O4—C41—O41	122.7 (4)	O10—C101—O101	123.0 (3)
O4—C41—C42	109.7 (4)	O10—C101—C102	111.8 (3)
O41—C41—C42	127.6 (4)	O101—C101—C102	125.2 (4)
C1′—O13—C13—C12	−92.0 (4)	O1′—C1′—C2′—C3′	−90.9 (5)
C1′—O13—C13—C14	146.1 (3)	C2′—C3′—N4′—C5′	−100.1 (4)
C13—O13—C1′—O1′	15.2 (5)	C2′—C3′—C31′—C32′	38.8 (6)
C13—O13—C1′—C2′	−161.4 (3)	O2′—C2′—C3′—N4′	−63.0 (4)
O13—C1′—C2′—O2′	−158.4 (3)	O2′—C2′—C3′—C31′	60.5 (4)
O13—C1′—C2′—C3′	85.6 (4)	C3′—N4′—C5′—O5′	−2.9 (6)
C1′—C2′—C3′—C31′	179.6 (3)	C3′—N4′—C5′—C51′	179.1 (4)
C1′—C2′—C3′—N4′	56.0 (4)	C31′—C3′—N4′—C5′	135.3 (4)
O1′—C1′—C2′—O2′	25.1 (6)	C32′—C31′—C3′—N4′	161.7 (4)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1′···O7^{i}	1.003	1.851	2.801	156.9
O7—H7′···O101	1.062	1.928	2.896	149.5
N2′—H22′···O1^{ii}	0.957	2.131	2.991	148.9
N2′—H21′···O9^{iii}	0.971	2.191	3.120	159.2
N4′—H4′···O21^{ii}	0.975	2.207	3.101	151.8

Symmetry codes: (i) $x, y, 1+z$; (ii) $\frac{3}{2}-x, \frac{1}{2}+y, 2-z$; (iii) $\frac{3}{2}-x, \frac{1}{2}+y, 1-z$.

The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985) and refined by full-matrix least-squares techniques using *MolEN* (Fair, 1990). The two hydroxyl H atoms in the molecule were located from difference Fourier maps and the positions of all the other H atoms were calculated from an idealized geometry with standard bond lengths and angles.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1123). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 298–301

2-Methyl-2*H*-1,2-benzisoselenazol-3-one

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(*Received* 8 *March* 1993; *accepted* 25 *January* 1994)

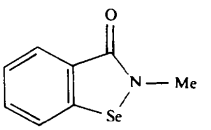
Abstract

The nearly planar molecules of C_8H_7NOSe form chains parallel to [001] with Se···O intermolecular distances of 2.600 (3) Å. The shortest contacts [2.362 (5) Å] occur between the methyl group H atoms of the neighbouring chains.

Comment

Within the last few years selenium has been recognized as an essential component of several biologically important macromolecules (Stadtman, 1990), *e.g.* glutathione peroxidase (GSH-Px), the enzyme which catalyzes reduction of hydroperoxides in the human organism (Parnham & Graf, 1987). An important stage in the enzyme's catalytic cycle is the modification of the selenomethionine at its active centre (Ladenstein, Epp & Wendel, 1983). The antioxidant activity of GSH-Px can be mimicked by relatively simple seleno-organic compounds such as 2-methyl-2*H*-1,2-benzisoselenazol-3-one (MBS). The best known is ebselen, a 2-phenyl analogue of MBS, which was reported to elicit anti-inflammatory (Dupont, Dideberg & Jacquemin, 1990) and immuno-stimulating (Młochowski & Inglot, 1991) activities. The anti-inflammatory effects of ebselen were suggested to be connected with its stimulating influence on the arachidonic acid metabolism (Leyck & Parnham, 1990). This results in inhibition of 5-lipoxygenase and isomerization of its product LTB_4 to a biologically inactive *trans*-LTB_4, as well as an inhibition of the generation of reactive oxygen species (Cotgreave, Johanson, Westergren, Moldeus & Brattsand, 1988). The nature of the likeness between the antioxidant activity of the seleno-organic compounds and GSH-Px is not yet understood.

