

The Crystal Structure of *O*-Ethyl *S*-(2-Carboxyethyl) Dithiocarbonate

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O-Ethyl *S*-(2-carboxyethyl) dithiocarbonate is triclinic (*PI*) with cell dimensions $a = 10.935(13)$, $b = 10.106(7)$, $c = 4.671(5)$ Å, $\alpha = 85.59(10)$, $\beta = 81.87(10)$ and $\gamma = 113.99(9)^\circ$. All intramolecular distances and angles are in agreement with those reported for the two homologues with a hexanoic and dodecanoic fatty acid residue. The molecules are V-shaped as the two homologues but whereas the bend in the latter occurs at the sulfur atom it takes place at the adjacent carbon atom in the title compound. The molecules pack as *Z*-shaped dimers with normal van der Waals contacts.

The title compound belongs to a series of dithiocarbonate fatty acids which have been studied at this Department. These examinations were proposed by Professor A. Fredga of Uppsala University who also provided the crystals for the X-ray work.

Previously the structures of *O*-ethyl *S*-(5-carboxypentyl) dithiocarbonate (ESP)¹ and *O*-ethyl *S*-(11-carboxyundecyl) dithiocarbonate (ESU)² have been determined. This present structure, *O*-ethyl *S*-(2-carboxyethyl) dithiocarbonate, was determined in order to make a comparison with a homologue with a short fatty acid residue.

CRYSTAL DATA

Molecular formula	$C_6H_{10}S_2O_3$
Unit cell, triclinic	$a = 10.935(13)$, $b = 10.106(7)$, $c = 4.671(5)$ Å, $\alpha = 85.59(10)$, $\beta = 81.87(10)$, $\gamma = 113.99(9)^\circ$
<i>V</i>	461.69 Å ³
Molecular weight	194.27
<i>Z</i>	2

D_c	1.397 g cm ⁻³
Space group	<i>P</i> $\bar{1}$
λ	1.54051 Å
μ	47.48 cm ⁻¹ for CuK α radiation

A crystal with dimensions $0.10 \times 0.19 \times 0.44$ mm was mounted along the *c*-axis. Intensity data were collected on a Picker FACS1 automatic diffractometer using the Vanderbilt disc-oriented program system.³ Reflexions were measured up to $2\theta = 120^\circ$ with a total scan width of 2.8° . 10 s background counts were taken on both sides of the peak. 1367 independent reflexions were recorded of which 221 were less than $3\sigma(I)$ and considered as unobserved. Corrections were made for the Lorentz and polarization factors and for absorption and extinction.

STRUCTURE DETERMINATION

The structure was solved with MULTAN 74⁴ with an E_{\min} of 1.4. The set with the highest figure of merit was used for an initial *E*-map which showed the positions of all non-hydrogen atoms.

All heavier atoms were refined with full matrix least-squares using isotropic temperature factors during the first three cycles and thereafter anisotropic ones. The structure refined to an *R*-value of 0.08 and a Fourier difference map now revealed the positions of all the hydrogen atoms. These atoms were included in the refinement using isotropic *B*-values and the structure refined to a final *R*-factor of 0.047. Shift/error values for all atoms, hydrogen atoms

included, were then less than 0.02 with an average value of 0.003. The weighting scheme used during the final stage of the refinement was $\omega = 1/[1 + \{(|F_o| - 5)/5\}^2]$. Atomic scattering factors were taken from Cromer and Mann⁶ except for hydrogen atoms where those of Stewart, Davidson and Simpson⁶ were used. The sulfur atoms were corrected for anomalous dispersion.⁷ A list of the observed and calculated structure factors may be obtained from this Department.

The calculations were performed on a DEC10 computer using the X-Ray System of Crystallographic Programs.⁸ System modifications for the DEC10 were made by Dr. Steve Ernst at University of Pittsburgh and by Dr. Robert Pearson at this Department. Interface routines between X-RAY72 and display programs⁹ have been written by Prof. S. Abrahamsson. They allow a direct inspection of the Fourier output on a graphic display and input of selected

atoms into the structure factor calculation program. By using these routines the time between reading the diffractometer data into the computer and obtaining a structure refined to an *R*-value of 0.08 was less than 2 h.

