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The Crystal Structure of Diethyldixanthogen

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The crystal structure of diethyldixanthogen, $(SSCOC_2H_5)_2$, is monoclinic with $a=18{\cdot}958$ (0·005), $b=4{\cdot}394$ (0·002), $c=6{\cdot}990$ (0·004) Å; $\beta=107{\cdot}27$ (0·03)°; the space group is $P2/a$ and $Z=2$. A molecule of $(SSCOC_2H_5)_2$ consists of two almost planar $SSCOC_2H_5$ groups linked by a twofold rotation axis at a S–S distance of 2·054 (0·004) Å, which is comparable with the S–S single bond distance. The dihedral angle C–S–S–C is 107·2 (1·0)°. The molecules are held together by van der Waals sulphur–sulphur, sulphur atom–alkyl group, sulphur atom–methyl end and methyl end–methyl end contacts.

Introduction

In connexion with the study of the action of xanthate on sulphide mineral surfaces in a froth flotation process, the determination of the molecular structure of dixanthogen, an oxidation product of xanthate, is important. Dixanthogen is supposed by some authors to play an important role in making sulphide mineral surfaces hydrophobic, (1) by coating the xanthate ions already adsorbed on the mineral surfaces by van der Waals forces (Leja, 1956), or (2) by being adsorbed dissociatively on the mineral surface so that one xanthate radical is coordinated to one metal atom in the substrate (Poling & Leja, 1963). In the present paper the molecular structure of diethyldixanthogen in the crysstalline state is reported.

Crystal data

The crystallographic data for diethyldixanthogen are as follows:

Cell constants and cell volume
$a=18{\cdot}958$ (0·005) Å, $b=4{\cdot}394$ (0·002),
$c=6{\cdot}990$ (0·004),
$\beta=107{\cdot}27$ (0·03)°, $V=556{\cdot}1$ (0·4) Å^3 .
Space group $P2/a$
Formula units per cell: $Z=2$
Observed and calculated density
$d_o=1{\cdot}30$ g.cm^{-3} (flotation)
$d_c=1{\cdot}28$ g.cm^{-3}
Linear absorption coefficient for Cu radiation
$\mu=85{\cdot}54$ cm^{-1}.

Experimental

Diethyldixanthogen was obtained by mixing aqueous solutions of purified potassium ethylxanthate and iodine drop by drop. The light yellowish green substance obtained in the form of an emulsion was dissolved in ethanol and crystallized by evaporation of the solvent at a temperature of about 15 °C. The crystal, in the shape of a rectangular plate, was stable in air up to the melting point (28·0 °C). The specimen used had a cross section of 0·35 × 0·85 mm in the *b*-axis setting and 0·14 × 0·08 mm in the *c*-axis setting of the crystal.

Equi-inclination photographs of the 0 to 4th layers around the *b* axis and the 0 to 5th layers around the *c* axis were taken with the use of an integrating cassette at a temperature of 12 ± 2°C with Ni-filtered Cu $K\alpha$ radiation. The intensity measurement was carried out with a microphotometer. Of the recorded 1121 independent reflexions, about 88 % of the total number of those observable with Cu $K\alpha$ radiation, 353 reflexions were too weak to give any numerical values. Observed intensities were corrected for Lorentz and polarization factors. An absorption correction, in which the crystal was approximated to a cylinder, and a spot-size correction (Phillips, 1956) were applied, but no extinction correction was made. The unit-cell dimensions were determined by the use of a Straumanis-type cassette.

Determination of the crystal structure

Systematic extinction showed the crystal to be monoclinic with space group $P2/a$ or Pa. Because the unit cell is thin in the b axis direction, the (010) Patterson projection was calculated and the image seeking method applied. The resultant molecular image possessed a twofold rotation axis in this projection. The three-dimensional Patterson function was calculated and the expected peaks were observed on the section $P(\frac{1}{2}+2x, 0, 2z)$.Thus the space group was determined to be $P2/a$ rather than Pa. The y coordinates of two sulphur atoms were determined from the section $P(\frac{1}{2},2y,0)$. On the basis of the atomic coordinates of the two sulphur atoms the coordinates of the oxygen and carbon atoms were determined from the electron density maps. Three cycles of isotropic least-squares refinement reduced the R value to 0·154. A further three cycles of anisotropic refinement reduced the R value to 0·108. An anomalous dispersion correction was applied to the sulphur atoms in the anisotropic refinement. On inclusion of the hydrogen atoms of the ethyl groups with an isotropic temperature factor $B=7{\cdot}0$ Å the R value fell to 0·106. The overall accuracy of the present analysis is still insufficient to reveal the hydrogen atom positions.

The final atomic coordinates and thermal parameters are given in Table 1 and the numbering of the atoms is shown in Figs. 1 and 2. The observed and calculated structure factors with the omission of the hydrogen atoms are shown in Table 2.

