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The crystal structure of benzeneseleninic acid anhydride, $C_{12}H_{10}O_3Se_2$

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Abstract

$C_{12}H_{10}O_3Se_2$, triclinic, $P\bar{1}$ (no. 2), $a = 9.1794(3)$ Å, $b = 11.5706(5)$ Å, $c = 12.3976(5)$ Å, $\alpha = 85.291(2)^\circ$, $\beta = 72.198(2)^\circ$, $\gamma = 74.084(2)^\circ$, $V = 1205.65(8)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0275$, $wR_{ref}(F^2) = 0.0698$, $T = 200$ K.

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The molecular structure is shown in the Figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The compound was obtained commercially (Sigma Aldrich). Crystals suitable for the diffraction study were taken directly from the provided product.

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Table 1: Data collection and handling.

Crystal:	Colourless rod
Size:	$0.52 \times 0.11 \times 0.07$ mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	6.13 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.4° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	20,955, 6011, 0.028
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4555
$N(\text{param})_{\text{refined}}$:	307
Programs:	Bruker [1, 2], SHELX [3], WinGX/ORTEP [4], Mercury [5], PLATON [6]

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å) and were included in the refinement in the riding model approximation, with $U(\text{H})$ set to $1.2U_{\text{eq}}(\text{C})$.

Comment

The Baeyer–Villiger reaction is a useful method to convert ketones into esters. A number of substrates in this context benefit significantly from the catalytic action of seleninic acids [7–9]. In continuation of our interest in structure–property relationships of esters [10–14] a preparative study aimed at the synthesis of novel esters was initiated. To prevent accidental isolation of the anhydride of benzeneseleninic acid (that was used as a precursor to generate the catalytically-active benzeneseleninic acid in situ) it was subjected to a diffraction study. The molecular and crystal structures of methylseleninic acid [15] and benzeneseleninic acid [16] have been reported in the literature. Only one report about the structure of a seleninic acid anhydride has appeared in print so far [17].

The structure solution shows the presence of two complete molecules of the title compound in the asymmetric unit. Se–O bond lengths for the formal Se=O double bonds cover a narrow range of only 1.635(2)–1.648(2) Å as well as an equally small range of 1.818(2)–1.843(2) Å for the Se–O single bonds. C–Se bonds are found in between 1.920(3)–1.932(3) Å. All mentioned atomic distances are in good agreement with corresponding values reported for

