2-Phenylselanyl-3,5-methano-2*H*-cyclopenta[*b*]furan-2-one

Thomas Francis,* D. Alan R. Happer and Ward T. Robinson

Chemistry Department, University of Canterbury, PO Box 4800, Christchurch 8004, New Zealand

Correspondence e-mail:
tfr13@student.canterbury.ac.nz

Key indicators

The title compound, $C_{14}H_{14}O_2Se$, crystallizes as separate neutral molecules each consisting of one norbornane moiety bridged through aa Se atom to a phenyl group and covalently bonded to both the C and O atoms of a carboxylate group forming a five-membered ring. It is a useful intermediate in the synthesis of larger organometallic complexes. One molecule of the title compound constitutes the asymmetric unit. The packing of molecules in well defined layers results in a number of C—H···Se 'agostic' interactions and weak C—H···O=C hydrogen bonds.

Comment

The title compound, (I), was prepared as part of our ongoing studies of the electrophilic addition reactions of phenyl selenenyl choride to 5-substituted-2-norbornenes. The synthetic usefulness of organoselenium compounds in biological studies (Nicolaou *et al.*, 1979) and natural product synthesis are of great interest to synthetic chemists (Kyriacos & William, 1977, Kyriacos *et al.*, 1979).
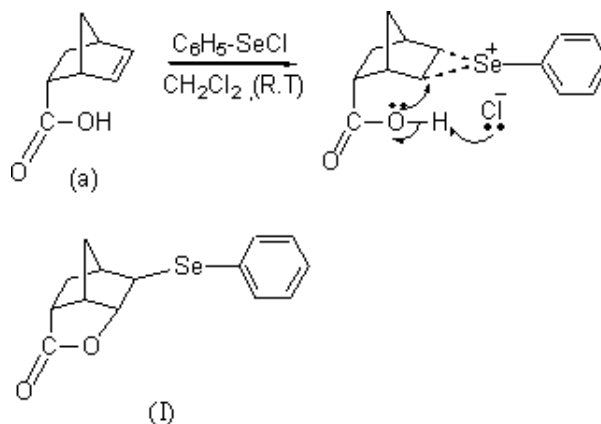
2-Norbornene-5-*endo*-carboxylic acid, (II), and its ability to form the lactone (I) is a well characterized reaction in the literature (Berson & Ben-Efraim, 1959; VanTamelen & Shamma, 1955). The cyclization reactions of various carboxylic acids in the presence of phenyl selenenyl sulfide, phenyl selenenyl bromide and phenyl selenenyl chloride under different experimental conditions have been reported (Nicolaou & Lysenko, 1977, Nicolaou *et al.*, 1979). The title compound, (I), has also been prepared by a different route using 5-*endo*-carbomethoxy-2-norbornene (Nicolaou, 1981) and phenyl selenenyl chloride in anhydrous methylene chloride at room temperature. It crystallizes as separate neutral molecules, each consisting of one norbornane moiety bridged through one Se atom to a phenyl group and covalently
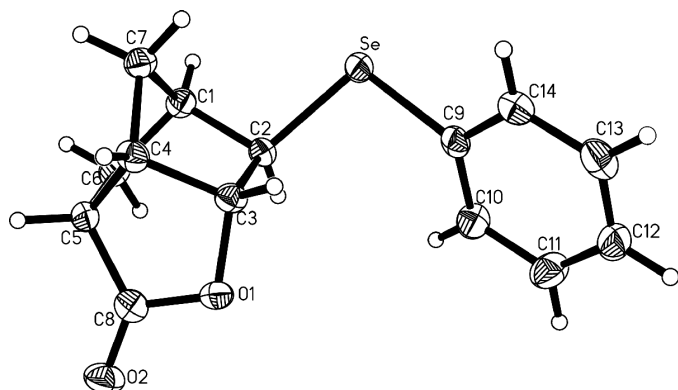
Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by spheres of arbitrary radii.
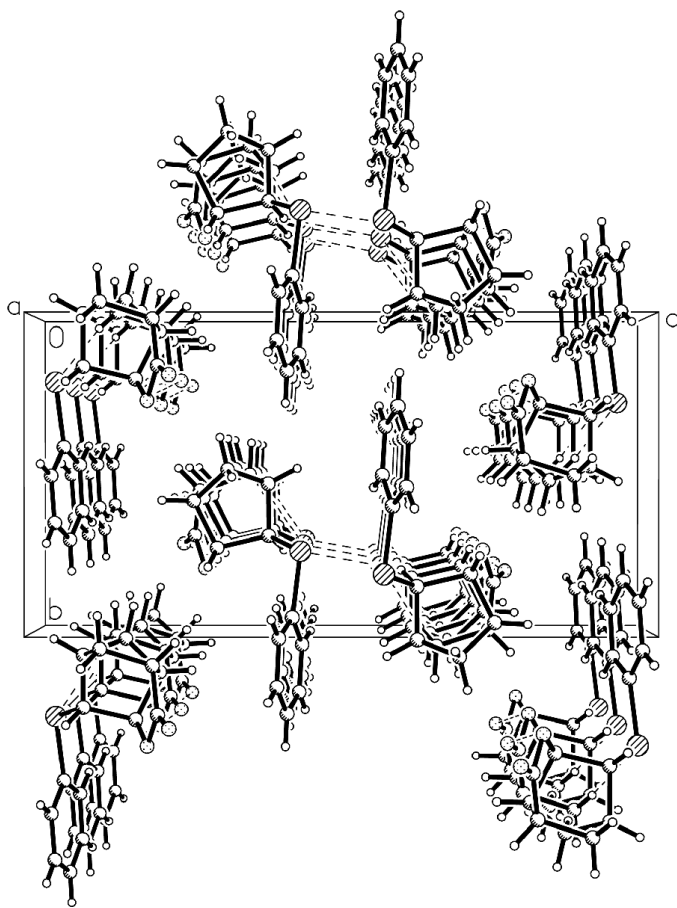