Discussion of the structure

Intramolecular configuration

The molecule of diethyldixanthogen, $(SSCOC_2H_5)_2$, consists of two $SSCOC_2H_5$ groups linked by a S–S single bond through a twofold rotation axis. The SSCO group is completely planar and two SSCO groups make an angle of 107·8 (1·3)°. The atoms C(1), C(2) and C(3) deviate from the plane defined by S(1), S(2) and O atoms by 0·00, 0·11 and −0·07 Å respec-

Table 1. *Atomic parameters with standard deviations*

Atomic coordinates ($\times 10^4$)

	x/a	y/b	z/c
S(1)	2051 (2)	1127 (9)	3740 (4)
S(2)	595 (2)	8526 (10)	2511 (5)
O	1575 (4)	7650 (20)	6108 (11)
C(1)	1376 (5)	8899 (30)	4245 (16)
C(2)	1012 (6)	5931 (33)	6699 (17)
C(3)	1424 (7)	4556 (34)	8761 (17)

Thermal parameters

The U_{ij} values as given here are defined by:

$$T=\exp\{-10^{-4}\,.\,2\pi^2(U_{11}h^2a^{*2}+\ldots+2U_{12}hka^*b^*+\ldots)\}$$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	437 (14)	604 (20)	477 (15)	66 (16)	139 (11)	118 (16)
S(2)	398 (14)	885 (29)	517 (17)	41 (18)	0 (12)	35 (20)
O	455 (40)	517 (52)	385 (38)	−60 (40)	131 (31)	−20 (38)
C(1)	363 (52)	481 (75)	509 (61)	72 (58)	162 (45)	−79 (62)
C(2)	460 (62)	629 (92)	518 (65)	−32 (66)	182 (52)	26 (70)
C(3)	765 (86)	596 (100)	437 (63)	−13 (75)	182 (60)	119 (64)

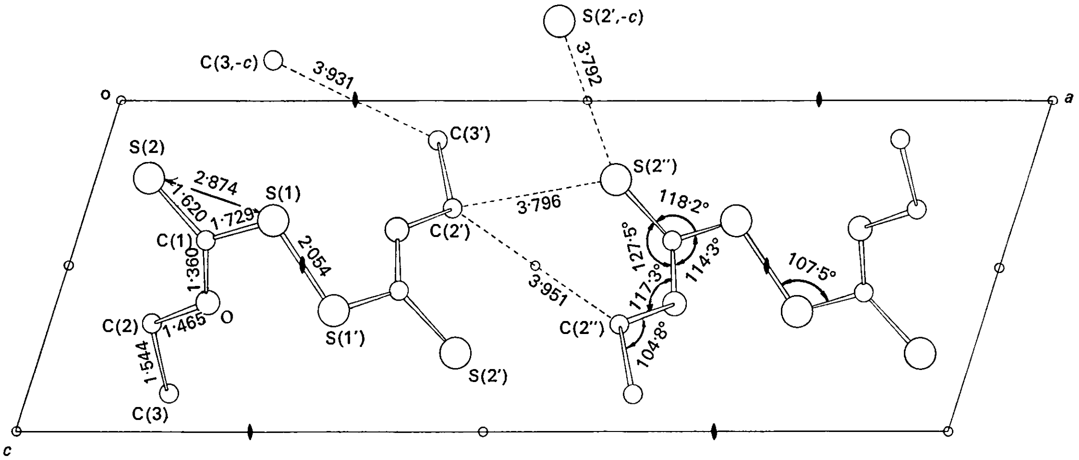

Fig. 1. Molecular configuration in the unit cell of diethyldixanthogen, $(SSCOC_2H_5)_2$, viewed along the b axis. The broken line shows van der Waals contact (*cf.* Table 3).