A possible explanation might be a similarity between the amide N-atom surrounding of the Se atom in the active selenazoles and in GSH-Px (Wendel, Fausel, Safayhi, Tiegs & Otter, 1984).



The determination of the crystal and molecular structure of MBS has been undertaken to find out which of its geometrical features and those of its analogues could be responsible for the differentiation of their biological activities.

Most of the bond lengths in both rings of MBS do not deviate by more than 3σ from standard values given in the literature. Certain elongation of the C7—O1 and C8—N1 bonds together with a shortening of the C7—N1 bond, in comparison to standard values, may be ascribed to the resonance form $O1^-$—C7=$N1^+$—C8 of the amide-like fragment of the five-membered ring.

Bond angles in both rings show a tendency for the molecule to be planar, the dihedral angle between the best planes through the five- and six-membered rings being 1.33 (1)°. The values of the endocyclic torsion angles do not exceed 2° in both rings. The O atom belongs to the plane of five-membered ring within 3σ accuracy. The deviations of atoms O1 and C8 from the least-squares plane through the five-membered ring (Se1—N1—C7—C6—C1) are 0.009 (3) and 0.096 (3) Å, respectively.

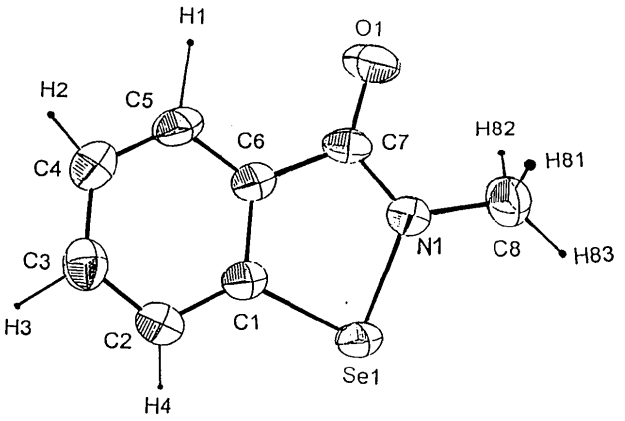


Fig. 1. An *ORTEP*II (Johnson, 1976) view of the molecule projected on the mean plane of the five- and six-membered rings. Displacement ellipsoids are plotted at 30% probability.

The packing of the molecules in the unit cell is shown in Fig. 2. The molecules form chains parallel to the z axis. The most important intermolecular interactions seem to occur between Se1 and O1 (x, $-y+0.5$, $z+0.5$) and between H atoms of the methyl groups of neighbouring chains [2.362 (5) Å]. The Se···O distance of 2.600 (3) Å is slightly longer than that observed by Dupont, Dideberg & Jacquemin (1990) in the crystal structure of ebselen [2.569 (3) Å]. Although, according to Dupont, Dideberg & Jacquemin (1990), the intermolecular interaction Se···O in the structure of ebselen has an intermediate length between that of a single bond and the sum of the van der Waals radii; in the case of MBS this bond seems to be closer to the latter. Using Pauling's relationship, $d(n) - d(1) = -c \log n$, where n is a fractional bond number, c is a constant characteristic for a given pair of atoms and $d(1)$ is the single bond length, we tried to calculate the bond number for the $d(n)$ = Se···O distance of MBS. In view of the lack of a value of c for the pairs of atoms, Se and O, we took c for S atoms adopted by Dunitz (1979), $c_{s-s} = 1.03$. The Se—O single-bond length, $d(1) = 1.774$ (3) Å, was that reported by Dupont, Dideberg & Jacquemin (1990) for ebselen. The bond number, $n = 0.16$ (obtained under these assumptions), is much lower than expected for the value intermediate between the single-bond length and van der Waals distance. This number is, however, only a first approximation. A more reliable calculation requires a precise determination of the constant c for the Se and O atoms, which can be done by the use of more crystal structure data for seleno-organic compounds.