Figure 2
Packing diagram for (I). The perspective view is parallel to the *a* axis. Dashed lines indicate intermolecular agostic interactions involving selenium.

bonded to both the C and O atoms of the carboxylate group, forming a five-membered ring. This is the first time the crystal structure of this phenylseleno lactone of norbornane has been studied. The bond connectivities of (I), previously determined by ¹H and ¹³C NMR, have been reported (Nicolaou *et al.*, 1979). Due to the strained molecular structure of (I) the angles and bond lengths are found to deviate from typical tetrahedral
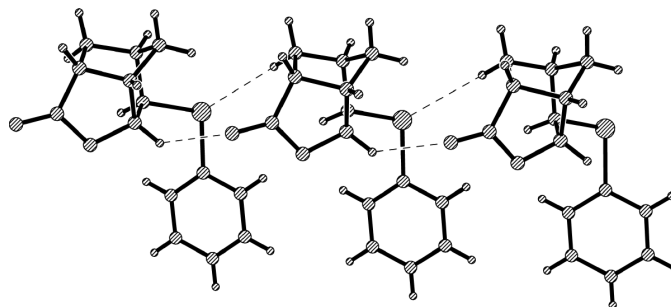

Figure 3
The agostic selenium interactions, plus 2.503 Å C—H···O hydrogen bonds parallel to the *c* axis.

angles and bond lengths. Selected geometrical parameters are listed in Table 1. The geometry about the selenium centre is best described as a distorted tetrahedron (Fig. 1).

This geometry found for the Se atom is consistent with the presence of stereochemically active lone pairs of electrons. The angles C2—Se—C9 [101.36 (10)°], C2—Se···H6A [111.39 (17)°] and C9—Se···H6A [116.78 (16)°] show a considerable spread is possible. From the packing diagram (Fig. 3), it is evident that the extended structure of (I) is a three-dimensional multilayer network with strong σ–π intermolecular interactions. There are no π–π stacking interactions between the phenyl rings. The bridging Se atom has a significant C—H···Se 'agostic' interaction (Cole *et al.*, 1998; Braga *et al.*, 1995) to two neighbouring molecules. Each Se atom has an agostic interaction, with a phenyl C10—H and a norbornane C2—H of one molecule [3.090 (1) and 3.003 (3) Å, respectively] and an agostic interaction to norbornane C6A—H of a different molecule [3.089 (1) Å]. An agostic interaction is a three-centre two-electron bond between an electron deficient metal atom and C—H σ bond (Desiraju, 2000). The other intramolecular interaction which stabilizes this crystal lattice is the presence of weak hydrogen bonds which are typical of organometallic compounds that have polar cabonyl O atoms. The terminal carbonyl O atom is hydrogen bonded to the norbornane C—H groups of two adjacent molecules, *viz.* C5—H···O2 [2.62 (4) Å] and C3—H···O2 [2.501 (9) Å]. The C5—H of these norbornane CH groups also hydrogen bonds to the ring atom O1 [2.669 (2) Å]. The combination of these weak interactions serve to stabilize the crystal and form the three-dimensional network observed in the packing diagram (Fig. 2).