Table 2. *Observed and calculated structure factors*

H	FO	FC
H	0	0
2	15.9	-20.8
4	34.5	-41.5
8	37.9	-42.1
10	12.9	-13.1
12	24.6	-25.3
14	30.0	29.8
16	6.3	5.8
18	7.1	6.3
20	17.5	16.1
22	8.6	-9.4
H	0	1
-22	11.5	10.7
-20	3.7	3.6
-18	5.8	5.4
-16	18.9	16.6
-14	49.0	-48.6
-12	7.8	-7.3
-10	19.1	-19.9
-8	7.8	-7.8
-6	67.2	69.0
-4	32.4	33.9
-2	56.4	63.1
0	70.6	-79.0
2	19.7	15.8
4	16.7	-15.6
6	86.4	-85.3
8	31.6	27.4
10	4.9	-5.5
12	36.5	30.9
14	25.8	22.7
20	20.4	-17.3
H	0	2
-22	5.6	5.5
-20	5.7	-5.0
-18	8.3	-7.0
-16	41.8	-39.7
-14	24.8	23.6
-12	5.9	6.6
-10	13.1	-11.2
-8	56.1	60.2
-6	4.0	1.3
-4	37.8	34.1
-2	69.6	-61.0
0	47.8	-42.9
2	21.2	-19.5
4	44.2	-40.7
6	53.0	58.5
8	13.1	12.2
10	29.6	29.4
12	5.0	2.7
14	27.8	-23.7
16	3.9	4.4
18	19.4	-16.8
20	4.5	-3.6
H	0	3
-22	17.5	-15.0
-18	6.9	-8.5
-16	10.2	10.6
-12	17.0	17.5
-10	53.0	52.1
-8	50.3	-50.0
-6	4.1	-2.3
-4	45.1	-41.0
-2	49.6	-42.5
0	38.4	36.9
2	5.3	2.0
4	41.7	43.6
8	10.9	11.1
10	5.0	-4.7
12	29.7	-28.8
16	17.6	-15.6
18	8.3	7.2
H	0	4
-24	9.4	-11.4
-22	5.8	4.8
-20	7.1	-5.0
-18	13.6	13.6
-16	18.6	18.5
-14	7.2	-8.3
-12	10.1	9.3
-10	35.7	-32.1
-8	6.0	-6.2
-6	24.3	-22.1
-4	6.9	5.8
-2	37.4	40.1
0	26.6	-25.0
2	49.7	51.0
4	10.2	10.2
6	27.2	-30.7
8	13.1	-14.4
10	18.2	-17.7
12	8.8	6.9
14	4.0	-3.1
16	15.2	14.1
H	0	5
-20	4.6	4.8
-18	5.7	4.7
-16	13.7	-14.0
-14	11.6	11.0
-12	26.6	-26.3
-10	6.2	-5.8
-8	10.0	8.4
-4	35.8	32.6
0	19.3	17.9
2	31.1	-31.1
4	24.4	-23.9
6	11.4	11.4
8	15.6	-16.4
10	10.5	11.1
12	11.6	9.2
H	0	6
-18	9.8	-9.8
-14	18.1	-20.9
-12	5.7	7.1
-10	24.6	25.7
-8	6.9	-5.7
-6	18.6	15.1
-4	9.7	-9.9
0	15.8	-16.1
2	12.1	-13.0
4	9.6	10.4
6	7.2	-6.9
8	18.6	18.0
10	9.5	7.8
H	0	7
-20	8.0	-8.0
-14	9.4	10.9
-12	2.1	3.8
-10	10.9	-11.1
-8	19.4	20.2
-6	14.1	-14.7
-4	13.7	-13.8
0	3.1	-4.6
2	10.6	12.2
6	11.8	12.2
H	0	8
-14	5.2	6.8
-12	3.8	-5.2
-8	12.1	-13.0
-4	4.1	5.0
0	12.2	14.6
H	1	0
0	40.6	55.5
1	12.9	14.8
2	10.6	-14.6
3	62.1	72.2
4	22.3	26.8
6	2.8	-3.2
7	7.7	8.7
8	30.4	-37.1
9	17.5	18.5
11	34.8	-39.5
12	17.5	-20.9
13	3.6	-2.3
14	18.4	19.1
15	9.4	-9.6
16	8.7	9.8
19	8.2	8.3
20	5.4	5.9
21	4.1	3.8
22	4.8	-6.2
H	1	1
-22	8.1	8.0
-20	2.9	2.8
-18	2.7	1.7
-17	15.7	16.0
-16	7.8	7.3
-15	10.0	10.2
-14	30.8	-31.2
-13	10.4	11.2
-12	6.5	5.6
-11	30.9	-35.2
-10	1.5	-2.2
-9	2.4	-4.6
-8	9.9	-8.9
-7	11.8	-13.4
-6	3.8	6.9
-5	52.6	-56.7
-4	13.2	9.8
-3	77.1	71.4
-2	89.8	89.7
-1	31.1	25.9
0	52.4	-44.8
1	12.6	13.5
2	37.0	-30.6
3	11.2	14.3
6	35.9	-36.7
7	9.5	-8.7
8	17.0	14.0
9	44.1	-43.4
11	4.5	2.8
12	25.3	22.4
13	3.2	-3.9
14	4.3	3.6
15	9.7	8.7
16	5.8	-5.6
17	20.2	17.9
18	9.7	8.4
20	12.0	-9.9
21	3.4	4.1
H	1	2
-21	3.2	3.8
-20	5.2	-4.5
-19	19.2	18.1
-18	2.7	2.7
-17	12.6	-12.6
-16	18.3	-19.3
-15	8.2	-7.6
-14	6.8	5.9
-13	11.1	-11.2
-12	9.1	-8.0
-11	8.8	-8.6
-10	4.8	4.8
-9	11.2	-8.8
-8	50.1	50.9
-7	6.0	-2.1
-6	17.5	-14.1
-5	66.7	60.6
-4	6.3	6.5
-3	14.6	-11.9
-2	40.3	-36.3
-1	34.6	28.7
0	18.6	-13.4
1	17.7	13.0
2	3.2	3.7
3	60.6	-59.4
4	24.4	-25.5
5	10.6	-9.5
6	31.4	30.7
7	17.7	-18.2
9	12.1	10.6
10	16.6	15.7
11	12.5	12.3
12	9.7	9.0
13	10.9	11.8
14	12.6	-13.3
15	10.5	10.3
17	7.8	-7.0
18	14.4	-12.3
19	2.3	2.1
H	1	3
-22	6.9	-7.5
-21	4.1	5.1
-19	16.2	-16.1
-18	12.2	-12.8
-16	13.9	14.8
-15	6.6	-7.5
-14	10.8	10.7
-13	14.9	-14.1
-12	4.4	-5.6
-11	20.0	19.7
-10	20.7	20.9
-9	10.7	9.2
-8	19.6	-16.6
-7	33.6	32.3
-6	5.6	3.9
-5	6.5	-3.8
-4	33.0	-28.1
-3	12.1	-8.6
-2	11.8	-10.3
-1	30.6	-26.2
0	19.8	17.1
1	32.4	-31.7
2	26.6	-23.4
3	21.7	19.8
4	39.1	38.4
5	17.8	-18.0
6	12.1	13.4
7	17.4	19.6
9	22.6	23.3
10	8.4	-8.3
12	16.5	-16.2
13	5.5	5.1
14	6.6	5.6
15	10.4	-9.4
16	9.9	-8.3
17	6.6	-6.2
18	2.4	3.3
19	7.2	-8.1
H	1	4
-22	5.2	5.6
-21	7.8	-9.8
-18	3.7	5.1
-14	4.2	-2.2
-13	26.0	25.7
-12	18.1	17.6
-11	8.6	-7.9
-10	26.7	-26.1
-9	14.8	12.5
-8	3.7	-4.4
-7	14.1	-10.8
-6	9.6	-7.6
-5	26.2	-22.7
-4	12.3	-9.4
-2	31.0	28.1
-1	20.0	-15.9
