

N1—C5—C4	118.7 (2)	O2—C7—C1	118.7 (1)
N1—C5—C6	119.4 (2)	O3—C8—O4	124.3 (2)
O1—C7—O2	124.3 (2)	O3—C8—C3	113.1 (2)
O1—C7—C1	117.1 (1)	O4—C8—C3	122.6 (2)

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

	D—H...A	D—H	H...A	D...A	D—H...A
a	N1—H1N...O2'	0.99 (2)	1.80 (2)	2.762 (2)	163 (2)
b	N1—H3N...O2''	1.00 (2)	1.97 (2)	2.905 (2)	155 (2)
c	O3—H3...O1'''	1.03 (2)	1.51 (2)	2.536 (2)	178 (2)
d	N1—H2N...O5''	0.99 (2)	1.83 (2)	2.796 (2)	163 (2)
e	O5—H5...O1	0.95 (2)	1.80 (2)	2.746 (2)	176 (2)

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

Table 3. *First- and basic second-level graph set descriptors involving hydrogen bonds between acid molecules which are designated a–c in the order given in Table 2*

	a	b	c
a	C(7)	$R_2^2(8)$	$C_2^2(11)$
b		$R_2^2(14)$	$C_2^2(11)$
c			C(8)

Fourier difference methods were used to locate the initial H-atom positions and the H atoms were then refined isotropically; refined C—H distances ranged from 0.98 (1) to 1.01 (1) Å, with a mean value of 0.99 (1) Å. Subsequently, the ring H atoms were made canonical, with C—H = 0.98 Å and $U_{iso} = 1.2U_{eq}$ of the attached C atom. Refined N—H and O—H distances are given in Table 2.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *MITHRIL84* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

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cis-4,6-Dimethyl-2-phenyl-1,3-diselenane

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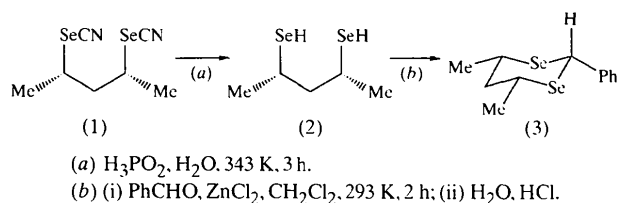
Abstract

In the crystal of the title compound, C₁₂H₁₆Se₂, the packing involves quadrupolar interactions, and the 1,3-diselenane cycle adopts a chair conformation. This compound was synthesized using diselenocyanate and benzaldehyde.

Comment

The 1,3-dithianes are very interesting synthetic intermediates. Seebach & Corey (1975) have shown that these compounds, when metallated in position 2, are synthetically equivalent to acyl anions. 1,3-Diselenanes are the selenium analogues of 1,3-dithianes. We have recently shown that those bearing at least one H atom at position 2 react selectively with *n*-butyllithium and lead to give products resulting from the cleavage at C-2, of the C—Se or of the C—H bond, depending upon the nature of the substituents present at the 2, 4 and 6 positions (Krief & Defrère, 1996). The title 1,3-diselenane, (3),

bearing methyl groups at C-4 and C-6, and a H atom and a phenyl substituent at C-2, can be readily synthesized from compound (1) and benzaldehyde (Clarembau *et al.*, 1985).



According to the Cambridge Structural Database [CSD, Version 5.14 (October 97); Allen & Kennard, 1993], compound (3) (Fig. 1) is the third published structure of a 1,3-diselenane; the first two (CSD codes SOJJK and SOJJUW) are 1,3-diselenane phosphonates published by Mikolajczyk *et al.* (1991). The introduction of Se atoms into the cyclohexane ring results in C—Se bonds longer than C—C bonds and C—Se—C valence angles smaller than the other valence angles. Puckering analysis (Evans & Boeyens, 1989; Cremer & Pople, 1975) of the Se1—C6 ring gives a total puckering amplitude (Q) of 0.727(3) Å, which is greater than the Q value of an ideal cyclohexane chair (0.63 Å; Cremer & Pople, 1975). However, the conformation is mainly chair (94%), with a small contribution (5%) of boat conformation [$\varphi(B)$ of 12°]. Similar structural features can be found in compound SOJJK; the r.m.s. deviation between these two 1,3-diselenane rings is 0.056 Å (coordinates of SOJJUW were not available in the CSD).

