Acta Cryst. (1974). B**30**, 721

The Crystal Structure of *O*-Ethyl *S*-(5-Carboxypentyl)dithiocarbonate

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(*Received* 19 *March* 1973; *accepted* 26 *November* 1973)

Crystals of *O*-ethyl *S*-(5-carboxypentyl)dithiocarbonate ($C_9H_{16}S_2O_3$) are triclinic ($P\bar{1}$) with $a=4{\cdot}752$, $b=8{\cdot}204$, $c=17{\cdot}458$ Å, $\alpha=91{\cdot}16$, $\beta=98{\cdot}18$ and $\gamma=111{\cdot}82°$. The ethyldithiocarbonate group is almost planar and forms an angle of 83·6° with the carbon-chain plane of the hexanoic acid part of the molecule. The molecule is slightly V-shaped at the bridging sulphur atom in that the chain axis makes an angle of 144° with the direction of maximum extension of the ethyldithiocarbonate group. The molecules are linked in dimers by hydrogen bonds (2·66 Å) between carboxyl groups. The planes of the latter are 0·099 Å apart and inclined 24·9° to the main-chain plane.

Introduction

In connexion with work on the general solid-state behaviour of lipids, compounds with sulphur atoms in the molecule have been studied at this laboratory. Abrahamsson & Westerdahl (1963) determined the crystal structure of 3-thiadodecanoic acid and Larsson (1963) the diglyceride of the same acid. In both cases the chain direction was broken at the sulphur atom, giving V-shaped molecules. Work is now in progress on the structure of some dithiocarbonate fatty acids, the present study dealing with hexanoic acid with an ethyldithiocarbonate group in the ω position.

Crystal data

O-Ethyl *S*-(5-carboxypentyl)dithiocarbonate (ESD)	
Molecular formula	$C_9H_{16}S_2O_3$
M.W.	236·36
Unit cell	Triclinic
	$a=4{\cdot}752$ (5), $b=8{\cdot}204$ (11),
	$c=17{\cdot}458$ (22) Å, $\alpha=91{\cdot}16$ (1),
	$\beta=98{\cdot}18$ (1), $\gamma=111{\cdot}82$ (1)°
Space group	$P\bar{1}$

$Z=2$
$D_c=1{\cdot}230$ g cm^{-3}
$D_m=1{\cdot}234$
$V=637{\cdot}8$ Å^3
$\mu=32{\cdot}66$ cm^{-1} for Cu $K\alpha$ radiation.

A single crystal with dimensions 0·03 × 0·06 × 0·41 mm was mounted along the *a* axis. X-ray reflexions were collected on a Picker FACS I diffractometer using graphite-monochromated Cu $K\alpha$ radiation. Reflexions were measured up to $2\theta=124°$ in the θ–2θ scanning mode with a speed of 1° min^{-1} and a scan width of 2·0°. The background level was determined from 10 s counts on each side of the reflexion. In all, 1972 independent reflexions were measured of which 1606 had an intensity greater than two standard deviations and were used in the structure analysis. The Lorentz and polarization factors were applied and a correction was made for absorption but not for extinction. The space group was assumed to be $P\bar{1}$, which was verified by the structure analysis.

Structure determination

All non-hydrogen atoms were easily found from a sulphur-phased electron density series. After a few cycles of block-diagonal least-squares refinement using anisotropic temperature parameters for the sulphur atoms, all hydrogen atoms except that attached to the hydroxyl oxygen were located from a difference series and included in the following calculations with isotropic temperature factors corresponding to those of the parent atom. All non-hydrogen atoms were then refined with anisotropic temperature factors to an *R* value of 0·06. A difference series showed two peaks close to the hydroxyl oxygen, of which one was at the expected position for a hydrogen bond. The refinement was now continued with the full matrix. The hydrogen atoms – their *B* values were not varied – and the rest of the molecule were treated in alternate cycles. The refinement was terminated at an *R* value of 0·058. The ratios between shifts and standard deviations then averaged 0·02.

