

Structure of Ethyl Phenyl Selenone

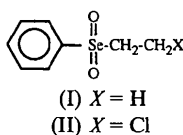
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Abstract. $C_8H_{10}O_2Se$, $M_r = 217.13$, monoclinic, $P2_1/n$, $a = 9.511$ (2), $b = 15.741$ (3), $c = 11.467$ (2) Å, $\beta = 91.31$ (2)°, $V = 1716.3$ (6) Å³, $Z = 8$ (two molecules per asymmetric unit), $D_x = 1.68$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 4.19$ mm⁻¹, $F(000) = 864$, $T = 295$ K, $R_{obs} = 0.060$ for 1944 unique reflections with $I > 2\sigma(I)$. The two molecules in the asymmetric unit are very similar; they differ only in the conformation of the ethyl side chain. There is considerable disorder in one molecule, that possibly can be represented by torsion about the Se—C(ethyl) bond. In each case the O atoms of the SeO₂ group lie near the plane of the phenyl group. Se—O···H—C interactions appear to be the only significant intermolecular interactions. These involve an H atom of the α -C atom of the ethyl group in addition to the H atoms of the phenyl group.

Introduction. Alkylating organoselenones (ArSeO₂R) have been studied as potential antitumor agents as a result of their tendency to undergo nucleophilic substitution by Se—C bond cleavage, probably related to the strong acidity of the seleninic acid (ArSeO₂H) leaving group (Kang & Spears, 1990). The structure of ethyl phenyl selenone (I), a monofunctional alkylating agent, was determined by X-ray diffraction techniques. Compounds with chloroethyl side chains (II) are bifunctional alkylating agents.



Experimental. The method of preparation of this compound has been reported (Kang & Spears, 1988, 1990). Colorless transparent crystals were grown from toluene containing a trace of *n*-heptane. An equidimensional rhomb, approximately 0.15 mm in each dimension, was cut from one of these crystals.

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The X-ray diffraction data were measured on a Nicolet/Siemens P3 four-circle automated diffractometer using variable θ - 2θ scans in the range 2.02–58.6° min⁻¹ (depending on reflection intensity) and monochromated Mo $K\alpha$ radiation. The lattice parameters were determined, using a least-squares procedure, from 14 centered reflections in the 2θ range 25.9–35.1°. All measurements were made at approximately 295 K. The index ranges of data were $h = 0$ to 12, $k = 0$ to 22, $l = -16$ to 16 and the number of data was 3254, from a total of 3463, measured to $\sin\theta/\lambda = 0.61$ Å⁻¹. R_{merge} was 0.030. Three standard reflections (200, 060 and 004) were measured at periodic intervals in order to check the crystal decay and a correction term of the form $I = I_0 + 0.0012t$ (t = time after initiation of measurement) was applied. The data were corrected for Lorentz and polarization effects. The weights for reflections used in the least-squares refinements, $w = 1/\sigma^2(F)$, were derived from counting statistics using the relation $\sigma(F) = (F/2)[\sigma^2(I)/I^2 + \delta^2]^{1/2}$ in which δ (= 0.0390) is an instrumental uncertainty based on the variation in the intensities of the standard reflections monitored throughout the data collections. Intensity data with $I > 2\sigma(I)$ were considered observed. No absorption correction was applied ($\mu = 41.9$ cm⁻¹).

The structure was determined by locating the Se atom by use of the Patterson map. Fourier maps were then computed so that the lighter atoms could be located. The structure was refined on F by a full-matrix least-squares procedure. Each non-H atom was refined, initially isotropically, then anisotropically. All intensity data considered to be observed at the 2σ level were used in the refinement (1944 in all). H atoms, placed in calculated positions with the isotropic temperature factors of the C atoms to which they are bonded, were included in further calculations but were not refined. For all crystallographic calculations in-house programs were used (Carrell, Shieh & Takusagawa, 1981). Thermal ellipsoid plots were produced with *SNOOPI* (Davies, 1983). The packing diagram was drawn with the program *VIEW* (Carrell, 1976), and comparisons between molecules were made with *MOLDOCK* (Carrell, 1991). Atomic scattering factors were taken

from *International Tables for X-ray Crystallography* (1974, Vol. IV). No corrections were made for anomalous scattering or extinction. Final $R_{\text{obs}} = 0.060$, $R_{\text{all}} = 0.120$, $wR_{\text{obs}} = 0.065$, $wR_{\text{all}} = 0.072$; number of parameters refined = 199; $S = 1.33$; $(\Delta/\sigma)_{\text{max}} = 0.07$; $(\Delta\rho)_{\text{max}} = 0.9$, $(\Delta\rho)_{\text{min}} = -0.6 \text{ e } \text{Å}^{-3}$.