1	12.0	10.2
2	24.0	22.1
3	4.1	3.8
4	12.1	-11.8
5	27.3	28.7
6	11.3	-11.0
7	8.6	7.8
8	5.2	3.2
9	15.0	-14.9
10	15.3	-15.5
11	2.7	2.4
13	15.4	-15.3
15	4.9	-4.7
16	7.6	7.0
H	1	5
-21	1.9	2.1
-20	3.0	4.4
-19	5.4	5.8
-18	4.9	4.9
-16	7.6	-8.8
-15	9.3	8.3
-14	6.8	6.3
-13	6.1	-5.8
-12	17.0	-20.0
-11	7.7	8.7
-9	19.9	-20.0
-8	12.1	11.5
-7	18.3	-17.4
-6	3.6	2.2
-5	15.4	14.6
-4	16.7	14.6
-3	13.7	-11.9
-2	12.2	-11.8
-1	21.2	20.1
0	17.7	16.7
1	17.0	16.3
2	8.1	-6.5
3	1.9	3.3
4	18.5	-19.5
5	7.4	-6.9
6	3.4	2.6
7	11.6	-12.2
8	6.6	-7.8
10	8.5	8.9
11	12.9	-12.8
12	3.9	4.0
13	1.8	2.6
14	4.3	5.0
H	1	6
-18	5.3	-7.1
-17	7.7	8.8
-16	2.4	2.8
-15	5.1	-6.6
-14	6.4	-7.8
-13	7.3	-9.0
-12	6.3	6.4
-11	6.5	-7.3
-10	6.7	6.7
-9	1.9	2.6
-8	9.4	-8.8
-7	11.3	10.4
-6	20.9	19.6
-5	8.8	-6.5
-4	5.8	-4.0
-3	23.2	22.6
-2	5.1	-5.9
0	9.9	-10.9
1	10.8	-11.3
2	5.8	-7.2
4	8.5	10.2
5	9.6	-12.2
6	3.0	-4.6
7	2.9	-3.1
8	8.3	9.9
10	4.0	3.4
11	7.5	8.1
H	1	7
-17	7.3	-9.0
-16	2.8	-4.0
-12	7.6	10.4
-11	3.5	-2.9
-10	4.4	-5.5
-9	6.6	7.0
-8	5.2	4.6
-7	3.2	2.0
-6	9.4	-9.8
-5	7.4	8.5
-4	2.6	-2.3
-3	6.0	-7.0
-1	7.1	-7.9
0	3.5	-4.6
2	8.1	10.8
3	8.1	-10.4
5	5.4	7.3
6	4.9	4.8
7	3.3	4.3
H	1	8
-12	3.9	-6.1
-11	6.5	9.3
-10	4.6	6.0
-8	5.0	-6.2
-6	2.9	-3.8
-5	2.5	-4.4
-3	3.7	-4.9
0	4.7	6.6
3	4.8	6.6
H	2	0
0	6.4	-5.1
1	9.9	-12.1
2	3.1	-5.0
3	41.8	45.5
5	4.4	4.7
6	4.8	-4.0
7	6.2	6.4
8	6.9	8.2
-4	4.6	4.8
-3	2.3	-2.3
-2	12.2	10.8
1	49.4	-41.5
2	12.8	-9.2
3	8.1	6.3
4	6.6	4.9
5	8.5	-9.0
6	7.8	-9.2
7	24.4	25.5
8	8.3	-7.9
9	16.8	17.2
10	11.0	11.0
11	6.7	-5.1
13	6.6	6.4
15	13.2	-12.9
16	3.7	2.5
17	4.3	-2.5
H	2	4
-21	10.5	-11.2
-18	2.7	3.1
-16	2.9	-4.0
-14	6.1	-5.6
-13	18.4	16.8
-12	8.1	9.0
-11	4.2	-3.4
-9	25.0	23.5
-8	2.0	-1.3
-7	19.8	-16.9
-6	12.8	11.8
-5	28.4	-24.9
-2	7.4	-7.0
-1	23.1	-19.4
0	7.6	-5.5
1	24.1	21.2
3	4.9	3.3
5	17.6	17.7
7	6.1	7.0
8	5.0	5.3
9	13.8	-14.1
11	6.4	5.6
12	4.5	4.1
13	14.1	-13.9
15	4.2	-4.5
H	2	5
-21	2.1	2.9
-19	2.7	3.2
-18	2.4	-1.1
-15	14.9	17.9
-13	7.8	-8.0
-10	7.7	7.7
-9	16.4	-15.5
-7	8.5	-7.5
-6	14.6	-13.0
-5	15.6	13.4
-4	8.1	6.9
-3	18.4	-15.9
-1	23.0	22.0
0	8.7	-8.3
1	8.8	7.6
2	6.5	4.7
3	3.1	3.4
4	3.0	4.0
6	3.0	2.7
7	15.2	-16.0
11	11.1	-11.5
12	2.3	-2.7
13	3.1	3.5
H	2	6
-19	2.1	-4.6
-17	5.7	7.3
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-9	6.0	-6.5
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0	4.7	6.6
1	10.2	-9.6
2	4.1	-5.8
3	3.4	-3.1
5	10.2	-13.5
9	22.0	26.2
10	12.8	13.2
11	33.5	-37.8
12	5.3	-6.3
13	7.4	-8.7
15	9.0	-10.2
17	5.4	4.6
18	5.8	-6.6
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11	9.0	7.6
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-17	9.4	-9.1
-13	18.3	-19.7
-12	7.4	5.9
-11	12.9	-11.9
-10	5.0	-3.6
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15	13.8	14.4
16	7.3	6.1
17	8.5	-7.3
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0	11.9	9.2
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-1	5.4	3.8
0	10.3	8.4
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3	11.6	-11.2
4	9.4	10.0
5	3.6	4.3
6	12.8	-12.8
7	14.3	-15.9
8	3.1	-4.8
9	11.8	13.4
10	9.9	-12.0
11	6.3	5.8
13	7.1	-7.2
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H	3	3
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3	4.3	5.3
4	18.3	-18.0
5	6.4	-5.9
7	7.7	8.5
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11	5.5	-5.5
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10	5.1	-6.4
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-1	7.0	-6.1
0	4.8	5.3
4	9.1	11.5
5	5.1	7.7
6	9.1	-10.8
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-4	13.2	10.7
-1	9.0	8.3
0	6.3	-5.8
2	7.1	9.2
4	12.3	-14.6
H	4	4
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-10	12.5	12.0
-3	8.4	5.9
-2	5.6	-4.6
2	9.4	-10.5
H	4	5
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-4	9.1	-9.4
H	4	6
-6	4.5	-6.2
-4	3.9	5.9