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962) except for hydrogen, for which the data of Stewart, Davidson & Simpson (1965) were used. The weight assigned to the observation in the least-squares refinement was (Mills & Rollett, 1961)

$$w=\left[1+\left(\frac{|F_o|-5F_{\min}}{5F_{\min}}\right)^2\right]^{-1}.$$

The calculations were performed on a Datasaab D21–PDP 15 dual computer system using programs developed at this laboratory except for the absorption correction (Coppens, Leiserowitz & Rabinovich, 1965) and the drawing of the vibrational ellipsoids (Johnson, 1965).

Results and discussion

The atomic parameters are given in Tables 1 and 2 and interatomic distances and angles are shown in Fig. 1

together with the atomic numbering, and with standard deviations in Tables 3 and 4. No corrections were made for thermal motion.*

The ethyldithiocarbonate group is nearly planar (Table 5). C(8) and C(9) are 0·04 and 0·12 Å respectively on each side of the plane through S(1), S(2), C(7) and O(3). The latter atoms are within 0·003 Å of the plane. C(6) is also close to the plane (0·04 Å).

Table 1. *Fractional atomic coordinates*

The standard deviations (in parentheses) are multiplied by 10^5 for the sulphur, 10^3 for hydrogen and 10^4 for the other atoms.

	x	*y*	*z*	*B* (Å^2)
S(1)	−0·26172 (21)	−0·05917 (12)	0·76060 (5)	
S(2)	0·20021 (24)	0·15503 (12)	0·89808 (6)	
O(1)	0·3946 (6)	0·7897 (3)	0·5200 (2)	
O(2)	0·2517 (7)	0·9912 (4)	0·5685 (2)	
O(3)	0·0296 (6)	−0·1822 (3)	0·8544 (1)	
C(1)	0·2441 (7)	0·8327 (4)	0·5616 (2)	
C(2)	0·0348 (8)	0·7059 (5)	0·6083 (2)	
C(3)	0·1110 (7)	0·5494 (4)	0·6296 (2)	
C(4)	−0·1135 (7)	0·4294 (5)	0·6766 (2)	
C(5)	−0·0461 (7)	0·2690 (5)	0·6997 (2)	
C(6)	−0·2747 (8)	0·1550 (5)	0·7471 (2)	
C(7)	0·0112 (7)	−0·0260 (4)	0·8440 (2)	
C(8)	0·2327 (10)	−0·2004 (5)	0·9213 (2)	
C(9)	0·2302 (14)	−0·3813 (7)	0·9121 (3)	
H(12)	0·371 (10)	1·054 (6)	0·538 (3)	8·7
H(21)	0·045 (8)	0·776 (5)	0·654 (2)	6·4
H(22)	−0·129 (9)	0·678 (5)	0·583 (2)	7·6
H(31)	0·103 (8)	0·485 (5)	0·583 (2)	6·2
H(32)	0·314 (8)	0·593 (5)	0·663 (2)	6·2
H(41)	−0·116 (7)	0·496 (4)	0·724 (2)	5·1
H(42)	−0·308 (8)	0·389 (5)	0·649 (2)	6·3
H(51)	−0·060 (8)	0·197 (4)	0·653 (2)	6·3
H(52)	0·169 (9)	0·311 (5)	0·730 (2)	7·6
H(61)	−0·267 (7)	0·214 (4)	0·795 (2)	5·2
H(62)	−0·464 (9)	0·129 (5)	0·720 (2)	7·1
H(81)	0·436 (9)	−0·106 (5)	0·921 (2)	7·2
H(82)	0·174 (8)	−0·166 (4)	0·970 (2)	5·7
H(91)	0·294 (12)	−0·415 (6)	0·865 (3)	10·4
H(92)	0·023 (10)	−0·457 (6)	0·913 (3)	8·6
H(93)	0·337 (10)	−0·403 (6)	0·961 (3)	9·1

The hexanoic acid part of the molecule shows a fairly regular zigzag chain between C(2) and C(6). The maximum deviation from the chain plane is 0·005 Å. C(1) is 0·009 Å off the plane and S(1) 0·332 Å. There is a slight bend in the chain axis within the plane as C(2) and C(6) are 0·04 Å further away from the chain axis than C(4). This is also obvious from the valence angles at C(3) and C(5), which are considerably smaller than those at C(2), C(4) and C(6). A similar type of bending was observed in 13-oxoisostearic acid (Dahlén, 1972).