The final positional parameters and equivalent isotropic temperature factors from values obtained from the least-squares refinement are listed in Table 1.*

Discussion. A diagram showing thermal ellipsoids for non-H atoms is given in Fig. 1. Bond distances, interbond angles and torsion angles are listed in Table 2. They are very similar (as shown in Table 2) to those reported in methyl phenyl selenone (Krief, Dumont & Denis, 1985). There are two molecules in the asymmetric unit and the coordinates show that equivalent atoms in the two independent molecules have approximately the same y values and are related to each other by a center of symmetry. The two molecules have been superposed on each other and the resulting similarities are shown in Fig. 2(a). The only substantial difference is in the disposition of the second C atom of the ethyl side chain (Fig. 2). This difference is also indicated by the appropriate torsion angles [involving Se and C(17) or C(27)] listed in Table 2. In each case the two O atoms attached to the Se atom lie near the plane of the benzene ring, while the ethyl group lies well out of this plane. An analogous arrangement is found in the crystal structure of methyl phenyl selenone (Krief, Dumont & Denis, 1985). In molecule 2 of the ethyl phenyl selenone (studied here), viewed down the Se(2)—C(27) (ethyl) bond, the terminal CH_3 group [C(28)] is *gauche*, whereas in molecule 1 [C(18)] it is *anti* (Fig. 2b). The Se—O bond lengths (1.58–1.63 Å) and Se—C bond lengths (1.91–1.95 Å) are near those normally expected for double-bonded Se=O (1.597 Å) and Se—C [averages 1.970 Å for C(sp^3)—Se and 1.930 Å for C(aryl)—Se], respectively (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987).

There is considerable disorder in molecule 2; this is evident in the final electron density map, in the thermal ellipsoids (Fig. 1), and in the anisotropic temperature factors.* Most of this disorder occurs in the ethyl group of molecule 2. The effect is best described as torsion, particularly about the Se(2)—C(27) bond. Attempts were made to fit a disordered

* Lists of calculated H-atom positions, anisotropic temperature factors and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55630 (47 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1004]

Table 1. Atomic coordinates and equivalent isotropic temperature factors (Å^2)

	x	y	z	B_{eq}
Se(1)	0.22718 (5)	0.05096 (3)	1.18251 (4)	3.99 (3)
Se(2)	0.23310 (5)	0.05145 (3)	0.70506 (4)	3.82 (3)
C(11)	0.2571 (5)	-0.0659 (3)	1.1391 (4)	3.7 (2)
C(12)	0.1871 (6)	-0.1279 (4)	1.2008 (5)	4.8 (3)
C(13)	0.2150 (6)	-0.2119 (3)	1.1732 (5)	4.8 (3)
C(14)	0.3082 (6)	-0.2321 (3)	1.0909 (5)	4.8 (3)
C(15)	0.3710 (6)	-0.1679 (4)	1.0340 (4)	5.0 (3)
C(16)	0.3460 (6)	-0.0838 (3)	1.0567 (4)	4.4 (3)
C(17)	0.0644 (5)	0.0874 (3)	1.0938 (4)	4.0 (3)
C(18)	0.0201 (6)	0.1753 (4)	1.1319 (5)	5.5 (3)
O(11)	0.1916 (6)	0.0546 (3)	1.3210 (3)	7.5 (3)
O(12)	0.3614 (4)	0.1050 (2)	1.1388 (4)	5.8 (2)
C(21)	0.2367 (5)	-0.0641 (3)	0.6554 (4)	3.2 (2)
C(22)	0.3170 (6)	-0.1205 (3)	0.7167 (4)	4.1 (3)
C(23)	0.3146 (6)	-0.2048 (3)	0.6839 (5)	4.5 (3)
C(24)	0.2320 (6)	-0.2299 (3)	0.5888 (5)	4.5 (3)
C(25)	0.1530 (6)	-0.1721 (3)	0.5265 (5)	4.5 (3)
C(26)	0.1554 (5)	-0.0877 (3)	0.5591 (5)	4.1 (3)
C(27)	0.4200 (8)	0.0971 (5)	0.6788 (8)	10.0 (5)
C(28)	0.4504 (9)	0.1031 (5)	0.5545 (9)	12.5 (6)
O(21)	0.2219 (7)	0.0509 (3)	0.8426 (4)	8.6 (3)
O(22)	0.1115 (5)	0.1031 (3)	0.6364 (4)	6.6 (2)

Table 2. Bond distances (Å), interbond angles ($^\circ$) and torsion angles ($^\circ$)

Values in square brackets refer to methyl phenyl selenone (Krief, Dumont & Denis, 1985). For torsion angles, e.s.d.'s are from 0.5 to 0.9 $^\circ$.

