

The Crystal Structure of Bis(6-hydroxy-4,4-dimethyl-2-oxo-6-cyclohexenyl) Selenide

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The crystal structure of the title compound, $(C_8H_{11}O_2)_2Se$, has been established by single-crystal X-ray diffraction techniques. The compound crystallizes in the tetragonal space group $P4_2bc$ with unit cell dimensions $a = 13.420(10)$ Å, $c = 9.278(5)$ Å and $Z = 4$. The structure was solved by the heavy atom method and refined to a final R value of 0.045 for 518 symmetry independent reflections. The molecule has C_2 symmetry, with selenium atom in the special position.

The Se–C distance is 1.916(10) Å and the C–Se–C angle 100.9(4)°. The bond lengths in the enol system show considerable degree of delocalization. Short intramolecular contacts indicate bifurcated Se-containing hydrogen bonds between the two six-membered rings of the molecule.

Selenium dioxide oxidation of some cyclic α - and β -diketones have afforded new organic selenium compounds: 1,3-oxaselenole derivatives,^{1–3} a selenoether of a reductone¹ and a representative of the 7-selenabicyclo[2.2.1]heptane series.^{3,4} Each model compound has been subjected to X-ray analysis.^{3–6} The title compound **1**^{7,8} and bis(2-hydroxy-4,4,6,6-tetramethyl-3-oxa-1-cyclohexenyl) selenide **2** reported earlier⁶ can be regarded as derivatives of the respective reductones (Fig. 1). Selenide **1** is a β -diketone derivative and selenide **2** an α -diketone derivative. To determine the crystal

structure of **1** and to compare the structural properties of these closely related selenides was the purpose of this present study.

EXPERIMENTAL

The title compound was prepared as described earlier and recrystallized from ethanol to give white crystals.^{7,8}

Preliminary photographic investigations indicated tetragonal symmetry and systematically absent reflections showed the space group to be $P4_2bc$ or $P4_2/mbc$. The crystal selected for the data collection had approximate dimensions $0.12 \times 0.12 \times 0.4$ mm³. The determination of the unit cell parameters and the data collection were carried out on a Syntex $P2_1$ four-circle diffractometer using graphite monochromatized $MoK\alpha$ -radiation. ω -scanning technique ($5^\circ < 2\theta < 50^\circ$) and variable scan speed (2–20°/min) were employed. Reflections having $h \leq k$ were measured and, of those, 518 had $F > 3\sigma(F)$ and were used in the structure analysis. The data were corrected for Lorentz and polarization effects.

CRYSTAL DATA

$(C_8H_{11}O_2)_2Se$, FW = 357.31,
space group $P4_2bc$ (No. 106).
 $a = 13.420(10)$, $c = 9.278(5)$ Å, $Z = 4$
 $D_{obs} = 1.43$ g cm⁻³, $D_{calc} = 1.420$ g cm⁻³,
 $\mu(MoK\alpha) = 24.3$ cm⁻¹.

STRUCTURE DETERMINATION AND REFINEMENT

The structure analysis showed the space group to be acentric $P4_2bc$. The structure was solved by the

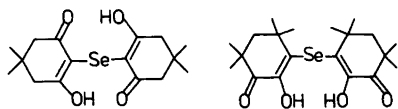


Fig. 1. Selenides **1** and **2**.

Table 1. Fractional atomic coordinates ($\times 10^4$) and thermal parameters^a ($\times 10^3$) for the non-hydrogen atoms.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Se	0	5000	2500 ^b	49(1)	53(1)	36(1)	8(1)	0	0
O1	1525(6)	6372(6)	4045(13)	48(6)	32(5)	115(8)	-6(3)	-9(6)	2(6)
O2	512(6)	3015(6)	4180(11)	44(5)	39(4)	77(6)	-5(4)	-6(5)	6(5)
C1	1055(7)	4686(7)	3815(12)	22(5)	35(5)	32(6)	17(4)	-5(5)	2(5)
C2	1711(9)	5457(9)	4265(16)	57(8)	32(6)	52(8)	-9(6)	10(8)	-4(7)
C3	2630(8)	5207(8)	5207(17)	41(6)	47(8)	48(8)	0(5)	8(7)	-16(8)
C4	2982(7)	4114(7)	5011(19)	35(5)	36(6)	56(7)	15(4)	12(9)	15(10)
C5	2071(8)	3445(7)	5223(17)	47(6)	33(5)	35(9)	10(9)	15(6)	11(6)
C6	1179(9)	3741(9)	4352(12)	39(7)	41(7)	36(5)	5(5)	9(6)	-6(6)
C7	3439(10)	3994(11)	3489(19)	43(8)	42(8)	82(11)	10(6)	18(8)	25(8)
C8	3764(11)	3849(12)	6165(18)	40(9)	68(11)	78(11)	4(7)	8(8)	-9(9)