The molecule is slightly V-shaped, owing to a bend at S(1). The angle between the axis of the chain within C(2) and C(6) and the axis of the tail of the ethyldithiocarbonate group [C(7), O(3), C(8) and C(9)] is 144·2°. The plane through the dithiocarbonate group forms an angle of 83·6° with the chain plane. Hereby, S(2) comes into close contact (2·85 Å) with H(61) in the same molecule. As the ethyl carbon atoms are close to the dithiocarbonate plane the S(2)···H(81) and S(2)··· H(82) distances are also very short (2·78 and 2·91 Å).

The carboxyl-group plane intersects at an angle of 24·9° with the chain plane. Hydrogen bonds between

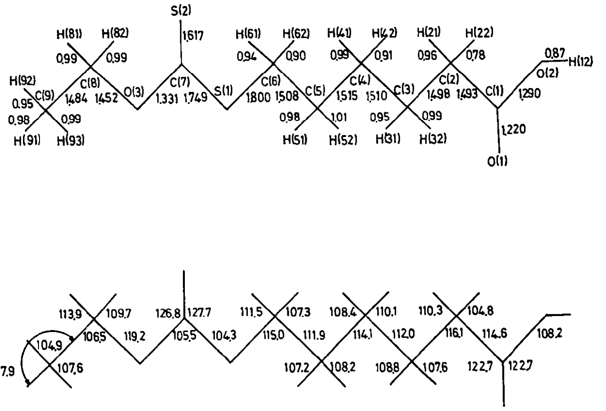

Fig. 1. Distances and angles of ESD.

Table 2. *Anisotropic thermal parameters in the form exp* $[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2klb^*c^*U_{23}+2lha^*c^*U_{31}+2hka^*b^*U_{12})]$

Standard deviations are given in parentheses. All values have been multiplied by 10^4.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{31}	U_{12}
S(1)	711 (5)	645 (5)	702 (5)	61 (4)	69 (4)	272 (4)
S(2)	911 (6)	654 (6)	747 (6)	−29 (4)	57 (5)	341 (5)
O(1)	907 (17)	766 (17)	989 (19)	245 (14)	452 (15)	423 (14)
O(2)	1098 (20)	761 (17)	1010 (20)	237 (14)	512 (17)	465 (16)
O(3)	800 (15)	624 (14)	779 (15)	109 (11)	108 (12)	344 (12)
C(1)	578 (17)	728 (21)	661 (20)	125 (16)	108 (14)	316 (16)
C(2)	672 (20)	804 (23)	826 (24)	217 (19)	264 (18)	391 (18)
C(3)	539 (17)	712 (21)	718 (21)	116 (16)	157 (15)	283 (15)
C(4)	582 (17)	781 (22)	712 (20)	164 (17)	206 (15)	354 (16)
C(5)	617 (18)	783 (22)	722 (21)	166 (17)	222 (16)	362 (17)
C(6)	632 (18)	795 (22)	726 (21)	171 (17)	204 (16)	385 (17)
C(7)	603 (17)	620 (18)	642 (19)	127 (15)	218 (15)	273 (15)
C(8)	966 (27)	776 (25)	757 (23)	149 (19)	106 (19)	468 (21)
C(9)	1516 (45)	898 (31)	1120 (37)	159 (27)	−61 (32)	664 (32)

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* A list of the final structure factors can be obtained from this laboratory and has also been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30303 (11 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Bond distances with standard deviations* ($\times 10^3$) *for the heavier atoms and for hydrogen* ($\times 10^2$)

S(1) —C(6)	1·800 (4) Å	H(22)–C(2)	0·78 (4) Å
S(1) —C(7)	1·749 (3)	H(31)–C(3)	0·95 (4)
S(2) —C(7)	1·617 (3)	H(32)–C(3)	0·99 (3)
O(1)—C(1)	1·220 (5)	H(41)–C(4)	0·99 (3)
O(2)—C(1)	1·290 (5)	H(42)–C(4)	0·91 (3)
O(3)—C(7)	1·331 (5)	H(51)–C(5)	0·98 (4)
O(3)—C(8)	1·452 (5)	H(52)–C(5)	1·01 (4)
C(1)—C(2)	1·493 (5)	H(61)–C(6)	0·94 (3)
C(2)—C(3)	1·498 (6)	H(62)–C(6)	0·90 (4)
C(3)—C(4)	1·510 (5)	H(81)–C(8)	0·99 (3)
C(4)—C(5)	1·515 (6)	H(82)–C(8)	0·99 (4)
C(5)—C(6)	1·508 (5)	H(91)–C(9)	0·98 (6)
C(8)—C(9)	1·484 (8)	H(92)–C(9)	0·95 (4)
H(12)–O(2)	0·87 (5)	H(93)–C(9)	0·99 (5)
H(21)–C(2)	0·96 (4)		

