factors were obtained from *International Tables for X-ray Crystallography* (1968), and,

Table 1. *Fractional atomic coordinates* $(\times 10^4$, *for* H $\times 10^3$) *with e.s.d.'s in parentheses*

	x	y	z
Se(1)	1603 (4)	1811 (1)	2143 (1)
Se(2)	−93 (5)	2008 (2)	3379 (1)
O(1)	3897 (35)	2017 (13)	1013 (8)
C(1)	963 (53)	4250 (18)	4197 (10)
C(2)	1323 (39)	3600 (15)	3479 (10)
C(3)	2806 (39)	4063 (14)	2904 (10)
C(4)	3188 (37)	3412 (13)	2223 (10)
C(5)	4619 (43)	3817 (16)	1638 (10)
C(6)	5022 (42)	3040 (18)	1001 (10)
C(7)	6730 (53)	3398 (22)	363 (12)
H(1,1)	178	518	426
H(1,2)	−141	430	427
H(1,3)	210	374	467
H(3,1)	369	498	297
H(5,1)	556	472	166
H(7,1)	766	433	35
H(7,2)	856	276	35
H(7,3)	513	336	−14

Table 2. *Equations of mean planes and atom deviations*
$(\text{Å} \times 10^3)$

Equations are referred to the a, b and c^* axes; distances of atoms not included in the calculations are in parentheses.

(I) $0 \cdot 8176x - 0 \cdot 3660y + 0 \cdot 4445z + 1 \cdot 2466 = 0$
(II) $0 \cdot 8334x - 0 \cdot 3580y + 0 \cdot 4210z + 1 \cdot 1475 = 0$
(III) $0 \cdot 8064x - 0 \cdot 3541y + 0 \cdot 4737z + 1 \cdot 3273 = 0$
(IV) $0 \cdot 8032x - 0 \cdot 3970y + 0 \cdot 4442z + 1 \cdot 1036 = 0$

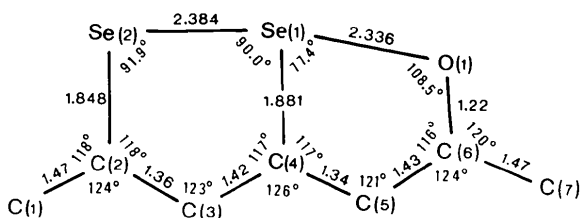|	(I)	(II)	(III)	(IV)
Se(1)	37	5	−11	(−38)
Se(2)	−44	−11	(−168)	(−126)
O(1)	−5	(−105)	15	(−57)
C(1)	−49	−7	(−240)	−50
C(2)	13	26	(−131)	−7
C(3)	19	−8	(−93)	25
C(4)	48	−5	−17	36
C(5)	57	(−37)	24	69
C(6)	1	(−117)	14	−9
C(7)	−77	(−238)	−26	−63

Fig. 1. Bond distances (Å), angles (°) and numbering of atoms for the title compound. Mean e.s.d.'s are: $\sigma_{C-C} = 0 \cdot 03$, $\sigma_{C-Se} = 0 \cdot 015$, $\sigma_{Se-Se} = 0 \cdot 003$ Å, $\sigma_{\hat{C}} = 1 \cdot 5$, $\sigma_{\widehat{Se}} = 0 \cdot 5°$.

for Se, a correction was applied for both the real and imaginary parts of anomalous dispersion (Dauben & Templeton, 1955).

Table 1 gives the final atomic parameters and Fig. 1 shows the numbering of the atoms, bond lengths and angles with e.s.d.'s. H atom coordinates have been calculated and not refined, with a mean C–H distance of 1·08 Å; for the two methyl groups the conformation with one H *trans* to Se and O was chosen on the basis of the *R* factor.*

Discussion. The title compound is related to the thio-thiophthene system, which has been studied by several authors. A list is given below of some derivatives and isosteres whose structures have been determined.

* Lists of structure factors, anisotropic thermal parameters and intermolecular distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33078 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

(a)   (b)
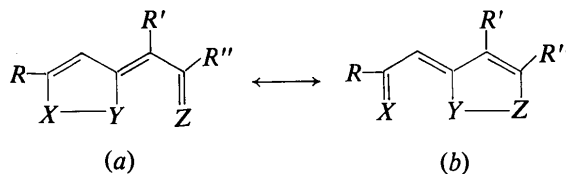
(I) $R = R'' = $ Me, $R' = $ H; $X = Y = Z = $ S (Bezzi, Mammi & Garbuglio, 1958; Leung & Nyburg, 1969)
(II) $R = R' = $ Ph, $R'' = $ H; $X = Y = Z = $ S (Hordvik, Sletten & Sletten, 1966)
(III) $R = R'' = $ Ph, $R' = $ H; $X = Y = Z = $ S (Hordvik, 1968)
(IV) $R = $ PhBr, $R' = $ PhCO, $R'' = $ SMe; $X = Y = Z = $ S (Johnson, Newton, Paul, Beer & Cartwright, 1967)
(V) $R = R' = $ Ph, $R'' = $ H; $X = Y = $ S, $Z = $ Se (Van den Hende & Klingsberg, 1966)
(VI) $R = R'' = $ Me, $R' = $ H; $X = Y = $ S, $Z = $ O (Mammi, Bardi, Traverso & Bezzi, 1961)
(VII) $R = R'' = $ Me, $R' = $ H; $X = Y = $ Se, $Z = $ O (present work).

