

The Crystal Structure of 2,2,4,4-Tetraacetyl-1,3-diselenetane

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Kivekäs, Raikko, Laitalainen, Tarja and Simonen, Tapio. 1986. The Crystal Structure of 2,2,4,4-Tetraacetyl-1,3 diselenetane. – Acta Chem. Scand. B 40: 98–100.

The crystal structure of the title compound has been established by single-crystal X-ray diffraction techniques. The compound crystallizes in the orthorhombic space group *Pbca* with unit cell dimensions $a = 9.477(2)$, $b = 10.184(3)$, $c = 12.512(5)$ Å and $Z = 4$. The structure was solved by the heavy atom method and refined to a final R value of 0.039 for 901 reflections. The molecule lies across a crystallographic centre of inversion at $(0, \frac{1}{2}, \frac{1}{2})$. Intermolecular interactions between Se and O atoms result in the formation of a two-dimensional network.

Introduction

The title compound, first prepared by Morgan^{1,2} and to which a 1,3-diselenetane structure was assigned by Dewar³ was subjected to X-ray analysis. This is the first example of a 1,3-diselenetane crystal structure determination.

Experimental

The title compound was prepared as described earlier^{1–3} and white crystals were obtained by very slow evaporation of a benzene solution. The specimen selected for intensity data collection was approximately $0.1 \times 0.3 \times 0.5$ mm³.

A computer-controlled Nicolet *P3* four-circle diffractometer was used to determine cell parameters and collect intensities. Systematically absent reflections of $0kl$, $k = 2n+1$; $h0l$, $l = 2n+1$; $hk0$, $h = 2n+1$ showed the space group to be *Pbca*. 901 reflections with $|F_0| > 5\sigma|F_0|$ were collected in the interval $5 < 2\theta < 55^\circ$ with ω -scan technique and variable scan speed. The monitored standard reflections of 400, 040, 008 showed no significant variation during data collection. The data were corrected for Lorentz and polarization effects and an empirical absorption correction based on ψ scans was applied (transmission coefficients 0.664–1.000).

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The structure was solved by the heavy atom method and refined by full-matrix least-squares with XRAY76.⁴ $\Sigma w(\Delta F^2)$ was minimized. The difference Fourier synthesis calculated after anisotropic refinement of the non-hydrogen atoms did not allow the location of all hydrogen atoms. Two hydrogen atom positions were idealized (C–H = 1.0 Å) with the aid of the strongest hydrogen atom maximum of both methyl groups. Final R value was 0.039, H atoms were not refined. The atomic scattering factors were those included in the program and anomalous dispersion corrections for Se were obtained from Ref. 5.

Crystal data

$C_{10}H_{12}O_4Se_2$, $FW = 354.1$, space group *Pbca*. $a = 9.477(2)$, $b = 10.184(3)$, $c = 12.512(5)$ Å, $Z = 4$, $D_{calc} = 1.95$ g cm⁻³, $\lambda(MoK\alpha) = 0.71069$ Å, $\mu = 65.8$ cm⁻¹.

Discussion

Fig. 1 shows the molecular structure with the numbering system. The molecule lies across a crystallographic centre of inversion at $(0, \frac{1}{2}, \frac{1}{2})$. Tables 1–3 present atomic coordinates, bond lengths and angles, torsional angles and deviations of atoms from the Se–C–Se¹–Cⁱ plane. The

2,2,4,4-TETRAACETYL-1,3-DISELENETANE

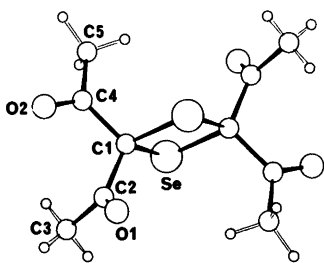


Fig. 1. A view of 2,2,4,4-tetraacetyl-1,3-diselenetane and the numbering.