carboxyl groups over centres of symmetry link the molecules in dimers. The planes of the carboxyl groups are separated by 0·099 Å. The hydroxyl hydrogen atoms are halfway between the planes.

The bond lengths in the dithiocarbonate group agree well with those reported for diethyldixanthogen (Watanabe, 1971). The C=S double bond lengths are thus 1·617 and 1·620 Å respectively and the C–S single bonds 1·749 and 1·729 Å. The angles at the carbon atom of the dithiocarbonate group are, however, different in that the O(3)–C(7)–S(1) angle has decreased to 105·5° in ESD as compared to the corresponding angle in diethyldixanthogen (DEX) of 114·3°. Because of the crowding round S(2) the C(7)–S(1) bond direction must change, which is also clear from the angle S(2)–C(7)–S(1) being increased by 9·5°. The dimensions of the rest of the ethyldithiocarbonate group are compared below with both diethyldixanthogen and cadmium ethylxanthate (CEX) (Iimura, Ito & Hagihara, 1972):

	ESD	DEX	CEX
C(7)–O(3)	1·331 Å	1·360 Å	1·331 Å
O(3)–C(8)	1·452	1·465	1·457
C(8)–C(9)	1·484	1·544	1·498
C(7)–O(3)–C(8)	119·2°	117·3°	120·9°
O(3)–C(8)–C(9)	106·5	104·8	106·3 .

The S(1)–C(6) distance of 1·800 Å is a usual single-bond value and the valence angle at S(1) of 104·3° is also normal.

The mean value of the C–C bonds in the chain [C(2) to C(6)] is 1·508 Å. This is a fairly short distance, as is usual for long chains uncorrected for thermal motion. In isostearic acid (Abrahamsson & Lundén, 1972) the corresponding value is 1·515 Å. This compound also shows dimensions for the carboxylic group comparable to those of ESD.

The C–H bond distances range from 0·78 to 1·01 Å (mean value 0·95 Å), the C–C–H angles from 104·8 to 117·9° (108·8°) and the H–C–H angles from 101·9 to 114·5° (108·3°).

The molecular packing is shown in Figs. 2 and 3 where the most important contacts are indicated. More complete data are given in Table 6. As Figs. 2 and 3, which are projections, do not give a correct impression of the packing, a stereoscopic drawing is also included (Fig. 4).

Table 4. *Bond angles* (*with standard deviations*)

C(6)–S(1) –C(7)	104·3 (0·2)°	C(4)—C(3)–H(31)	108·8 (2·0)°
S(1) –C(7)–S(2)	127·7 (0·2)	C(3)—C(4)–H(42)	110·1 (2·3)
S(1) –C(7)–O(3)	105·5 (0·2)	C(5)—C(4)–H(41)	108·4 (2·1)
S(2) –C(7)–O(3)	126·8 (0·2)	C(4)—C(5)–H(52)	108·2 (2·5)
S(1) –C(6)–C(5)	115·0 (0·3)	C(6)—C(5)–H(51)	107·2 (1·9)
C(7)–O(3)–C(8)	119·2 (0·3)	C(5)—C(6)–H(62)	107·3 (2·5)
O(1)–C(1)–O(2)	122·7 (0·3)	C(9)—C(8)–H(81)	113·9 (2·8)
O(1)–C(1)–C(2)	122·7 (0·4)	C(8)—C(9)–H(91)	117·9 (3·2)
O(2)–C(1)–C(2)	114·6 (0·4)	C(8)—C(9)–H(92)	104·9 (3·3)
O(3)–C(8)–C(9)	106·5 (0·3)	C(8)—C(9)–H(93)	107·6 (2·8)
C(1)–C(2)–C(3)	116·1 (0·3)	H(21)–C(2)–H(22)	109·3 (4·3)
C(2)–C(3)–C(4)	122·0 (0·3)	H(31)–C(3)–H(32)	114·1 (3·4)
C(3)–C(4)–C(5)	114·1 (0·3)	H(41)–C(4)–H(42)	107·1 (3·3)
C(4)–C(5)–C(6)	111·9 (0·3)	H(51)–C(5)–H(52)	109·8 (3·6)
S(1) –C(6)–H(61)	111·5 (2·2)	H(61)–C(6)–H(62)	107·4 (3·6)
C(1)–O(2)–H(12)	108·2 (3·6)	H(81)–C(8)–H(82)	101·9 (2·9)
O(3)–C(8)–H(82)	109·7 (2·2)	H(91)–C(9)–H(93)	114·5 (4·7)
C(1)–C(2)–H(22)	104·8 (3·1)	H(91)–C(9)–H(92)	108·5 (3·8)
C(3)–C(2)–H(21)	110·3 (2·5)	H(92)–C(9)–H(93)	101·9 (3·7)
C(2)–C(3)–H(32)	107·6 (2·3)		