Experimental

2-Norbornene-5-*endo*-carboxylic acid (Nicolaou & Lysenko, 1977; 50 mg, 0.36 mmol) was dissolved in anhydrous methylene chloride (1 ml) at room temperature. To this, phenyl selenenyl chloride (80 mg, 0.41 mmol) dissolved in anhydrous methylene chloride (1 ml) was added dropwise and the solution stirred at room temperature for 10 min. The solvent was removed *in vacuo* and the crude product purified on silica gel (1:20, compound to silica gel by weight), eluting with methylene chloride (yield 116 mg, 97%). Recrystallization from dry chloroform provided crystals suitable for X-ray analysis (m.p. 376 K).¹H NMR (CDCl₃, 500 MHz): δ 1.66 (*dd*, 1H, *J* = 1.5, 11.2 Hz,

H7*s*), 1.78 (*t*, 1H, *J* = 2.0 Hz, H6*n*), 2.09 (*m*, 1H, H6*x*), 2.20 (*dd*, 1H, *J* = 1.5 Hz, H7*a*), 2.51 (*d*, 1H, *J* = 2.9 Hz, H1), 2.56 (*dd*, 1H, *J* = 4.4, 11.2 Hz, H5*x*), 3.23 (*dd*, 1H, *J* = 1.0, 4.9 Hz, H4), 3.32 (*bd*, 1H, *J* = 2.0 Hz, H2*n*), 4.73 (*d*, 1H, *J* = 4.9 Hz, H3*x*), 7.27 (*dd*, 1H, *J* = 2.9, 7.8 Hz, H12), 7.28 (*m*, 2H, H11, H13), 7.50 (*m*, 2H, H10, H14). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 35.09 (C6), 36.60 (C7), 38.14 (C5), 42.12 (C1), 49.15 (C2), 86.26 (C3), 46.29 (C4), 127.39 (C12), 128.53 (C9), 129.25 (C10, C14), 132.84 (C11, C13), 179.98 (C8) (*x* = *exo* proton, *n* = *endo* proton, *s* = proton *syn* to phenyl ring on C7 and *a* = proton *anti* on C7).

Crystal data

C$_{14}$H$_{14}$O$_2$Se
M_r = 293.21
Orthorhombic, $P2_12_12_1$
a = 6.2771 (13) Å
b = 9.792 (2) Å
c = 19.073 (4) Å
V = 1172.4 (4) Å^3
Z = 4
D_x = 1.661 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 4814 reflections
θ = 4.3–53.0°
μ = 3.19 mm^{-1}
T = 293 (2) K
Prism, colourless
0.79 × 0.25 × 0.15 mm

Data collection

Bruker SMART CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.26, T_{max} = 0.62
5977 measured reflections

2344 independent reflections
2176 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 26.3°
$h = -7 \rightarrow 7$
$k = -12 \rightarrow 12$
$l = -23 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.054
S = 1.01
2344 reflections
154 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0193P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.55 e Å^{-3}
Absolute structure: Flack (1983), 951 Friedel pairs
Flack parameter = 0.070 (11)

Table 1
Selected geometric parameters (Å, °) for (section).

Se—C9	1.913 (2)	C3—C2	1.544 (3)
Se—C2	1.954 (3)	C2—C1	1.534 (3)
C3—C4	1.534 (3)		
C9—Se—C2	101.36 (10)	C1—C2—C3	102.73 (17)
C4—C3—C2	103.26 (18)	C3—C2—Se	113.39 (17)

All H atoms were included in calculated positions using a riding model, with Csp^3—H bond distances of 0.97 Å and U_{iso} values equal to $1.5U_{eq}$(C), and Csp^2—H bond distances of 0.93 Å and U_{iso} values equal to $1.2U_{eq}$(C).

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*'; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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