Table 1. Final atomic coordinates ($\times 10^4$) with e.s.d.s in parentheses. The equivalent isotropic thermal parameters ($\times 10^3$) have been calculated by $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

| | x | y | z | $U_{eq}(\text{\AA}^2)$ |
|------|---------|---------|---------|------------------------|
| Se | -9(1) | 3830(1) | 4332(1) | 27(1) |
| O(1) | 2822(5) | 6532(5) | 4571(4) | 40(3) |
| O(2) | 3095(6) | 4363(7) | 6507(5) | 55(4) |
| C(1) | 1358(6) | 4802(6) | 5226(5) | 21(3) |
| C(2) | 2596(7) | 5354(6) | 4576(5) | 25(3) |
| C(3) | 3498(8) | 4414(8) | 3983(6) | 38(4) |
| C(4) | 1904(7) | 4084(7) | 6210(5) | 28(3) |
| C(5) | 1012(8) | 3110(7) | 6794(6) | 37(4) |

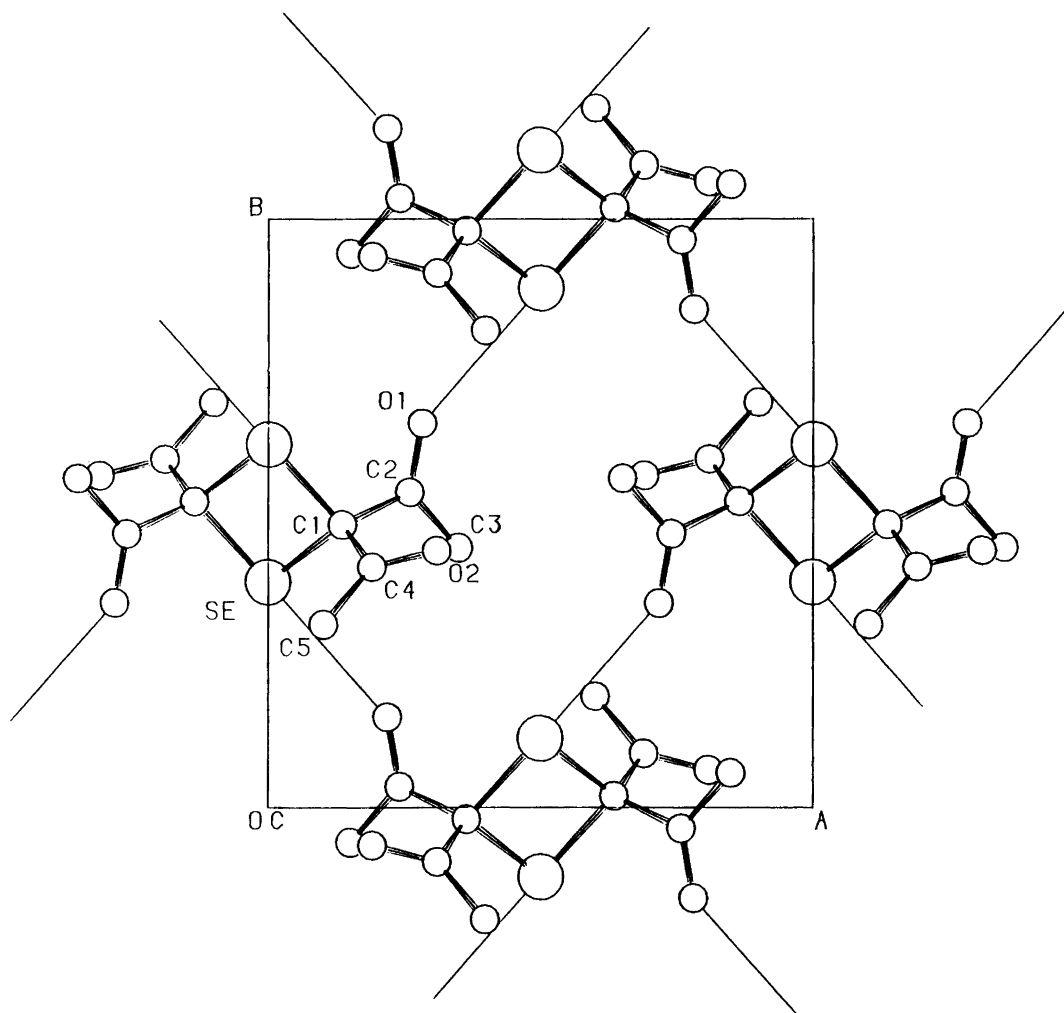


Fig. 2. The intermolecular Se...O interactions in the crystal of 2,2,4,4-tetraacetyl-1,3-diselenetane.