DESCRIPTION OF THE STRUCTURE

The final atomic parameters are given in Table 1. The atomic numbering and interatomic distances and angles are shown in Figs. 1 and 2.

Intramolecular distances and angles are all in agreement with the corresponding ones found in ESP and ESU. The C-H bonds range from 0.91 to 1.01 Å with a mean value of 0.94 Å. The C-C-H angles are 105–115° with a mean value of 110° and the H-C-H angles are 100–118° with a mean value of 108°.

The conformation of the ethyldithiocarbonate group is very similar to that observed in the two homologues. It is nearly planar (Table 2) with

Table 1. Fractional atomic coordinates and thermal parameters with standard deviations. The anisotropic temperature factors are in the form

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})].$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
(a) All values have been multiplied by 10 ⁴									
S(1)	3318(1)	3423(1)	6415(2)	509(4)	493(4)	669(5)	242(4)	-67(4)	-163(4)
S(2)	2663(1)	285(1)	5501(2)	610(5)	465(4)	734(5)	241(4)	-42(4)	-92(4)
O(1)	796(3)	4527(3)	7351(6)	826(17)	583(15)	819(17)	404(13)	-373(14)	-269(13)
O(2)	-400(3)	3143(3)	4406(6)	736(17)	551(15)	717(16)	341(13)	-226(14)	-169(12)
O(3)	4786(2)	2715(2)	2939(5)	484(13)	550(13)	643(13)	226(11)	7(11)	-134(11)
C(1)	311(3)	3355(3)	6455(6)	385(15)	526(18)	444(16)	231(14)	8(13)	-90(14)
C(2)	487(3)	2045(4)	7685(8)	496(19)	486(18)	535(19)	218(15)	51(15)	-16(16)
C(3)	1744(4)	2418(4)	8997(7)	650(22)	596(21)	443(17)	347(18)	-28(15)	-63(16)
C(4)	3616(3)	2038(3)	4817(7)	453(17)	507(17)	525(17)	240(14)	-133(14)	-125(14)
C(5)	5314(4)	1836(5)	1239(9)	626(23)	727(24)	663(23)	389(20)	-73(19)	-218(20)
C(6)	6598(5)	2904(7)	-782(14)	592(26)	1088(40)	944(35)	314(27)	60(24)	-306(32)
(b) All values have been multiplied by 10 ³ . The isotropic temperature factors are given as <i>U</i> 's.									
H(21)	45(3)	144(3)	622(7)	40(7)					
H(22)	-33(4)	149(4)	907(8)	65(10)					
H(31)	179(4)	157(4)	975(8)	58(10)					
H(32)	180(4)	307(4)	1027(9)	65(11)					
H(51)	546(4)	123(5)	265(10)	78(12)					
H(52)	461(5)	128(5)	28(10)	87(13)					
H(61)	638(7)	353(7)	-191(15)	142(27)					
H(62)	729(6)	349(6)	38(12)	105(16)					
H(63)	702(6)	238(7)	-175(13)	123(19)					
H(24)	-55(5)	377(5)	393(10)	76(14)					