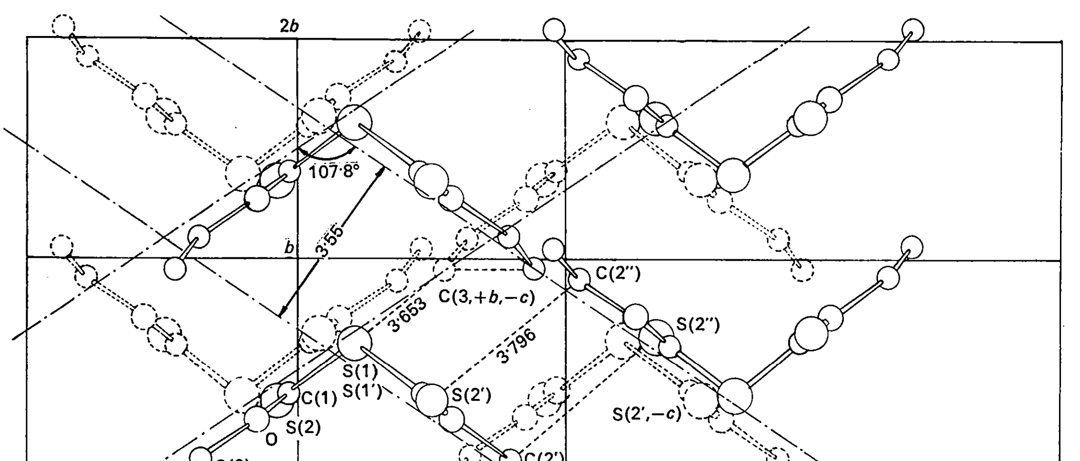

Fig. 2. Molecular configuration of diethyldixanthogen, $(SSCOC_2H_5)_2$, viewed along [103]. The molecules present at $z<0$ are drawn with broken lines. Chained lines show the planes of four xanthate groups related by a centre of symmetry.