Table 5. *Various least-squares planes through the molecule*

(Equations are referred to the crystal axes.)

	Atoms defining plane (*)	Equation
I	C(2), C(3), C(4), C(5), C(6)	$0·10842X+0·18494Y+0·97675Z-0·72834=0$
II	S(1), S(2), O(3), C(7)	$0·29625X-0·02621Y-0·95475Z+0·80209=0$
III	O(1), O(2), C(1)	$0·25152X-0·05403Y+0·96634Z-0·55912=0$

Table 5 (*cont.*)

Distances from the various planes (Å)

	I	II	III
S(1)	−0·332	−0·001*	1·334
S(2)	2·671	−0·001*	4·131
O(1)	−0·423	5·042	*
O(2)	0·504	3·864	*
O(3)	1·015	−0·001*	3·343
C(1)	0·009	3·970	*
C(2)	0·001*	2·675	−0·009
C(3)	0·003*	2·755	0·559
C(4)	−0·005*	1·397	0·505
C(5)	−0·003*	1·423	1·070
C(6)	0·004*	0·042	1·006
C(7)	1·239	0·003*	3·071
C(8)	2·141	−0·041	4·718
C(9)	1·568	0·119	4·721

Table 6. *Intermolecular van der Waals contacts*

i and ii refer to the equivalent positions x, y, z and $-x, -y, -z$.

A	*B*	Unit translation of atom *B*	
O(2) ····	O(2^{ii})	(0, 2, 1)	3·18 Å
S(1) ····	H(21^{i})	(0, −1, 0)	3·09
S(1) ····	H(21^{i})	(−1, −1, 0)	3·31
S(1) ····	H(32^{i})	(−1, −1, 0)	3·11
S(1) ····	H(81^{i})	(−1, 0, 0)	3·30
S(2) ····	H(61^{i})	(1, 0, 0)	3·21
S(2) ····	H(81^{ii})	(1, 0, 2)	3·48
S(2) ····	H(82^{ii})	(0, 0, 2)	3·13
S(2) ····	H(82^{ii})	(1, 0, 2)	3·47
S(2) ····	H(91^{i})	(0, 1, 0)	3·46
S(2) ····	H(93^{ii})	(1, 0, 2)	3·16
O(1) ····	H(22^{i})	(1, 0, 0)	2·84
O(1) ····	H(31^{ii})	(0, 1, 1)	2·93
O(1) ····	H(42^{ii})	(0, 1, 1)	3·17
O(1) ····	H(12^{ii})	(1, 2, 1)	1·79
O(2) ····	H(51^{i})	(0, 1, 0)	3·10
O(2) ····	H(51^{i})	(1, 1, 0)	3·19
O(2) ····	H(62^{i})	(1, 1, 0)	2·79
O(2) ····	H(12^{ii})	(0, 2, 1)	3·15
O(2) ····	H(12^{ii})	(1, 2, 1)	2·86
C(1) ····	H(12^{ii})	(1, 2, 1)	2·63
C(7) ····	H(81^{i})	(−1, 0, 0)	3·10
H(12)···	H(12^{ii})	(1, 2, 1)	2·29
H(22)···	H(32^{i})	(−1, 0, 0)	3·03
H(32)···	H(42^{i})	(1, 0, 0)	2·90
H(41)···	H(91^{i})	(0, 1, 0)	2·81
H(42)···	H(52^{i})	(−1, 0, 0)	2·91
H(52)···	H(62^{i})	(1, 0, 0)	2·71
H(81)···	H(82^{ii})	(1, 0, 2)	2·79
H(92)···	H(93^{ii})	(0, −1, 2)	2·96
H(93)···	H(93^{ii})	(1, −1, 2)	2·84