Table 2. Bond lengths (Å) and angles (°).

| | | | |
|---------------------------|----------|----------------|-----------|
| Se-C(1) | 1.977(6) | C(1)-C(2) | 1.534(9) |
| Se-C(1) ⁱ | 1.970(6) | C(1)-C(4) | 1.523(9) |
| O(1)-C(2) | 1.219(8) | C(2)-C(3) | 1.482(10) |
| O(2)-C(4) | 1.222(9) | C(4)-C(5) | 1.494(10) |
| C(1)-Se-C(1) ⁱ | 85.0(2) | O(1)-C(2)-C(1) | 119.9(6) |
| Se-C(1)-Se ⁱ | 95.0(2) | O(1)-C(2)-C(3) | 122.1(6) |
| Se-C(1)C(2) | 112.6(4) | C(1)-C(2)-C(3) | 118.0(6) |
| Se-C(1)-C(4) | 116.1(4) | O(2)-C(4)-C(1) | 116.6(6) |
| C(2)-C(1)-C(4) | 110.2(5) | O(2)-C(4)-C(5) | 121.9(6) |
| C(2)-C(1)-Se ⁱ | 112.7(4) | C(1)-C(4)-C(5) | 121.5(6) |
| C(4)-C(1)-Se ⁱ | 109.5(4) | | |

ⁱSymmetry code -x, 1-y, 1-z

intermolecular Se...O interactions are shown in Fig. 2.

A few 1,3-diselenetanes are known.⁶ An electron diffraction study⁷ of tetrafluoro-1,3-diselenetane has been reported, in which the planarity of the ring system was established. They found Se-C distances of 1.968(4) Å and the Se-C-Se angle of 98.5(4)°. For the planar ring system of the title compound we found approximately similar Se-C distances [1.977(6) and 1.970(6) Å] but a smaller Se-C-Se bond angle [95.0(2)°] and therefore also a shorter Se...Se contact distance [2.911(2) Å], which is considerably closer to the covalent bond distance (2.34 Å)⁸ than the sum of the van der Waals' radii (4.00 Å).⁹ For tetrafluoro-1,3-diselenetane the Se...Se contact distance of 2.981(3) Å has been reported.⁷ According to their CNDO/2 approximation there exists a strong bonding interaction between the selenium atoms which amounts to about one fourth of a normal single bond strength. In the case of the title compound the strong bonding interaction could be likewise explained mainly by the overlap between the 4s and 4p orbitals of one selenium atom with the 4d orbitals of the other.

The acetyl groups of the title compound are differently oriented as can be seen from the torsional angle values and deviations of atoms from the Se-C-Seⁱ-Cⁱ plane (Table 3), and only O(1) participates in intramolecular [3.021(5) Å] and intermolecular [3.140(5) Å] Se...O interactions. The intermolecular Se...O interactions result in the formation of a two-dimensional network, which might be one reason for the observation that the compound is only sparingly soluble in common solvents. Similar low solubility has been found for 2,4-dibenzylidene-1,3-ditellurethane.¹⁰

Acknowledgements. The financial support of the Finnish Academy and the E. Aaltonen Foundation is gratefully acknowledged (T.L.).

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Received April 15, 1985.

Table 3. Torsional angles (°) and deviations of atoms (Å) from the Se-C(1)-Seⁱ-C(1)ⁱ plane.

| | | | | | | |
|---------------------------------|----------|---------------------------------|-----------|----------|---------|---------|
| Se ⁱ -C(1)-C(2)-O(1) | 15.0(8) | Se-C(1)-C(4)-O(2) | 150.2(6) | | | |
| Se-C(1)-C(2)-O(1) | 121.1(6) | Se ⁱ -C(1)-C(4)-O(2) | -103.7(6) | | | |
| atom | O(1) | O(2) | C(2) | C(3) | C(4) | C(5) |
| deviation | -1.98(1) | 1.09(1) | -1.26(1) | -1.54(1) | 1.24(1) | 2.59(1) |