tively. The 'best-fit' equations for the two groups are expressed by

$$-0{\cdot}4814\,X+0{\cdot}8028\,Y+0{\cdot}4788\,Z=1{\cdot}541$$

and

$$0{\cdot}4814\,X+0{\cdot}8028\,Y-0{\cdot}4788\,Z=2{\cdot}757$$

respectively, where X, Y, Z are coordinates with respect to the crystal axes in Å.

The intramolecular distances and angles are given in Table 3 and are shown in Fig. 1. The S–S bond distance, S–S–C bond angle, S–C and S=C bond distances, and the angle with which two SSC groups meet are listed in Table 4 and compared with corresponding values of similar compounds.

The S(1)–S(1′) distance in diethyldixanthogen, 2·054 (0·004) Å, is longer than the 2·000 (0·005) Å in tetraethylthiuram disulphide, $[\mathrm{SSCN(C_2H_5)_2}]_2$ (Karle, Estlin & Britts, 1967), and 2·032 (0·004) Å in hexagonal L-cystine, $[\mathrm{SCH_2CH(NH_2)COOH}]_2$ (Oughton & Harrison, 1959), but is the same as the 2·05 (0·01) Å in L-cystinediamide dihydrochloride,

$$[\mathrm{SCH_2CH(NH_2HCl)CONH_2}]_2$$

(Chaney & Steinrauf, 1968), or the 2·04 (0·02) Å in diformamidinium disulphide dihalide monohydrate dibromide, $[\mathrm{(H_2N)_2CSSC(NH_2)_2}]\mathrm{Br_2}$ (Foss, Johnsen & Tvedten, 1958). The S(1)–C(1) distance in diethyldixanthogen, 1·729 (0·013) Å, is shorter than the sum of the single-bond radii of sulphur and carbon atoms, namely 1·04 + 0·77 = 1·81 Å, but is longer than the sum of their double-bond radii, namely 0·67 + 0·94 = 1·61 Å (Pauling, 1960). Table 4 shows that when the S–S distance is longer then the S–C distance will be shorter. The dihedral angle C(1)–S(1)–S(1′)–C(1′), 107·2 (1·0)°, is somewhat larger than those in the other compounds.

As to the bond angles in the xanthate group, S(1)–C(1)–S(2), 118·2 (1·0)°, is close to 120°, but S(1)–C(1)–O, 114·3 (0·7)°, and S(2)–C(1)–O, 127·5 (0·9)° both deviate considerably from it. Table 5 and Fig. 3 show a comparison of the configurations of the SSCO group in diethyldixanthogen and in the metal xanthate in which the metal atom is bonded to the two sulphur atoms of a xanthate group in the form $\mathrm{Me}\overset{S}{\underset{S}{<>}}\mathrm{C{-}O{-}}$, as deduced from the large difference in the metal–sulphur distance. As for the C–S, C=S and C–O distances no particular feature is observed. However, the bond angles S–C=S, S–C–O and S=C–O observed in diethyldixanthogen are in good agreement with those in a branch of lead ethylxanthate (Hagihara & Yamashita, 1966), whereas they differ from the corresponding values in antimonious ethylxanthate (Gottardi, 1961) and a branch of lead isopropylxanthate–pyridine (Hagihara, Yoshida & Watanabe, 1969). These latter values are also in good agreement with each other. The values of the S–C=S angle in arsenious ethylxanthate (Carrai & Gottardi, 1959), antimonious ethylxanthate and lead isopropylxanthate–pyridine are almost the same (130°).

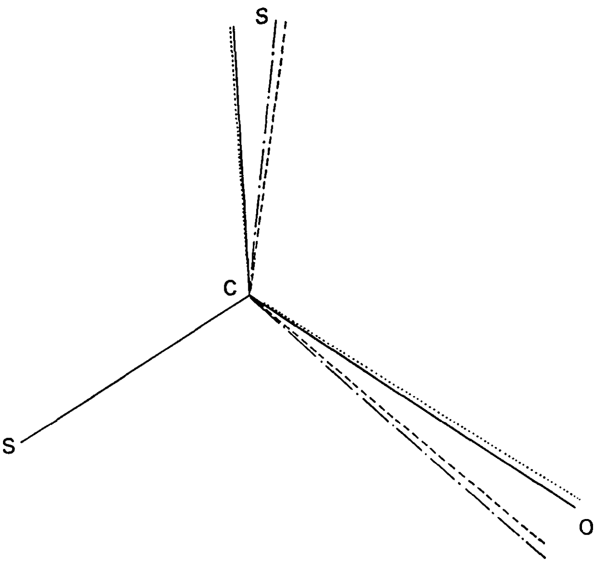

Fig. 3. Atomic configurations of diethyldixanthogen and metal xanthates in the SSCO plane drawn with the S–C bond in common (see Table 5). Solid line: $\mathrm{(EX)_2}$; dotted line: $\mathrm{Pb(EX)_2}$; dashed line: $\mathrm{Sb(EX)_3}$; chained line: $\mathrm{Pb(isoPX)_2}$–pyridine.