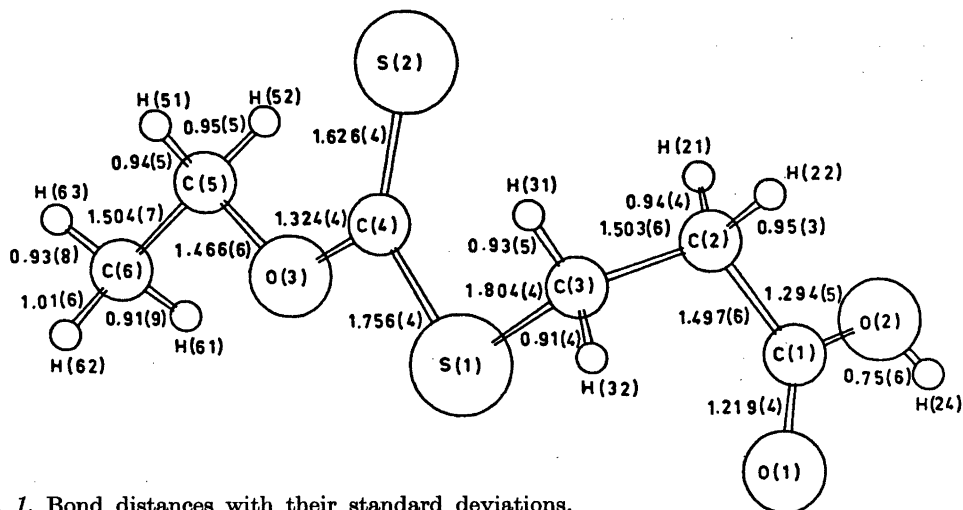


Fig. 1. Bond distances with their standard deviations.

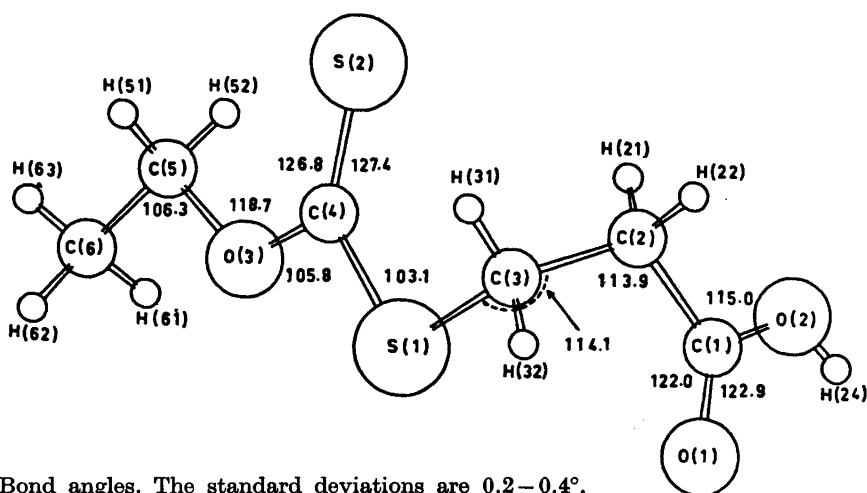


Fig. 2. Bond angles. The standard deviations are 0.2–0.4°.

all atoms within 0.003 Å of the plane through S(1)–S(2)–C(4)–O(3) except C(6) which deviates 0.069 Å. The molecule is V-shaped with a sharp bend at the ω -atom in the hydrocarbon chain. The torsion angle S(1)–C(3)–C(2)–C(1) is 62.3°. The molecules in ESP and ESU are also V-shaped but the bend there occurs at the sulfur atom S(1).

The carboxyl group forms an angle of 25.7° with the plane through the short hydrocarbon chain while these angles are 24.9 and 17.6°, in ESP and ESU respectively.

The molecular packing is shown in a stereoscopic drawing (Fig. 3) and in Fig. 4. The molecules are hydrogen bonded over centres of symmetry to Z-shaped dimers. The planes of the carboxyl groups are separated by 0.148 Å with the two hydrogen atoms halfway (0.07 Å) between these two planes. The O...O and H...O contacts are 2.653(5) and 1.91(6) Å, respectively, and the O–H...O angle is 174(5)°. These values are in agreement with those observed in ESP and ESU and in long chain fatty acids.

Table 2. Distances from some least-squares planes through the molecule.

