O4	0.3391 (4)	1.1911 (4)	−0.0442 (2)	0.0477 (5)
C1	−0.0826 (7)	0.9249 (5)	0.5688 (3)	0.0478 (6)
C2	0.1187 (8)	0.6690 (6)	0.6104 (4)	0.0558 (7)
C3	0.3220 (8)	0.6302 (6)	0.4686 (4)	0.0526 (7)
C4	0.2669 (6)	0.8631 (5)	0.3212 (3)	0.0370 (5)
C5	0.2037 (6)	0.7533 (5)	0.1723 (3)	0.0381 (5)
C6	0.1122 (7)	0.9958 (6)	0.0339 (3)	0.0438 (6)

Table 5. *Selected geometric parameters* (Å, °) *for* (3)

O1—C1	1.361 (3)	C1—C2	1.448 (4)
O1—C4	1.448 (3)	C2—C3	1.321 (4)
O2—C1	1.212 (3)	C3—C4	1.484 (4)
O3—C5	1.423 (3)	C4—C5	1.526 (3)
O4—C6	1.415 (3)	C5—C6	1.512 (4)
C1—O1—C4	109.1 (2)	O1—C4—C5	109.7 (2)
O2—C1—O1	119.5 (2)	C3—C4—C5	114.2 (2)
O2—C1—C2	132.1 (2)	O3—C5—C6	110.9 (2)
O1—C1—C2	108.4 (2)	O3—C5—C4	104.4 (2)
C3—C2—C1	109.0 (3)	C6—C5—C4	112.9 (2)
C2—C3—C4	109.5 (3)	O4—C6—C5	113.0 (2)
O1—C4—C3	103.9 (2)		
C4—O1—C1—O2	177.5 (3)	C2—C3—C4—C5	−120.8 (2)
C4—O1—C1—C2	−2.2 (3)	O1—C4—C5—O3	177.7 (2)
O2—C1—C2—C3	−178.3 (3)	C3—C4—C5—O3	−66.1 (3)
O1—C1—C2—C3	1.4 (3)	O1—C4—C5—C6	57.0 (3)
C1—C2—C3—C4	0.0 (3)	C3—C4—C5—C6	173.2 (3)
C1—O1—C4—C3	2.2 (3)	O3—C5—C6—O4	−56.1 (3)
C1—O1—C4—C5	124.7 (2)	C4—C5—C6—O4	60.8 (3)
C2—C3—C4—O1	−1.3 (3)		

Table 6. *Hydrogen-bonding geometry* (Å, °) *for* (3)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3A···O4^{i}	0.83 (6)	1.91 (5)	2.730 (3)	172 (4)
O4—H4A···O2^{ii}	0.72 (3)	2.11 (3)	2.761 (3)	150 (3)

Symmetry codes: (i) $x, y-1, z$; (ii) $1+x, y, z-1$.

Both structures were solved by direct methods and refined by full-matrix least-squares technique. All the H atoms in the two structures were located from difference Fourier maps and refined isotropically.

For both compounds, data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELX*90 (Sheldrick, 1990*a*); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*); software used to prepare material for publication: *SHELXL*93; *PARST* (Nardelli, 1983*b*).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1146). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-Phenyl-1,3(4*H*)-benzoselenazine-2,4(3*H*)-dione

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Abstract

The title compound, 3-phenyl-1,3(4*H*)-benzoselenazine-2,4(3*H*)-dione, $C_{14}H_9NO_2Se$, was found to crystallize in space group $P2_12_12_1$. The ten atoms in the benzoselenazine ring system are planar to within 0.040 (3) Å, with both carbonyl O atoms being slightly out of this plane. The dihedral angle between the phenyl ring and benzoselenazine system is 87.41 (8)°.

Comment

Work in our laboratories has been directed towards the design and understanding of synthetic methods involving free-radical homolytic substitution at selenium. Recently, we began to explore the use of pyridine-2-thionoxycarbonyl (PTOC) carbamates as precursors to amidyl radicals for the preparation of analogues of the anti-inflammatory compound ebselen. Following the procedure described by Esker & Newcomb (1994), we reacted 2-benzylseleno-*N*-trimethylsilylbenzanilide with phosgene. To our surprise, we were unable to observe the expected carbamoyl chloride, rather a crystalline solid was isolated in 60% yield which proved to be the title compound, (1) (Fong & Schiesser, 1995). This

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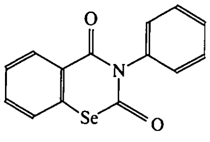
result is important as it provides an efficient synthetic route to a biologically important heterocyclic ring system rarely encountered in a reaction which involves a novel addition–elimination sequence with selenium as nucleophile. Given that the selenazinedione (1) and ebselen display remarkably similar NMR spectral properties, the structure determination was undertaken to unambiguously confirm the identity of this unexpected reaction product.