Table 3. *Bond distances and angles with standard deviations*

Notation: unprimed (x,y,z), single primed $(\frac{1}{2}-x,y,1-z)$, double primed $(x+\frac{1}{2},1-y,z)$.

Intramolecular distances and angles

S(1)–S(1′)	2·054 (0·004) Å	C(1)–S(1)–S(1′)	107·5 (0·4)°
S(1)–C(1)	1·729 (0·013)	S(1)–C(1)–S(2)	118·2 (0·7)
S(1)–S(2)	2·874 (0·004)	S(1)–C(1)–O	114·3 (0·7)
S(2)–C(1)	1·620 (0·009)	S(2)–C(1)–O	127·5 (0·9)
C(1)–O	1·360 (0·014)	C(1)–O——C(2)	117·3 (0·8)
O——C(2)	1·465 (0·016)	O——C(2)–C(3)	104·8 (0·9)
C(2)–C(3)	1·544 (0·016)		

Intermolecular distances (van der Waals distances)

C(2′)–S(2″)	3·796 (0·013) Å
C(2′)–C(2″)	3·951 (0·015)
S(1)—C(3, $+b,-c$)	3·653 (0·012)
C(3′)–C(3, $-c$)	3·931 (0·018)
S(2″)–S(2′, $-c$)	3·792 (0·005)

The C(1)–O distance, 1·360 (0·014) Å, O–C(2) distance, 1·465 (0·016) Å and bond angle C(1)–O–C(2), 117·3 (0·8)°, are in agreement with the corresponding values in potassium ethylxanthate (Mazzi &Tadini, 1963) which contains the lightest metal atom among the metal xanthates so far analysed.

Molecular packing

Intermolecular atomic distances are given in Table 3. The molecules are stacked in the *b*-axis direction through van der Waals contact between the S(1) atom and the methyl end of the ethyl group C(3, +*b*, −*c*) at a distance of 3·653 (0·012) Å. In the *c*-axis direction the atoms S(2″) and S(2′, −*c*), related by a centre of symmetry, and the methyl group end atoms C(3′) and C(3, −*c*), related by a twofold rotation axis, each come into van der Waals contact at distances of 3·792 (0·005) and 3·931 (0·018) Å respectively. In the *a*-axis direction the atom C(2′) of the methylene group comes into van der Waals contact with the atom C(2″) of the methylene group through the symmetry centre at a distance of 3·951 (0·015) Å, and with the sulphur atom S(2″) at a distance of 3·796 (0·013) Å. These distances can be accounted for in terms of the van der Waals radii of sulphur, 1·85 Å, and carbon in a methyl or methylene group, 2·0 Å (Pauling, 1960).

Two SSCOCC groups of adjacent molecules related by a symmetry centre lie on a plane as shown by chained lines in Fig. 2; there are two sets of parallel planes on which the planar SSCOCC groups lie.

The equations to the best fit planes are:

$$-0{\cdot}4408\,X+0{\cdot}8079\,Y+0{\cdot}5043\,Z=1{\cdot}778$$

and

$$0{\cdot}4408\,X+0{\cdot}8079\,Y-0{\cdot}5043\,Z=2{\cdot}404$$

The maximum and mean deviations of atoms from the plane are 0·14 and 0·005 Å respectively. The two planes meet at an angle of approximately 107·8 (1·3)°. Each set of parallel planes is stacked with the SSCOCC planes 3·55 (0·14) Å apart. The sulphur atoms and the methylene or methyl groups belonging to adjacent planes are in van der Waals contact as described above.

Table 4. *A comparison of bond distances and angles in the thio-compounds similar to diethyldixanthogen, with standard deviations*

	S–S	S–S–C	S–C	S=C	(CSS)–(SSC)*
$(SSCOC_2H_5)_2$	2·054 Å (0·004)	107·5° (0·4)	1·729 Å (0·013)	1·620 Å (0·009)	107·2 Å (1·0)
$[SSCN(C_2H_5)_2]_2$	2·000 (0·005)	103·6 (0·4)	1·813 (0·010)	1·662 (0·009)	96·4
		103·4 (0·4)	1·818 (0·010)	1·634 (0·009)	
$[SCH_2CH(NH_2)COOH]_2$	2·032 (0·004)	114·5 (0·4)	1·820 (0·012)	—	116·0 (1·0)
$[(H_2N)_2CSSC(NH_2)_2]Br_2$	2·04 (0·02)	104·0 (1)	1·76 (0·04)	—	89·2
$[SCH_2CH(NH_2HCl)CONH_2]_2$	2·05 (0·01)	102·9 (0·7)	1·76 (0·02)	—	81·4

* The dihedral angle C–S–S–C.