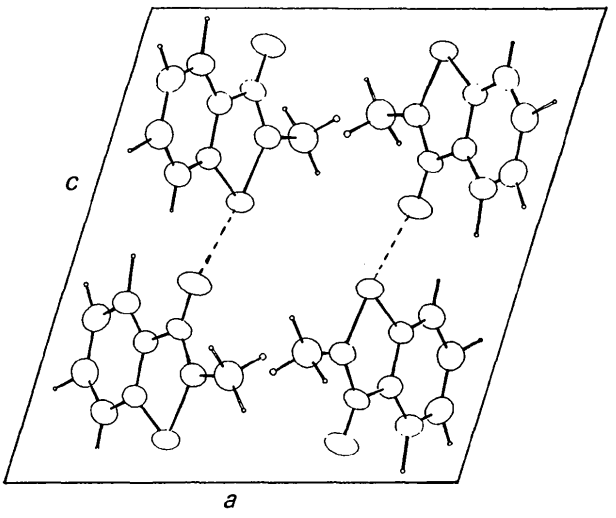


Fig. 2. Projection of the unit cell along the y axis. Intermolecular S···O interactions are indicated with dashed lines.

On the basis of the structural studies of MBS and ebselen, it has been found that the geometries described by bond lengths and angles, as well as the conformtions for both molecules, are very similar. This similarity suggests that a more important role in the biological activity is probably played by the nature of the substituent at the N atom. These substituents may modulate the electron density on the Se atom, as shown experimentally by Dakova and coworkers (Dakova, Kauffmann, Evers, Lamberts & Patriarche, 1990). Thus the substituents, methyl in the case of MBS and phenyl in the case of ebselen, seem to be responsible for the differentiation of biological activity of these two compounds.

Experimental

The crystals of the title compound (MBS) were kindly supplied by Professor J. Młochowski (Technical University, Wrocław). The most prominent faces belonged to the forms {110} and {100}. The density was measured by the suspension method.

Crystal data

C_8H_7NOSe	Cu $K\alpha$ radiation
M_r = 212.04	λ = 1.5418 Å
Monoclinic	Cell parameters from 25 reflections
$P2_1/c$	θ = 8–65°
a = 11.118 (2) Å	μ = 5.447 mm^{-1}
b = 6.167 (3) Å	T = 293 K
c = 12.296 (2) Å	Prism
β = 107.28 (2)°	0.17 × 0.13 × 0.10 mm
V = 804.95 (3) Å^3	Slightly yellowish
Z = 4	
D_x = 1.632 Mg m^{-3}	
D_m = 1.632 (1) Mg m^{-3}	

Data collection

KM-4 diffractometer	R_{int} = 0.0281
$\omega/2\theta$ scans	θ_{max} = 82°
Absorption correction: numerical (*SHELXS*86; Sheldrick, 1985)	$h = -15 \rightarrow 15$
	$k = -9 \rightarrow 9$
	$l = 0 \rightarrow 17$
T_{min} = 0.483, T_{max} = 0.646	3 standard reflections monitored every 50 reflections
3494 measured reflections	intensity decay: <5%
1711 independent reflections	
1687 observed reflections [$\lvert F_o\rvert \geq 2\sigma(F_o)$]	

Refinement

Refinement on F	$w = 1.37702[\sigma^2(F_o) + 0.003416(F_o)^2]$
R = 0.033	$(\Delta/\sigma)_{max}$ = 0.001
wR = 0.047	$\Delta\rho_{max}$ = 0.54 e Å^{-3}
S = 1.204	$\Delta\rho_{min}$ = −0.94 e Å^{-3}
1687 reflections	Extinction correction: none
129 parameters	Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)
All H-atom parameters refined	