The two methyl groups (C7 and C8) are related by an approximate molecular mirror plane. Despite this fact, the atomic displacement parameters are very different [$U_{eq}(C7) = 0.0866(12)$ and $U_{eq}(C8) = 0.1036(18)$ Å²]. This is also the case for the two symmetric Se atoms [$U_{eq}(Se1) = 0.0544(2)$ and $U_{eq}(Se3) = 0.0626(2)$ Å²].

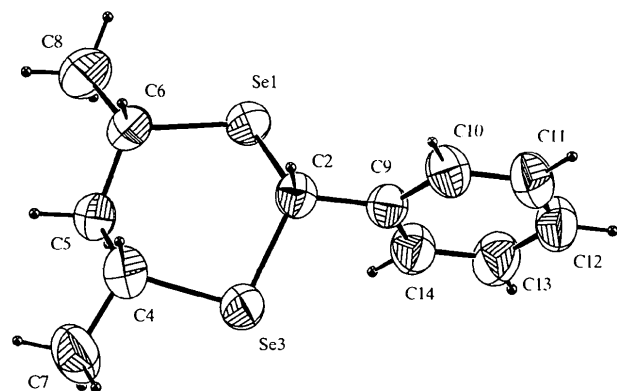


Fig. 1. The molecular structure of compound (3). Displacement ellipsoids are drawn at the 50% probability level.

The packing in the crystal can be explained mainly in terms of an intermolecular interaction between the H12 atom, attached to the phenyl group, and the aromatic ring C9ⁱ—C14ⁱ [symmetry code: (i) $-\frac{1}{2} + x, y, \frac{1}{2} - z$]. The distance between H12 and the centroid of the ring is 3.27 Å. The angle between the planes defined by the two rings is 78.13°. This situation can be explained by the fact that the phenyl substituents behave electrostatically like quadrupoles (Williams, 1993; Luhmer *et al.*, 1994) and that the Coulomb forces between these groups tend to place them in a 'T-shaped' arrangement.

Experimental

Compound (1) (252 mg, 1 mmol; M_r 252) was placed in a two-necked flask under argon and covered with aqueous hypophosphorous acid (3 ml of a 50% mixture, 29 mmol; M_r 66) and degassed over 30 min with argon. The mixture was heated to 343 K for 2 h, and the reaction was followed by TLC [ether/pentane eluent (7:3 v/v); R_f of compound (1) = 0.495]. The resulting mixture was then extracted four times with 2 ml of dry degassed CH_2Cl_2 , then poured into a pear-shaped flask under argon containing small amounts of $CaCl_2$ and 2 ml of dry CH_2Cl_2 . The resulting solution was then poured into another 25 ml two-necked flask under argon containing $ZnCl_2$ (68.2 mg, 0.5 mmol; M_r 136) in 2 ml of CH_2Cl_2 under agitation. Freshly distilled $PhCHO$ (106 mg, 1 mmol; M_r 106) dissolved in 5 ml of dry CH_2Cl_2 was added and the reaction mixture stirred vigorously for 12 min, then hydrolyzed with (i) 10 ml water and (ii) 10 ml of a 10% solution of HCl, and finally extracted four times with CH_2Cl_2 (25 ml). The organic phases were washed two times with 20 ml of a 10% solution of HCl, two times with a saturated solution of $NaHCO_3$, and three times with 20 ml of water, and finally dried with $MgSO_4$. The solvents were evaporated under reduced pressure and 230 mg of crude product was obtained as a solid, which was recrystallized in pentane to obtain 0.505 mmol (160 mg; 50.5% yield) of compound (3) ($C_{12}H_{16}Se_2$; M_r 318.17; m.p. 341–342 K; analysis found: C 45.74, H 5.09%; calculated: C 45.30, H 5.07%). The crystals of compound (3) used for single-crystal X-ray diffraction study were grown overnight by evaporation of a hexane solution at room temperature.