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Se11	0.64277(3)	0.65469(3)	0.47094(3)	0.01928(8)
Se12	0.33592(3)	0.62604(3)	0.64134(3)	0.01874(8)
Se21	0.17898(3)	0.62597(3)	0.40703(2)	0.01887(8)
Se22	0.02400(3)	0.46463(3)	0.31419(2)	0.01857(8)
O11	0.8000(3)	0.6490(2)	0.51098(19)	0.0297(5)
O12	0.1820(2)	0.7164(2)	0.60964(19)	0.0271(5)
O13	0.4814(3)	0.7146(2)	0.59715(19)	0.0258(5)
O21	0.3711(2)	0.5719(2)	0.3776(2)	0.0284(5)
O22	−0.1338(2)	0.5356(2)	0.27528(18)	0.0253(5)
O23	0.1410(3)	0.5736(2)	0.28425(18)	0.0266(5)
C111	0.6136(4)	0.8058(3)	0.3909(3)	0.0219(6)
C112	0.4707(4)	0.8936(3)	0.4206(3)	0.0338(8)
H112	0.383085	0.880011	0.480027	0.041*
C113	0.4578(5)	1.0009(3)	0.3623(4)	0.0399(9)
H113	0.360885	1.062079	0.382593	0.048*
C114	0.5834(5)	1.0204(3)	0.2753(3)	0.0397(9)
H114	0.573920	1.095019	0.236392	0.048*
C115	0.7235(5)	0.9309(4)	0.2446(3)	0.0425(9)
H115	0.809076	0.943558	0.182830	0.051*
C116	0.7408(4)	0.8236(3)	0.3023(3)	0.0327(8)
H116	0.838063	0.762897	0.281860	0.039*
C121	0.2900(4)	0.6619(3)	0.7986(3)	0.0221(6)
C122	0.1924(4)	0.7719(3)	0.8402(3)	0.0276(7)
H122	0.155233	0.832237	0.790999	0.033*
C123	0.1490(5)	0.7931(4)	0.9564(3)	0.0391(9)
H123	0.082718	0.868795	0.987131	0.047*
C124	0.2023(5)	0.7043(4)	1.0261(3)	0.0447(10)
H124	0.169892	0.718316	1.105437	0.054*
C125	0.3017(5)	0.5954(4)	0.9833(3)	0.0429(10)
H125	0.338852	0.535506	1.032798	0.051*
C126	0.3478(4)	0.5728(3)	0.8685(3)	0.0316(8)
H126	0.417362	0.498026	0.837968	0.038*
C211	0.1595(4)	0.7863(3)	0.3461(3)	0.0210(6)
C212	0.0258(4)	0.8756(3)	0.3963(3)	0.0329(8)
H212	−0.054430	0.858349	0.459853	0.039*
C213	0.0110(5)	0.9907(3)	0.3524(4)	0.0426(10)
H213	−0.079507	1.053575	0.386491	0.051*
C214	0.1268(5)	1.0140(3)	0.2598(4)	0.0387(9)
H214	0.115641	1.093092	0.229716	0.046*
C215	0.2589(5)	0.9239(3)	0.2101(4)	0.0411(9)
H215	0.337637	0.940598	0.145198	0.049*
C216	0.2770(4)	0.8090(3)	0.2544(3)	0.0292(7)
H216	0.369361	0.746866	0.221938	0.035*
C221	0.1526(3)	0.3731(3)	0.1791(3)	0.0205(6)
C222	0.3017(4)	0.2991(3)	0.1762(3)	0.0304(8)
H222	0.340371	0.293075	0.239802	0.037*
C223	0.3915(4)	0.2350(4)	0.0788(3)	0.0381(9)
H223	0.494058	0.184812	0.074650	0.046*
C224	0.3340(4)	0.2429(3)	−0.0131(3)	0.0346(8)
H224	0.396669	0.197398	−0.079576	0.042*
C225	0.1860(4)	0.3167(3)	−0.0089(3)	0.0317(8)
H225	0.147487	0.322856	−0.072623	0.038*
C226	0.0937(4)	0.3817(3)	0.0885(3)	0.0255(7)
H226	−0.009063	0.431551	0.092705	0.031*

comparable compounds as found in the Cambridge Structural Database [18]. The least-squares planes as defined by the non-hydrogen atoms of the aromatic moieties within the two individual molecules enclose angles of 48.1(2)° and 68.76(19)°, respectively.

In the crystal, C–H...O contacts whose range falls by more than 0.1 Å below the sum of van-der-Waals radii of the atoms participating in them are observed. These are established between one of the hydrogen atoms on each of the two molecules present in the asymmetric unit as donors as well as – invariably – one of the formally double-bonded oxygen atoms on each of the two molecules present in the asymmetric unit as acceptors. In one case, the hydrogen atom is found in the *ortho*, in the other case in the *meta* position to the selenium atom the phenyl group is bonded to. The donor-acceptor interaction exclusively appears in between the two symmetry-independent molecules. In terms of graph-set analysis [19, 20], the descriptor for these contacts is *DD* level and *C*₂²(15) at the binary level. In total, the two molecules are connected to infinite strands along the crystallographic *a* axis. Furthermore, dispersive Se...O contacts whose range falls by up to more than 0.6 Å below the sum of van-der-Waals radii of the two chalcogen atoms are apparent. A number of potential C–H...π interactions actually exhibit D–H...A angles that deviate significantly from a linear arrangement. π-Stacking is not a prominent feature as the shortest distance between two centers of gravity was measured at 4.346(3) Å.

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