The results have shown that only compound (I) has a perfectly symmetric structure (two condensed five-membered rings); this is because of a 'no-bond resonance' between the two equivalent structures (a) and (b), which accounts for its aromatic character (Klingsberg, 1969, and references therein). In the unsymmetrically substituted compounds, the $X-Y$ and $Y-Z$ distances are not equal: one is slightly longer than a single bond and the other is even longer, but still well below the sum of the van der Waals radii. However, aromaticity is maintained in these compounds, as well as in the isosteres (where S is substituted by Se, which only slightly perturbs the electronic distribution).

A different effect seems to occur on substituting one lateral S with O, as in the present compound. The
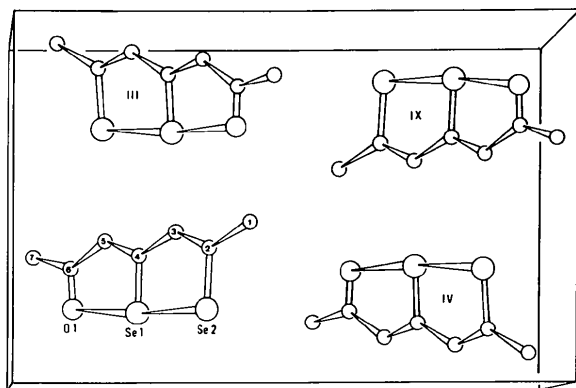
Fig. 2. Perspective view of the unit cell along [100]. The *a* axis is into the page, the *b* axis is up and the *c* axis is to the right.

Se···O intramolecular distances of 2·305 (19) Å (Baiwir, Llabres, Dideberg, Dupont & Piette, 1975) and 2·378 (3) Å (Dahlén, 1973) have been interpreted as evidence for the formation of five-membered rings.

We may conclude that the electronic distribution in the present molecule may be described by the ketonic formula (*a*) with a partial contribution of formula (*b*). Such a situation agrees with the reported chemical (Traverso, 1958) and spectroscopic properties (Pietra, Garbuglio & Mammi, 1964).

The molecular packing is shown in Fig. 2; all the intermolecular contacts are within the limits of the sum of the van der Waals radii. No special feature is to be found. It may be noted that Se and O atoms are mainly surrounded by H atoms.

molecule is roughly planar, but may be better described by the two planes through Se(1), Se(2), C(1), C(2), C(3), C(4) and Se(1), O(1), C(4), C(5), C(6), C(7): the two five-membered rings are inclined to each other at an angle of 3·4°, calculated from the mean planes reported in Table 2. This bending is also observed in other compounds of the series [6·6° in (V) and 3·0° in (VI) (Bardi, unpublished)].

An important feature of the molecule is the presence of alternating C—C bond distances, typical of a conjugated system, which extends to the C—O bond, whose length (1·22 Å) is very near to the double-bond value. The C—Se and Se—Se distances are consistently near to the single-bond value. A detailed review of observed values has been reported by Aleby (1972). C—Se bond distances of about 1·89 Å have been observed in aromatic heterocyclic compounds (Aleby, 1972; Bernier, Conde & Márquez, 1974), while larger values (1·91 ~ 1·95 Å) are reported for Se single bonds to aromatic or conjugated C atoms (Aleby, 1972; Dexter, 1972; Llabres, Dideberg & Dupont, 1972; Dahlén, 1973). A smaller value of 1·83 (2) Å has been observed for a partial C—Se double bond (Conde, López-Castro & Márquez, 1972). Our values of 1·88 and 1·85 Å are therefore slightly shorter than expected for a single bond.

Apart from a single value of 2·380 (6) Å (Villa, Nardelli & Tani, 1970), the Se—Se bond lengths reported in the literature (Aleby, 1972) range from 2·28 to 2·33 Å, lower than the sum of the covalent radii (2·34 Å, Pauling, 1960). Our value is therefore slightly larger than expected for a single bond.

It is interesting to note that the Se(1)···O(1) distance of 2·34 Å is much shorter than the van der Waals value (3·4 Å) but longer than the sum of the covalent radii (1·91 Å, Pauling, 1960). The observed value suggests a positive interaction between Se and O, not simply required by steric conditions, as indicated by the inner valence angles of C(6) and C(4) of less than 120°.

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