Table 5. *Configuration of the xanthate group in diethyldixanthogen and branches of metal xanthates, with standard deviations, in which* C=S *bond character is manifested*

Notation of the compounds: EX; ethyl xanthate group, isoPX; isopropyl xanthate group.

	C–S	C=S	S–C=S	S–C–O	S=C–O	C–O	Me–S	Me···S
$(EX)_2$	1·729 Å (0·013)	1·620 Å (0·009)	118·2° (0·7)	114·3° (0·7)	127·5° (0·9)	1·360 Å (0·014)	—	—
$As(EX)_3$	1·66 (0·04)	1·65 (0·04)	129·5 (3)	112·5 (3)	112·5 (3)	1·31 (0·04)	2·28 Å (0·007)	2·94 Å (0·007)
$Sb(EX)_3$	1·70 (0·02)	1·59 (0·02)	130·5 (2)	108·0 (2)	121·0 (2)	1·36 (0·025)	2·52 (0·006)	3·00 (0·006)
$Pb(EX)_2$	1·78 (0·10)	1·66 (0·10)	118·0 (6)	116·0 (7)	127·0 (7)	1·28 (0·14)	2·79 (0·03)	2·95 (0·03)
$Pb(isoPX)_2$-pyridine	1·73 (0·05)	1·60 (0·05)	128·3 (3·7)	106·5 (3·4)	122·2 (4·0)	1·35 (0·08)	2·722 (0·019)	3·057 (0·016)

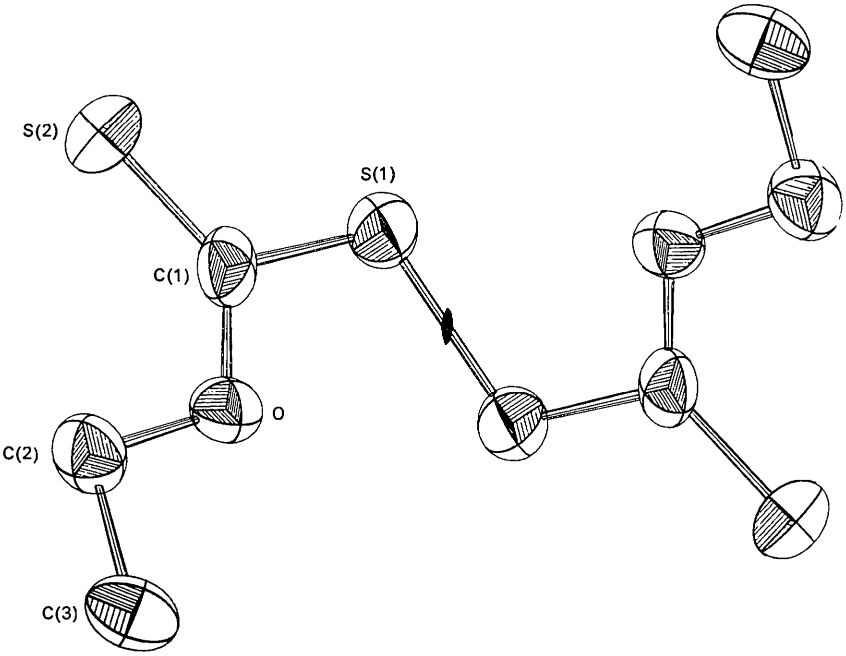

Fig. 4. Thermal ellipsoids of a molecule of diethyldixanthogen, drawn with the same magnitudes.

Thermal parameters

The thermal parameters of the atoms of diethyldixanthogen are listed in Table 2 and their thermal ellipsoids, which were calculated using the *ORTEP* program (Johnson, 1965), are shown in Fig. 4. The mean-square amplitudes of the b^*-axis component (U_{22}) are generally larger than those of the a^*- and c^*-axis components (U_{11} and U_{33} respectively). But U_n, the U component normal to the SSCOCC plane, is not larger than U_p, the U component parallel to the plane, for each atom. The U_n values are 806, 697, 610, 603, 505 and 317 for the atoms S(2), C(3), C(2), S(1), O and C(1) respectively. Each atom is restricted within the SSCOCC plane but the atom S(2) which has the largest deviation 0·11 Å from the plane vibrates with the largest amplitude along the direction normal to the plane.

Most of the calculations were carried out on the FACOM 270-20/30 computer of this institute and the HITAC 5020 computer of Tokyo University with a universal crystallographic computation program, *UNICS* (Sakurai, Ito, Iwasaki, Watanabe & Fukuhara, 1967).

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