Crystal data

$C_{12}H_{16}Se_2$
 $M_r = 318.17$
 Orthorhombic
Pbca
 $a = 8.582(5)$ Å
 $b = 9.609(5)$ Å
 $c = 31.213(5)$ Å
 $V = 2574(2)$ Å³
 $Z = 8$
 $D_x = 1.642$ Mg m⁻³
 D_m not measured

Cu $K\alpha$ radiation
 $\lambda = 1.54178$ Å
 Cell parameters from 25 reflections
 $\theta = 40\text{--}50^\circ$
 $\mu = 6.865$ mm⁻¹
 $T = 292(2)$ K
 Hexagonal prism
 $0.39 \times 0.19 \times 0.12$ mm
 Transparent, colourless

Data collection

Enraf–Nonius CAD-4
 diffractometer

2276 reflections with
 $I > 2\sigma(I)$

$\omega/2\theta$ scans
 Absorption correction:
 analytical (PLATON;
 Spek, 1990)
 $T_{\min} = 0.227$, $T_{\max} = 0.508$
 3079 measured reflections
 2522 independent reflections
 $R_{\text{int}} = 0.044$
 $\theta_{\max} = 71.94^\circ$
 $h = -10 \rightarrow 6$
 $k = -11 \rightarrow 0$
 $l = -38 \rightarrow 0$
 3 standard reflections
 frequency: 60 min
 intensity decay: 16.4%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.103$
 $S = 1.077$
 2522 reflections
 130 parameters
 H atoms constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0601P)^2 + 1.0789P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.0001$
 $\Delta\rho_{\max} = 0.442 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.466 \text{ e } \text{\AA}^{-3}$
 Extinction correction:
 SHELXL97 (Sheldrick, 1997a)
 Extinction coefficient:
 0.0055 (2)
 Scattering factors from
 International Tables for
 Crystallography (Vol. C)

Table 1. Selected geometric parameters ($\text{\AA}$, $^\circ$)

Se1—C2	1.950 (3)	Se3—C4	1.960 (3)
Se1—C6	1.966 (3)	C4—C5	1.512 (4)
C2—Se3	1.966 (3)	C5—C6	1.511 (4)
C2—Se1—C6	100.64 (13)	C5—C4—Se3	113.6 (2)
Se1—C2—Se3	112.65 (13)	C6—C5—C4	116.1 (3)
C4—Se3—C2	99.91 (13)	C5—C6—Se1	113.1 (2)
C6—Se1—C2—Se3	53.42 (17)	Se3—C4—C5—C6	−71.2 (3)
Se1—C2—Se3—C4	−53.47 (17)	C4—C5—C6—Se1	70.4 (3)
C2—Se3—C4—C5	57.7 (2)	C2—Se1—C6—C5	−57.1 (3)

The non-H atoms were refined with anisotropic displacement parameters and the H atoms were subject to constrained refinement.

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1992). Cell refinement: CAD-4 EXPRESS. Data reduction: HELENA (Spek, 1997). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1997b). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a). Molecular graphics: PLATON (Spek, 1990). Software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1184). Services for accessing these data are described at the back of the journal.

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Methylamine and Dimethylamine Salts of the Hydrogen Maleate Ion

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Abstract

Methylammonium hydrogen maleate, $\text{CH}_3\text{N}^+\cdot\text{C}_4\text{H}_3\text{O}_4^-$, crystallizes in space group $Pnam$ with two independent anions in the asymmetric unit having crystallographic mirror planes bisecting the $\text{C}=\text{C}$ bonds. Dimethylammonium hydrogen maleate, $\text{C}_2\text{H}_5\text{N}^+\cdot\text{C}_4\text{H}_3\text{O}_4^-$, crystallizes in space group $P2_1/n$ without crystallographic symmetry constraints on the hydrogen maleate ion and this anion also possesses almost perfect mirror-plane symmetry. One of the anions in the methylammonium salt displays significant deviation from planarity [$-12.00(9)^\circ$]. The symmetry of the three anions and the difference in their conformations are rationalized from the hydrogen-bond interactions in the two salts.

Comment

Hydrogen maleate ions possess a short intramolecular hydrogen bond with corresponding $\text{O}\cdots\text{O}$ distances around 2.42 Å. One would expect that a short hydrogen bond like this would lead to a fairly rigid geometry. However, significant variations are observed with