Though the molecule contains a fairly regular carbon chain there are no regions in the structure with normal side packing of chains (*cf.* Abrahamsson, Ställberg-Stenhagen & Stenhagen, 1963). More extended contacts between the chain parts exist only in the **a** direction. Because of the bulky dithiocarbonate group the dimers are translated relative to each other so that S(2) finds space between the ethyl end groups. It is seen from Fig. 3 that the intermolecular sulphur contacts with hydrogen are all longer than 3·09 Å, as compared with the intramolecular contacts of about 2·8 Å. This indicates that the closest intermolecular

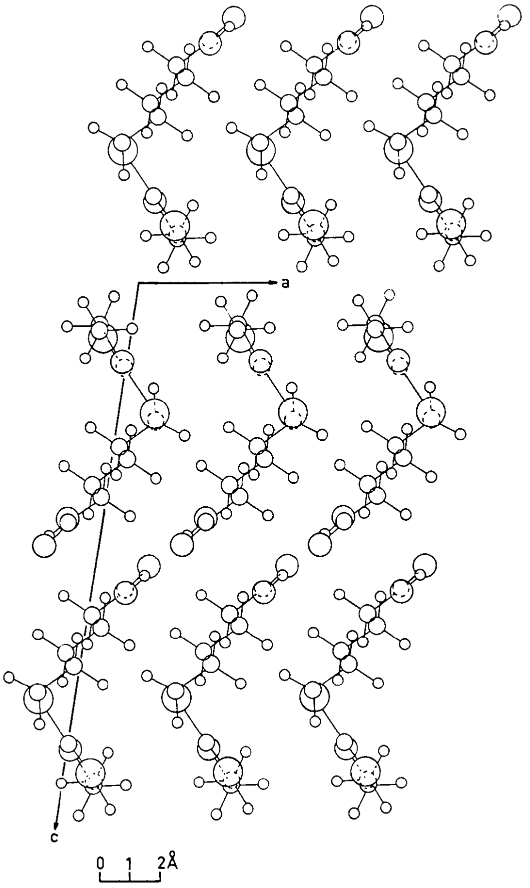

Fig. 2. Projection of ESD along the *b* axis.

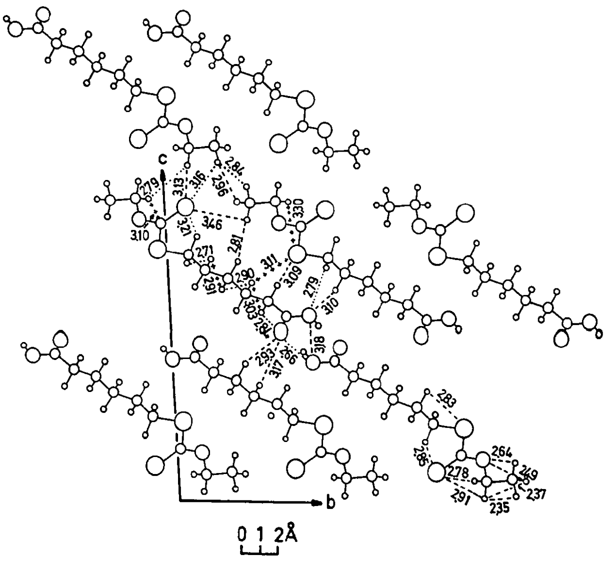

Fig. 3. Molecular packing of ESD as seen along the *a* axis. The more important inter- and intramolecular contacts (lower right) are indicated. (····· and + + + + + indicate contacts to molecules translated +*a* and −*a* respectively).