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

U_{iso} for H atoms; $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	y	z	U_{iso}/U_{eq}
Se1	0.32707 (3)	0.18781 (5)	0.40948 (2)	0.0397 (2)
C1	0.2279 (2)	0.4042 (4)	0.3166 (2)	0.0360 (7)
C2	0.1714 (2)	0.5833 (4)	0.3513 (2)	0.0435 (8)
C3	0.1027 (3)	0.7230 (5)	0.2673 (3)	0.0467 (9)
C4	0.0900 (3)	0.6893 (4)	0.1518 (3)	0.0494 (10)
C5	0.1462 (2)	0.5114 (5)	0.1198 (2)	0.0444 (8)
C6	0.2147 (2)	0.3667 (4)	0.2020 (2)	0.0364 (7)
C7	0.2804 (2)	0.1748 (4)	0.1763 (2)	0.0370 (8)
C8	0.4220 (3)	−0.1164 (5)	0.2742 (3)	0.0506 (10)
N1	0.3431 (2)	0.0708 (3)	0.2732 (2)	0.0393 (7)
O1	0.2825 (2)	0.1140 (4)	0.0802 (2)	0.0513 (7)
H1	0.1282 (46)	0.4449 (79)	0.0218 (48)	0.0795 (145)
H2	0.0435 (58)	0.7576 (95)	0.0815 (59)	0.0822 (141)
H3	0.0481 (41)	0.8409 (71)	0.3017 (42)	0.0608 (117)
H4	0.1816 (31)	0.5894 (51)	0.4266 (33)	0.0408 (72)
H81	0.4784 (3)	−0.2040 (5)	0.3479 (3)	0.0832 (155)
H82	0.4832 (3)	−0.0333 (5)	0.2341 (3)	0.0199 (404)
H83	0.3628 (3)	−0.2289 (5)	0.2144 (3)	0.0916 (164)

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

Se1—C1	1.885 (2)	C4—C5	1.376 (4)
Se1—N1	1.880 (3)	C5—C6	1.393 (3)
C1—C2	1.398 (4)	C6—C7	1.473 (4)
C1—C6	1.392 (4)	C7—N1	1.350 (3)
C2—C3	1.387 (4)	C7—O1	1.246 (4)
C3—C4	1.400 (5)	C8—N1	1.448 (4)
C1—Se1—N1	85.7 (1)	C5—C6—C7	123.9 (2)
Se1—C1—C6	111.2 (2)	C1—C6—C7	116.2 (2)
Se1—C1—C2	127.6 (2)	C6—C7—O1	126.5 (2)
C2—C1—C6	121.2 (2)	C6—C7—N1	110.6 (2)
C1—C2—C3	117.5 (3)	N1—C7—O1	122.9 (3)
C2—C3—C4	122.0 (3)	C7—N1—C8	122.6 (2)
C3—C4—C5	119.4 (3)	Se1—N1—C8	121.1 (2)
C4—C5—C6	120.0 (3)	Se1—N1—C7	116.3 (2)
C1—C6—C5	119.9 (2)		

The space group was determined from systematic absences on Weissenberg photographs (Ni-filtered Cu $K\alpha$ radiation). The position of the Se atom was found from Patterson synthesis and the positions of all non-H atoms were obtained from the first difference Fourier map. All H atoms were located on the difference Fourier maps after the last cycle of the isotropic refinement. The positional and displacement parameters (anisotropic for non-H atoms, isotropic for H atoms) were refined using full-matrix least-squares methods. Data were corrected for Lorentz and polarization effects but secondary-extinction correction was not applied.

Calculations were performed on an IBM compatible PC. The computer programs used were *SHELX*76 (Sheldrick, 1976) [from the Polish version of *CRYSRULER* (Rizzoli, Sangermano, Calestani & Andreetti, 1987)], *PARST* (Nardelli, 1982), *XANADU* (Roberts & Sheldrick, 1972) and *ORTEP*II (Johnson, 1976).