Se(1)—O(11)	1.632 (4)	Se(2)—O(21)	1.584 (5)
Se(1)—O(12)	1.623 (4)	Se(2)—O(22)	1.605 (5)
Se(1)—C(11)	1.929 (5)	Se(2)—C(21)	1.907 (5)
Se(1)—C(17)	1.921 (5)	Se(2)—C(27)	1.947 (8)
C(11)—C(12)	1.385 (8)	C(21)—C(22)	1.358 (7)
C(11)—C(16)	1.313 (7)	C(21)—C(26)	1.384 (7)
C(12)—C(13)	1.387 (8)	C(22)—C(23)	1.379 (7)
C(13)—C(14)	1.347 (8)	C(23)—C(24)	1.387 (8)
C(14)—C(15)	1.349 (8)	C(24)—C(25)	1.371 (7)
C(15)—C(16)	1.371 (8)	C(25)—C(26)	1.380 (7)
C(17)—C(18)	1.514 (8)	C(27)—C(28)	1.464 (10)
C(11)—Se(1)—C(17)	105.6 (2)	C(21)—Se(2)—C(27)	106.4 (3)
C(11)—Se(1)—O(11)	108.6 (2)	C(21)—Se(2)—O(21)	107.1 (2)
C(11)—Se(1)—O(12)	107.4 (2)	C(21)—Se(2)—O(22)	110.7 (2)
C(17)—Se(1)—O(11)	108.8 (2)	C(27)—Se(2)—O(21)	103.8 (3)
C(17)—Se(1)—O(12)	108.0 (2)	C(27)—Se(2)—O(22)	112.7 (3)
O(11)—Se(1)—O(12)	117.6 (2)	O(21)—Se(2)—O(22)	115.2 (3)
Se(1)—C(11)—C(12)	117.6 (4)	Se(2)—C(21)—C(22)	118.8 (4)
Se(1)—C(11)—C(16)	119.4 (4)	Se(2)—C(21)—C(26)	118.7 (4)
C(12)—C(11)—C(16)	122.8 (5)	C(22)—C(21)—C(26)	122.4 (4)
C(11)—C(12)—C(13)	117.2 (5)	C(21)—C(22)—C(23)	118.8 (5)
C(12)—C(13)—C(14)	121.1 (5)	C(22)—C(23)—C(24)	119.6 (5)
C(13)—C(14)—C(15)	117.9 (5)	C(23)—C(24)—C(25)	120.9 (5)
C(14)—C(15)—C(16)	123.3 (5)	C(24)—C(25)—C(26)	119.5 (5)
C(11)—C(16)—C(15)	117.4 (5)	C(21)—C(26)—C(25)	118.6 (5)
Se(1)—C(17)—C(18)	110.2 (3)	Se(2)—C(27)—C(28)	112.0 (6)
C(17)—Se(1)—C(11)—C(12)	-87.7	C(27)—Se(2)—C(21)—C(22)	67.6
C(17)—Se(1)—C(11)—C(16)	95.2	C(27)—Se(2)—C(21)—C(26)	-113.4
O(11)—Se(1)—C(11)—C(12)	28.9	O(21)—Se(2)—C(21)—C(22)	-43.0
O(11)—Se(1)—C(11)—C(16)	-148.2	O(21)—Se(2)—C(21)—C(26)	136.0
O(12)—Se(1)—C(11)—C(12)	157.2	O(22)—Se(2)—C(21)—C(22)	-169.5
O(12)—Se(1)—C(11)—C(16)	-20.0	O(22)—Se(2)—C(21)—C(26)	9.5
C(11)—Se(1)—C(17)—C(18)	173.0	C(21)—Se(2)—C(27)—C(28)	67.4
O(11)—Se(1)—C(17)—C(18)	56.5	O(21)—Se(2)—C(27)—C(28)	-179.7
O(12)—Se(1)—C(17)—C(18)	-72.3	O(22)—Se(2)—C(27)—C(28)	-54.3
C(16)—C(11)—C(12)—C(13)	0.5	C(26)—C(21)—C(22)—C(23)	-1.9
C(12)—C(11)—C(16)—C(15)	-1.3	C(22)—C(21)—C(26)—C(25)	1.9
C(11)—C(12)—C(13)—C(14)	1.1	C(21)—C(22)—C(23)—C(24)	0.8
C(12)—C(13)—C(14)—C(15)	-1.6	C(22)—C(23)—C(24)—C(25)	0.2
C(13)—C(14)—C(15)—C(16)	0.8	C(23)—C(24)—C(25)—C(26)	-0.1
C(14)—C(15)—C(16)—C(11)	0.7	C(24)—C(25)—C(26)—C(21)	-0.9