^aThe anisotropic thermal parameters are given by $\exp[-2\pi^2(h^2a^*U_{11} + \dots + 2hka^*b^*U_{12} + \dots)]$. ^bThe z-coordinate of selenium has been fixed.

heavy atom method. The selenium atom occupies the special position $0, 1/2, z$ and for fixing of the origin the z-value was fixed at 0.25. After anisotropic least-squares refinements of all non-hydrogen atoms the R factor was 0.059. In the difference Fourier map a maximum of $0.38 \text{ e } \text{Å}^{-3}$ was found at a distance of 0.94 Å from O2 and the other hydrogen atom maxima were found in the expected places, the C-H distances varying between 0.86 and 1.15 Å . Because of the poor observed reflections/parameter ratio the coordinates and the thermal parameters (0.05 Å^2) of the hydrogen atoms were fixed. For the same reason, the estimated standard deviations of the bond lengths and angles are somewhat large. The estimated standard deviations of the O-C and C-C bond lengths are 0.014 – 0.018 Å except of those including methyl carbons (0.021 and 0.024 Å). The deviations of the Se-C-C and C-C-C bond

angle values are 0.8 and 0.8 – 1.2° , respectively. The final R value was 0.045.

Scattering factors for Se, O and C were from Cromer and Mann⁹ and those for H from Stewart, Davidson and Simpson.¹⁰ The calculations were carried out on a Univac 1108 computer using the X-RAY 76 program system.¹¹

DISCUSSION

Positional parameters are listed in Table 1. Fig. 2 shows the molecule with the important structural parameters and intramolecular hydrogen bonds. A list of structure factors is obtainable from the authors on request.

The asymmetric unit of the structure comprises one half of the molecule. The structure consists of discrete molecules having C_2 symmetry with the

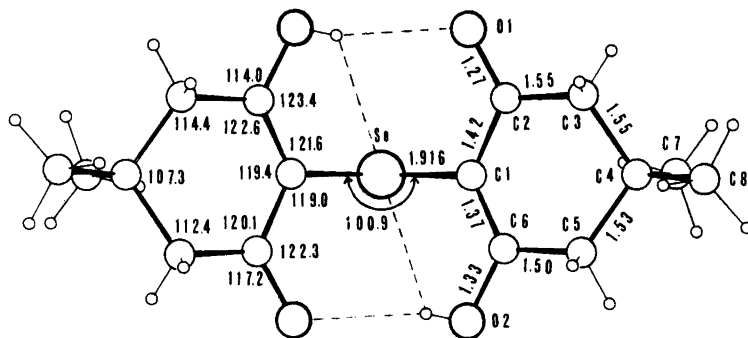


Fig. 2. A view of the molecule of 1 along the z-axis.

selenium atom in the special position. Although the estimated standard deviations of the bond parameters are fairly large, all bond lengths and angles in the conjugated system as well as the position of the hydroxyl hydrogen atom maxima indicate the C_{2v} symmetry to be impossible.

Geometrical constraints evidently determine the intramolecular contacts: the Se—O1 distance of 3.101(10) Å and the Se—O2 distance of 3.162(9) Å. The O1*—O2 distance (O1* at $-x, 1-y, z$) 2.857(12) Å and the distances of the H1 atom from O2 (0.94 Å), from selenium (2.53 Å) and from O1* (2.23 Å) suggest a bifurcated hydrogen bond between these atoms. Generally, the ability of selenium to participate in H-bonding is small.^{12,13} The resonance structure where selenium carries a negative charge coupled with the general trend of H-atoms to be donated to regions of large electron density might explain this arrangement.¹² The partial negative charge was assumed to explain also that the high field ⁷⁷Se NMR chemical shift of **1** appears nearly in the region of selenole anions.¹⁴

To allow comparison of the structural parameters and the solid state interactions of **1** and **2**, the molecular packing diagram of **2** with the numbering scheme and some relevant bond lengths is shown in Fig. 3.