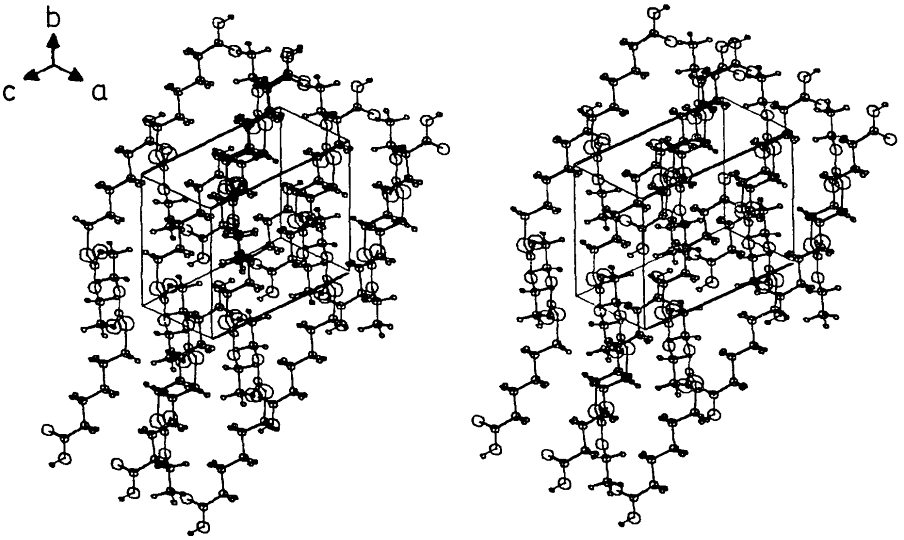

Fig. 4. Stereoscopic drawing of ESD.

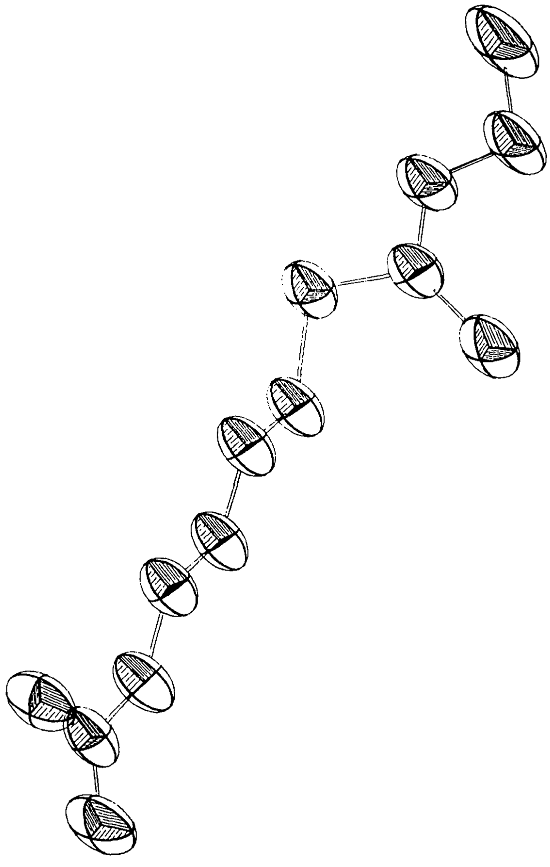

Fig. 5. Drawing of ESD showing the thermal ellipsoids as viewed along the *a* axis.

contacts are between hydrogen atoms. The ethyldithiocarbonate groups are in packing contact both with each other and the hexanoic acid chain. However, the axes – as described above – of the two parts of the molecule cross so that C(6) is close to the carboxyl group in one molecule and H(91) is in packing contact with H(31) of the equivalent molecule translated by **a**. There is considerable anisotropy in the thermal vibrations as can be seen in Fig. 5. The largest thermal motion is found, as expected, in the ethyl end group.

We wish to thank Professor A. Fredga for supplying the compound. Grants in support of the Crystallography Group were obtained from the Swedish Medical and the Swedish Natural Science Research Councils, the Swedish Board for Technical Development, the Tercentenary Fund of the Bank of Sweden and the U. S. Public Health Service (GM-11653).

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