The authors are grateful to Dr K. Stadnicka for her guiding assistance in use of the diffractometer and for advice on the problem of absorption.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: KA1040). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 301–304

5-Fluoro-1-indanone and 2,2-Dimethyl-5-fluoro-1-indanone

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(*Received* 9 *December* 1993; *accepted* 17 *May* 1994)

Abstract

There are two independent molecules in the asymmetric unit of 5-fluoro-1-indanone (1), C_9H_7FO. The cyclopentene ring is planar in one of the molecules and slightly distorted into an envelope conformation in the other, with the CH_2 group adjacent to the carbonyl group lying 0.033 (2) Å out of the best plane of the other four atoms. The maximum deviation from coplanarity of all the non-H atoms of (1) is 0.038 (2) Å for one molecule and 0.019 (2) Å for the other. The two molecules are nearly parallel in the crystal, their best planes forming a dihedral angle of 4.1 (3)°. 2,2-Dimethyl-5-fluoro-1-indanone (2), $C_{11}H_{11}FO$, lies on a mirror plane in the crystal. Molecules of both (1) and (2) pack in hypercentric arrays. The C—F distances are 1.354 (2) and 1.360 (3) Å for (1) and 1.355 (2) Å for (2). The C=O distances are 1.218 (2) and 1.212 (3) Å for (1) and 1.220 (2) Å for (2).

Comment

The synthesis of 5-fluoro-1-indanone (1) and 2,2-dimethyl-5-fluoro-1-indanone (2) was required for their use as standards for 5-[^{18}F]fluoro-1-indanone and 2,2-dimethyl-5-[^{18}F]fluoro-1-indanone. This work is part of an ongoing study involving nucleophilic substitution reactions with the [^{18}F]fluoride ion on nitro-1-indanones and nitro-1,3-indandiones (Enas, Garcia, Mathis & Gerdes, 1993; VanBrocklin, Enas, Garcia & Hanrahan, 1993). Compound (1) was prepared according to the literature method of Quere & Maréchal (1971) and compound (2) was prepared by reacting 2,2-dimethyl-5-nitro-1-indanone with KF in dimethyl sulfoxide (Enas, Garcia, Mathis & Gerdes, 1993). Suitable crystals of (1) and (2) had m.p.'s of 303–304 and 336–337 K, respectively.

(1) (2)

Structural data for compounds (1) and (2) are in agreement with those of indan-2,2-dicarboxylic acid (Garcia, Enas & Fronczek, 1994), 2-ethyl-2-nitroindan-1,3-dione (Garcia, Enas, Chang & Fronczek, 1993), 8-acetyl-2,2-difluoro-4-methyl-6*H*-1,3,2-indenodioxaborinane and 8-bromo-2,2-difluoro-4-methyl-6*H*-1,3,2-indenodioxaborinane (Garcia, Enas, VanBrocklin & Fronczek, 1993), 2-acylindan-1-one (Garcia, Enas & Fronczek, 1993) and 2,2-dimethyl-4,5-dinitroindan (Garcia, Enas & Fronczek, 1995).

The packing of molecules in the structure of (1) (Fig. 3) is hypercentric. The two independent molcules are related by a pseudocenter near $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ (0.263, 0.244, 0.257). The F and O atoms, however, do not conform to the pseudo-inversion and the molecules deviate slightly from being parallel, forming a dihedral angle of 4.1 (3)° with one another. The

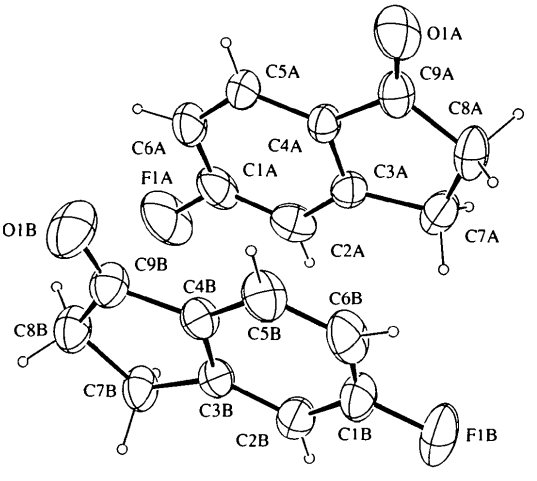

Fig. 1. *ORTEP* drawing (Johnson, 1965) of the asymmetric unit of (1) representing heavy atoms as 30% probability ellipsoids and H atoms as circles of arbitrary radii.

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