model to the electron density map but they were not successful, although it appears that any variation in the position for C(28) does not alter the Se(2)···C(28) distance, which is approximately 2.84 Å.

The packing of the molecule in the crystal is illustrated in Fig. 3 (Carrell, 1976). There are no strong forces between individual molecules. Some C—H···O—Se distances are listed in Table 3 but none appear to be shorter than the sum of the van der Waals radii of O and H atoms. Their directionality might, however, be considered to indicate

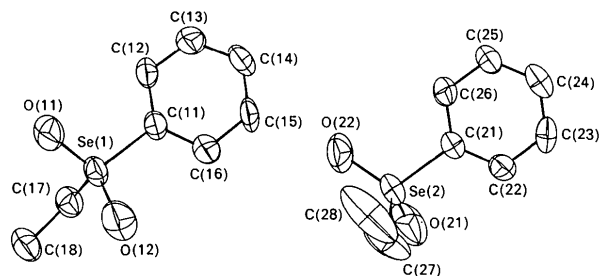


Fig. 1. Thermal ellipsoid (50%) representation and atomic numbering.

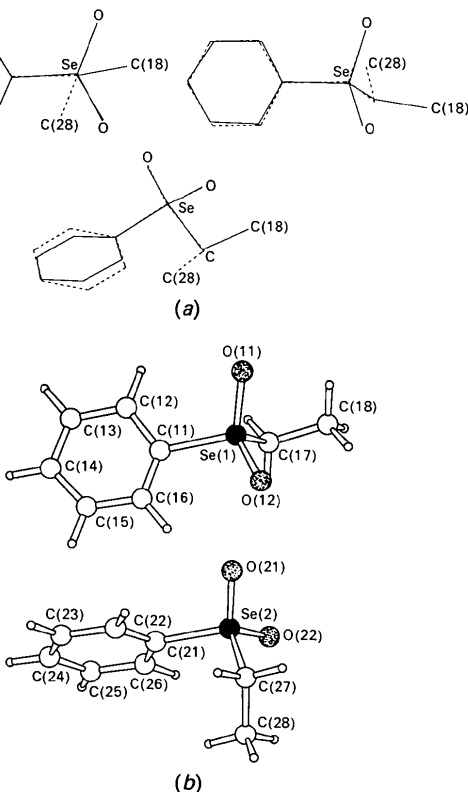
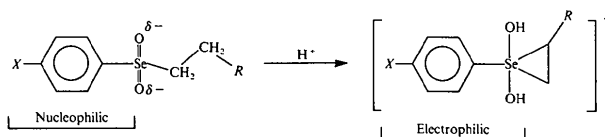


Fig. 2. (a) Three different views of the conformations of the two molecules in the asymmetric unit. Molecule 1 solid line. Molecule 2 dashed line. (b) Ball-and-stick drawings of molecules 1 and 2, indicating their *anti* and *gauche* conformations.

some interaction, as they appear to be the only intermolecular forces holding the crystal together. They mostly involve interactions between the phenyl H atoms and the Se—O groups, but one interaction [C(17)—H(171)···O(21) = 2.58 Å with an angle of 174°] involves an H atom of the ethyl group of molecule 1. If this H atom [H(171)] were to move onto O(21) from C(17) this would imply some degree of seleninic character [$RSe(OH)_2^+$] for molecule 2. The disorder in molecule 2 does not, however, show evidence of a three-membered Se—C—C ring which would be expected as an intermediate in the alkylating action of this selenone. Thus, in the crystal structure, C(28) is no nearer to Se(2) (2.84 Å) than C(18) is to Se(1) (2.83 Å). The expected reaction is shown below:



A slow pericyclic intramolecular mechanism (Reich, 1983) can be envisioned for aryl selenones, with subsequent *syn* elimination of olefin and seleninic acid (analogous to the elimination reaction of selenoxides to form olefins and selenenic acid). The results obtained here are consistent with a postulated 'umpolung' mechanism (Seebach, 1979) for