(I)

Bond lengths and angles, apart from those involving the Se atom, are similar to those of 3-phenyl-2,4(1*H*,3*H*)-quinazolinedione (Kitano, Kashiwagi & Kinoshita, 1972). In particular, the N atom is trigonal, with the N—C(2) and N—C(4) distances being shorter than the N—C(9) distance. The ten atoms of the benzoselenazine ring system are coplanar, the maximum deviation being 0.040 (3) Å for atom C(4), while C(9) and both of the carbonyl O atoms lie slightly out of the plane. The phenyl ring is almost perpendicular to this ring, with the dihedral angle between the two planes being 87.41 (8)°. This compares with 3-phenyl-2,4(1*H*,3*H*)-quinazolinedione (Kitano, Kashiwagi & Kinoshita, 1972), where the dihedral angle between the quinazolinedione and phenyl rings was found to be 65.0°.

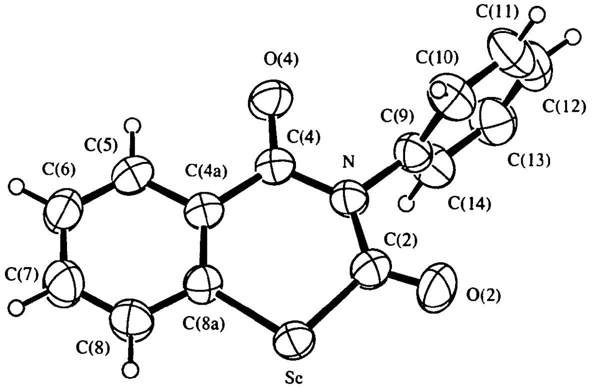


Fig. 1. *ORTEP*II (Johnson, 1976) diagram of (1) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

Crystal data

$C_{14}H_9NO_2Se$
$M_r = 302.18$
Orthorhombic
$P2_12_12_1$
$a = 11.8054\ (10)$ Å
$b = 5.0922\ (10)$ Å
$c = 20.0693\ (13)$ Å
$V = 1206.5\ (3)$ Å^3
$Z = 4$
$D_x = 1.664$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54180$ Å
Cell parameters from 25 reflections
$\theta = 26.6$–$41.7°$
$\mu = 4.159$ mm^{-1}
$T = 293\ (1)$ K
Needle
0.67 × 0.16 × 0.11 mm
Colourless

Data collection

Enraf–Nonius CAD-4 MachS diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical (indexed crystal faces)
$T_{\min} = 0.305$, $T_{\max} = 0.707$
3810 measured reflections
2487 independent reflections

2427 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0289$
$\theta_{\max} = 75.12°$
$h = -1 \rightarrow 14$
$k = -1 \rightarrow 6$
$l = -25 \rightarrow 25$
3 standard reflections
frequency: 150 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0333$
$wR(F^2) = 0.0894$
$S = 1.123$
2487 reflections
173 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0552P)^2 + 0.3368P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.002$

$\Delta\rho_{\max} = 0.657$ e Å^{-3}
$\Delta\rho_{\min} = -0.618$ e Å^{-3}
Extinction correction: $F_c^* = kF_c[1 + (0.001 \times \chi F_c^2\lambda^3/\sin 2\theta)]$
Extinction coefficient: 0.0021 (4)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Se	0.06024 (3)	0.14766 (6)	0.46713 (2)	0.05003 (14)
O(2)	0.2718 (3)	0.3332 (7)	0.4667 (2)	0.0826 (10)
O(4)	0.2456 (2)	−0.2530 (5)	0.29945 (13)	0.0557 (6)
N	0.2541 (2)	0.0236 (5)	0.38612 (13)	0.0437 (6)
C(2)	0.2131 (3)	0.1777 (7)	0.4379 (2)	0.0517 (7)
C(4)	0.1948 (3)	−0.1547 (6)	0.34559 (13)	0.0408 (6)
C(4a)	0.0754 (3)	−0.2231 (5)	0.35889 (14)	0.0400 (6)
C(5)	0.0287 (3)	−0.4185 (7)	0.3181 (2)	0.0480 (7)
C(6)	−0.0822 (3)	−0.4979 (8)	0.3254 (2)	0.0559 (8)
C(7)	−0.1481 (3)	−0.3832 (9)	0.3741 (2)	0.0620 (9)
C(8)	−0.1049 (3)	−0.1913 (7)	0.4150 (2)	0.0546 (8)
C(8a)	0.0071 (3)	−0.1112 (6)	0.4074 (2)	0.0422 (6)
C(9)	0.3746 (3)	0.0484 (7)	0.3727 (2)	0.0457 (7)
C(10)	0.4136 (3)	0.2365 (8)	0.3283 (2)	0.0597 (9)
C(11)	0.5292 (4)	0.2487 (9)	0.3160 (2)	0.0688 (11)
C(12)	0.6029 (3)	0.0849 (8)	0.3475 (2)	0.0643 (10)
C(13)	0.5624 (3)	−0.1015 (9)	0.3918 (2)	0.0654 (9)
C(14)	0.4479 (3)	−0.1194 (7)	0.4042 (2)	0.0570 (8)