That **1** is intramolecularly and **2** intermolecularly hydrogen bonded may be due to the tendency of the molecules to maximize H-bonding. The hydrogen bonding may affect the electronic structure of the participating moieties elsewhere in the molecule, too.¹⁵ Such changes are however small, about 0.01 Å in the bond lengths. Additional changes may occur

when hydrogen bonds are formed between molecules having delocalized π -bonding systems. The selenide **1** displays considerable degree of delocalization whereas **2** does not show any delocalization owing to the lack of a suitable conjugated system. A comparison of **1** and dimedone^{16,17} reveals that the Se atom and the differences in the H-bonding have only a minor effect on the conjugated system also in the solid state and both compounds display a similar extent of delocalization. Only small differences in the planarity of the conjugated systems of the two compounds can be discovered.

The Se—C bond lengths in **1** and **2** are equal (1.916(10), 1.916(4) and 1.917(4) Å), but the C—Se—C angle in **2** (103.9(2)°) is opened compared with **1** (100.9(4)°). The magnitudes of these parameters are as usually found in aromatic selenides (*ca.* 1.93 Å¹⁸ and 96–106°¹⁹). The dihedral angle C2—C1—Se—C1* of 91.3(10)° in **1** (C1* at $-x, 1-y, z$) and the dihedral angles C2—C1—Se—C11 of 41.6(4)° and C1—Se—C11—C12 of 46.9(3)° in **2**⁶ (*cf.* Table 2) show roughly differences in the distortion of the six-membered rings around Se—C bonds. The planarity of the conjugated systems in **2** and the conformation of the six-membered rings of both compounds can be seen from Table 4. The conformation of the rings in **1** can be described in the first place as half-boat, the conformation of the rings in **2** as half-chair. Small differences in the geometry of the rings in **2**⁶ (*cf.* Table 2) are reflected in the dihedral angle values of O1—C2—C3—O2 (1.5(6)°) and O3—C12—C13—O4 (9.5(5)°).

In the liquid state both selenides are fully

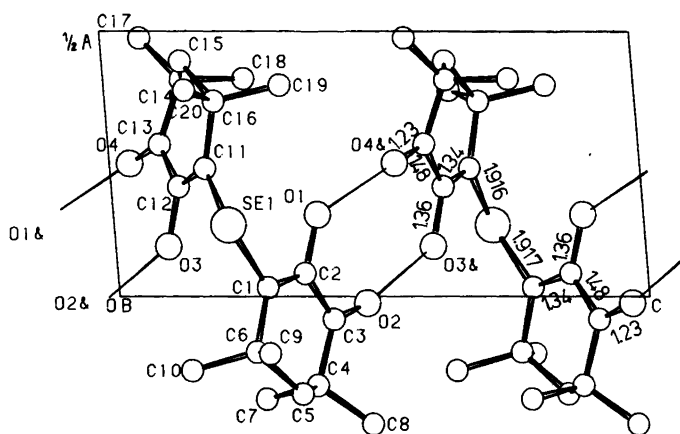


Fig. 3. Molecular packing diagram of **2**.

Table 2. Deviations (Å) of atoms from the least-squares planes.

Compound 1

Plane through C2, C3, C5 and C6.

C2	C3	C5	C6	C1	C4	O1	O2	Se
-0.01	0.01	-0.01	-0.01	-0.09	-0.65	0.17	0.17	-0.29

Compound 2

Plane through C1, C2, C3 and C6.

C1	C2	C3	C6	C4	C5	O1	O2
-0.03	0.03	-0.01	0.01	-0.21	0.42	0.09	0.03

Compound 2^a

Plane through C11, C12, C13 and C16.

C11	C12	C13	C16	C14	C15	O3	O4
0.02	-0.02	0.01	-0.01	0.35	-0.30	-0.07	-0.18

^aThe values for 2 have been calculated from coordinates previously published.⁶

enolized^{3,8} and 1 appears as C_{2v} symmetric due to the rapid proton exchange on the NMR time scale.

Acknowledgements. Financial support from the E. Aaltonen Foundation and from the Leo and Regina Wainstein Foundation is gratefully acknowledged (TL).

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Received April 1, 1982.