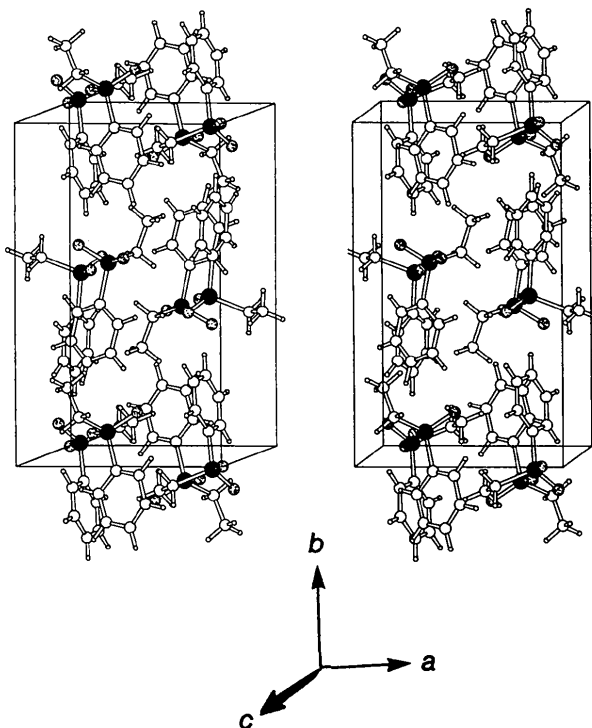


Fig. 3. Stereoview of packing in the unit cell.

Table 3. *Some intermolecular C—H...O distances (Å with e.s.d. 0.08 Å)*

Molecule 1	H...O	Symmetry position of O
C(12)—H(12)...O(22)	2.51	$-x, -y, 2-z$
C(14)—H(14)...O(11)	2.71	$0.5-x, y-0.5, 2.5-z$
C(15)—H(15)...O(12)	2.61	$1-x, -y, 2-z$
C(17)—H(17)...O(21)	2.58	$-x, -y, 2-z$
Molecule 2		
C(22)—H(22)...O(12)	2.62	$1-x, -y, 2-z$
C(23)—H(23)...O(22)	2.82	$0.5-x, y-0.5, 1.5-z$
C(24)—H(24)...O(21)	2.74	$0.5-x, y-0.5, 1.5-z$
C(25)—H(25)...O(22)	2.61	$-x, -y, 1-z$
C(26)—H(26)...O(11)	2.86	$x, y, z-1$
C(26)—H(26)...O(22)	2.77	$-x, -y, 1-z$

pericyclic formation of an electrophilic ethylene seleninic acid intermediate. This seleninic acid species would be expected to be a soft highly polarizable electrophile, that provides one explanation for the very high nucleophilic selectivities of alkylating aryl selenones.

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Structure of the Molecular Complex of Anthracene with 1,8:4,5-Naphthalenetetracarboxylic Dianhydride

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Abstract. $C_{14}H_{10}$ · $C_{14}H_4O_6$, $M_r = 446.42$, monoclinic, $P2_1/a$, $a = 17.572$ (10), $b = 7.727$ (4), $c = 7.398$ (4) Å, $\beta = 101.90$ (4)°, $V = 982.9$ (9) Å³, $Z = 2$, $D_x = 1.508$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.100$ mm⁻¹, $F(000) = 460$, $T = 293$ K, $R = 0.050$ for 1429 unique reflections with $I > 3\sigma(I)$. The molecules stack with alternating rows of anthracene and dianhydride molecules. The two types of molecule do not lie parallel to each other in these stacks, possibly as a result of interactions between the peripheral H atoms of the anthracene and O atoms of the anhydride.

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Introduction. Crystal structures of complexes of polycyclic aromatic hydrocarbons with many flat molecules such as trinitrobenzene, pyromellitic dianhydride and 1,8:4,5-naphthalenetetracarboxylic dianhydride are nicely crystalline and the structures of many of these have been investigated by X-ray diffraction techniques (Prout & Wright, 1968; Foster, 1969; Herbstein, 1971; Mayoh & Prout, 1972; Munnoch & Wright, 1974, 1975; Foster, Iball, Scrimgeour & Williams, 1976). The general feature of such molecular complexes of polycyclic aromatic hydrocarbons is the parallel stacking of alternate donor and acceptor molecules. The planes in which these molecules lie are approximately 3.4-3.5 Å apart,