Atoms defining plane (*)

I C(1), C(2), C(3)

II S(1), S(2), O(3), C(4)

	Distances (Å)	
	I	II
S(1)	1.464	0.001*
S(2)	2.423	0.001*
O(1)	-0.454	-1.863
O(2)	0.502	-3.508
O(3)	3.726	0.001*
C(1)	*	-2.254
C(2)	*	-1.307
C(3)	*	0.042
C(4)	2.633	-0.002*
C(5)	4.897	0.000
C(6)	5.944	-0.069

The dimers are arranged so that rows of parallel carboxyl group planes run in the *c*-axis direction. The rows are enclosed by ethyl end groups pointing towards the centres of the carboxyl group dimers. The shortest ethyl contacts are O(1)···H(62) (2.66 Å) and O(2)···H(63) (2.89 Å).

In order to accommodate the bulky S(2) atom the dimers are translated relative to each other so that S(2) finds space between ethyl groups and carboxyl groups of neighbouring molecules (Fig. 4). S(2) also forms close intramolecular contacts to H(31) (2.72 Å) and to H(52) (2.80 Å) and is furthermore in contact with molecules in the *c*-axis direction with the shortest S···H contacts of 3.23 and 3.32 Å. The shortest methylene group contacts are 2.92 Å in the ethyl end (H(51)···H(51)) and 2.81 Å (H(22)···

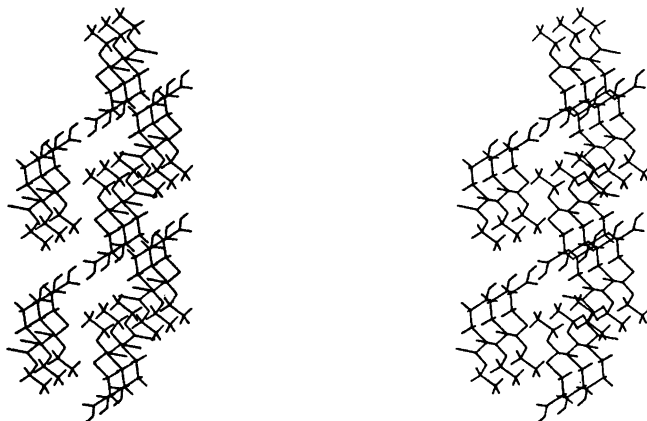


Fig. 3. Stereoscopic drawing.

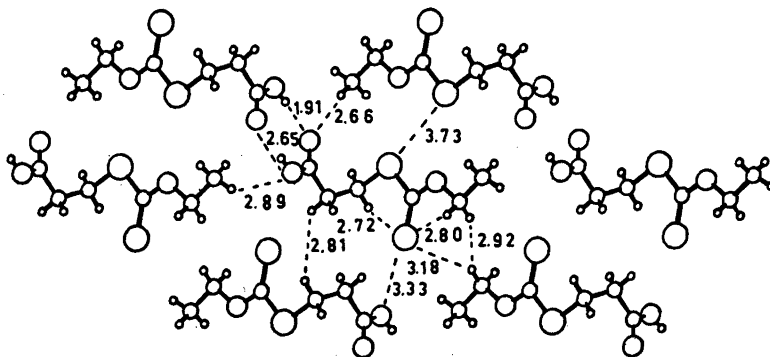


Fig. 4. The molecular packing as seen along the *c*-axis. Important inter- and intramolecular contacts are indicated.

H(31)) in the propionic acid residue. On the more smooth side the molecular separation is determined by the contacts between carbonyl oxygens and methyl ends as mentioned above and by the S(1)...S(1) distance of 3.73 Å.

The packing arrangement is different from that in the two homologues where the carboxyl groups are forced into a hydrocarbon chain matrix and the S(2) atom is accommodated between ethyl end groups.

I wish to thank Professor A. Fredga for providing the crystals, Professor S. Abrahamsson for valuable comments and Mr. M. Lundmark for technical assistance. Grants in support of the Department were obtained from the Swedish Medical Research Council, the Swedish Board for Technical Development, the Wallenberg Foundation and the U.S. Public Health Service (GM-11653).

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Received December 16, 1976.