Table 2. *Selected geometric parameters* (Å, °)

Se—C(8a)	1.889 (3)	N—C(2)	1.390 (4)
Se—C(2)	1.903 (3)	N—C(4)	1.406 (4)
O(2)—C(2)	1.200 (4)	N—C(9)	1.454 (4)
O(4)—C(4)	1.211 (4)	C(4)—C(4a)	1.476 (4)
C(8a)—Se—C(2)	100.13 (14)	O(4)—C(4)—C(4a)	120.9 (3)
C(2)—N—C(4)	128.6 (3)	N—C(4)—C(4a)	121.5 (2)
C(2)—N—C(9)	115.5 (3)	C(8a)—C(4a)—C(5)	118.2 (3)
C(4)—N—C(9)	115.9 (3)	C(4a)—C(8a)—Se	122.6 (2)

O(2)—C(2)—N	122.0 (3)	C(8)—C(8a)—Se	116.8 (2)
O(2)—C(2)—Se	117.0 (3)	C(14)—C(9)—C(10)	121.2 (3)
N—C(2)—Se	121.0 (2)	C(14)—C(9)—N	118.6 (3)
O(4)—C(4)—N	117.6 (3)	C(10)—C(9)—N	120.2 (3)

The structure was solved by the heavy-atom method using *SHELXS*86 (Sheldrick, 1990). Refinement was performed by *SHELXL*93 (Sheldrick, 1993) using full-matrix least squares, with anisotropic displacement parameters for all non-H atoms. H atoms were included at calculated positions and refined using a riding model with isotropic displacement parameters assigned. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: KH1013). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Three Polymorphic Forms of 2-Ethyl-3-hydroxy-4-pyranone (Ethyl Maltol)

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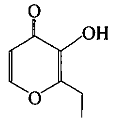
Abstract

The crystal structures of three polymorphic forms of ethyl maltol (2-ethyl-3-hydroxy-4-pyranone), $C_7H_8O_3$, have been determined. The polymorphs exhibit different molecular arrangements through intermolecular hydrogen bonding. Form (1) contains nearly planar chains of molecules, (2) contains three-dimensional or spiral chains and (3) contains hydrogen-bonded dimers.

Comment

Pyranones are biologically important chelating ligands which may be used for removing metal overloads from the body or the introduction of metals for therapy or NMR imaging (Hider & Hall, 1991; Burgess, 1993). Maltol (3-hydroxy-2-methyl-4-pyranone) is a naturally occurring pyranone much used in the baking industry. The ethyl analogue of maltol has been found in three polymorphic forms, all of which were crystallized as minor components; polymorph (1) was isolated from the attempted reaction between crude 3-benzyloxy-2-ethyl-4-pyranone and 4-fluoroaniline while (2) and (3) were obtained from preparations of the metal complexes of Si and Sb, respectively. This is not unexpected, as the potential of these compounds as drug-transport systems depends on the very similar solubilities of the ligand and the metal complexes.



Ethyl Maltol

In each of the structures the hydroxyl H atom H(1) bonded to O(1) is involved in intermolecular hydrogen bonding to a terminal carbonyl O atom O(2). In polymorphs (1) and (2) the hydrogen bonds link the molecules to form infinite chains. In the case of polymorph (1) the result is a near-planar chain (Fig. 1) in which adjacent molecules are related by a crystallographic twofold screw axis. Polymorph (2) contains a three-dimensional chain (Fig. 2) in which adjacent molecules spiral along a crystallographic threefold screw axis. In polymorph (3) pairs of molecules form hydrogen-bonded dimers mutually linked across a crystallographic centre of symmetry (Fig. 3). In all three forms the H atom H(1) was located as the highest residual electron-density peak after all other atoms were included in the refinement (other H atoms were included in calculated positions) and was subsequently included in a riding position in the final least-squares cycles. The intermolecular contact distances between the hydroxyl O atoms O(1) and O(2) (Table 2) are similar [2.724 (4), 2.676 (1) and 2.711 (2) Å for the polymorphic forms (1), (2) and (3), respectively] and are consistent with hydrogen bonding. Although the positions of the bridging H atoms were not refined, their locations are chemically reasonable, with H(1)···O(2) distances of 1.89, 1.87 and 1.81 Å and O(1)—H(1)···O(2) angles of 146, 155 and 152° for forms (1), (2) and (3), respectively.

Maltol (3-hydroxy-2-methyl-4-pyranone) has also been found in two polymorphic forms (Burgess, Fawcett, Llewellyn & Russell, 1995), one of which contains a planar chain similar to that found in (1) and the