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The Crystal and Molecular Structure of the Enol Form of 3,3′-Dithiobis-(2,4-pentanedione)

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The crystal structure of the enol form of 3,3′-dithiobis-(2,4-pentanedione), $C_{10}H_{14}O_4S_2$, has been determined using three-dimensional X-ray diffraction data (Mo $K\alpha$ radiation) collected by counter methods. A report [Power & Jones, *Inorg. Nucl. Chem. Lett.* (1971), **7**, 887–890] outlining what is now known to be the incorrect structure, has previously been published. The compound crystallizes in the orthorhombic space group $Pna2_1$ and has cell dimensions $a=14.852$ (5), $b=12.264$ (4) and $c=6.935$ (2) Å; $d_m=1.36$, $d_c=1.38$ g cm^{-3} for $Z=4$. The structure was refined, on F, by full-matrix, least-squares methods to an R value of 0·053 and wR of 0·038 for 1297 measured reflexions. The molecule exists as the enol tautomer and the short, intramolecular hydrogen bonds formed [O···O contacts of 2·418 (6) and 2·444 (7) Å] are asymmetric. There is evidence for alternating single and double bonds in the enol ring. The S–S distance is 2·082 (2) Å and the C–S distances are 1·744 (5) and 1·743 (4) Å. From comparison with other organic sulphides, a dependence of the C–S bond length on the state of hybridization of the carbon atom is indicated. The C–S–S–C torsion angle is 68·6°.

Introduction

Bis-β-diketones are very useful as ligands because of their ability to form polymeric chelate compounds with transition metals (Fernelius, 1956; Kluiber & Lewis, 1960; Oh, 1961; Oh & Bailar, 1962; Jones & Power, 1971). The enol tautomer is of particular interest because of the large downfield shift of the enol proton in the PMR spectrum (Dewar, Fergusson, Hentschel, Wilkins & Williams, 1964; Jones, 1969). Such shifts are indicative of very strong, intramolecular hydrogen bonding. Some of these compounds have already been studied by diffraction methods. In 3,3′-trithiobis-(2,4-pentanedione) (Power & Jones, 1971*a*), the O···O contact was very short and this has been confirmed by neutron diffraction studies (Power, Turner, Moore & Jones, 1975). Similar short contacts were found in 2,2′-dithiobis-(1-phenyl-1,3-butanedione) (Power & Jones, 1971*c*) and tetraacetylethane (Schaefer & Wheatley, 1966; Power, Turner & Moore, 1975).

A report on the X-ray structure of the present compound has been published (Power & Jones, 1971*b*, denoted P&J). Even though the structure had been refined to an R value ($R=\sum||F_o|-k|F_c||/\sum|F_o|$) of 0·093, bond lengths differed significantly from expected values. Although this anomaly could be due to disorder, a possibility if the space group was $Pnam$ rather than the assumed $Pna2_1$, the electron-density difference map did not indicate it. The correct structure is now reported and the reason for the previously incorrect structure determination discussed.

Experimental

3,3′-Dithiobis-(2,4-pentanedione), ($acac_2S_2$), was prepared by the method of Vaillant (1894). Pale yellow crystals were recrystallized from acetone and then by slow sublimation. Two forms of the compound were identified, a fact overlooked in the previous study (P&J). One form, that reported here and the assumed form in the P&J study, was orthorhombic and had the space group *Pna*2_1 or *Pnam*. Because of the symmetry restrictions required for four molecules in *Pnam*, *Pna*2_1 was assumed and successful analysis carried out in this space group.

Crystal data

$C_{10}H_{14}O_4S_2$, $M=262{\cdot}35$, orthorhombic. $a=14{\cdot}852$ (5), $b=12{\cdot}264$ (4), $c=6{\cdot}935$ (2) Å, $U=1263{\cdot}2$ Å^3. $d_m=1{\cdot}36$, $d_c=1{\cdot}38$ g cm^{-3} for $Z=4$. $F(000)=552$. Mo $K\alpha$ radiation, $\lambda=0{\cdot}71069$ Å, μ(Mo $K\alpha$)$=4{\cdot}06$ cm^{-1}.

The other form was monoclinic with cell dimensions $a=14{\cdot}924$ (3), $b=24{\cdot}552$ (4), $c=6{\cdot}927$ (1) Å and $\beta=89{\cdot}93$ (2)°. From systematically absent spectra, the space group was deduced to be $P2_1/a$. The second form has a b axis which is twice that in the orthorhombic form whilst a and c axes are virtually the same. It was noticed that reflexions with k odd were very weak. From X-ray photographs and optical inspection, there was no evidence for twinning in either form. The two forms could result from crystal packing differences, a different dihedral angle at the S–S bond or from the 2,4-pentanedione moieties being *trans*, in one case, and *cis*, in the other, with respect to the S–S bond. A related problem has been reported recently by Donohue & Chesick (1975).

Data collection

A crystal in the shape of a rectangular parallelepiped and measuring $0{\cdot}5\times0{\cdot}4\times0{\cdot}2$ mm was used to determine the cell dimensions and measure the intensity data. It was coated with shellac and mounted so that the c^* axis was slightly offset from the φ axis of a Stoe, four-circle goniostat. Cell dimensions were determined from the least-squares fit of the 2θ values of several high-angle reflexions which had been carefully centred. Intensity data were collected by the θ–2θ step-scan method using Mo $K\alpha$ radiation. The detector was a reverse-biased, surface barrier diode, kept at liquid nitrogen temperature. The detector allows energy discrimination such that only Mo $K\alpha$ radiation is detected (Beech & Eberhardt, 1973). Each reflexion was scanned 1·3° in 2θ in the 2θ range 0–20°, 1·4 in the range 20–35° and 1·5 in the range 35–50°. Each step was 0·01° in 2θ and the diffracted radiation was counted for 0·5 s at each step. At the limits of the scan, the background was counted for a time which allowed the optimization of the counting statistics (Elcombe, Cox, Pryor & Moore, 1971). After every 20 reflexions, the reflexion 080 was scanned. The maximum deviation from the mean intensity of this reflexion was 1·8%. One quadrant of data was measured, representing two equivalent sets.

Intensities were corrected for background and absorption. For each reflexion, the variance, σ_I^2, was determined from $\sigma_I^2=[\sigma_C^2+\sigma_A^2+(0{\cdot}018I)^2]$ where σ_C^2 is due to counting statistics, σ_A^2 is due to absorption (Elcombe *et al.*, 1971) and I is the net intensity. The equivalent reflexions were combined to yield 1279 unique reflexions. If the variance due to averaging was greater than $\sigma_C^2+\sigma_A^2$, the former value was used in lieu of the latter to determine σ_I^2. If the intensity was negative, it was set to a small positive quantity but the variance remained unchanged. I and σ_I were reduced to F and σ_F. Five reflexions (011, 020, 040, 410 and 411) were very intense and caused severe 'flooding' in the counting chain. They were not used in the analysis.

Structure refinement

It was thought that the coordinates determined by P&J might be a reliable starting point. With reasonable isotropic thermal parameters, the R value was 0·16 for reflexions with $I\geq2{\cdot}3\sigma_I$. Full-matrix, least-squares refinement did cause some large parameter shifts initially but they settled and refinement with isotropic temperature factors converged to an R of 0·12. The function minimized was $\sum w(|F_o|-k|F_c|)^2$ and each reflexion was assigned unit weight. Refinement was continued with anisotropic thermal parameters. All data were used (Moore, 1972) and weights were derived from $w=\sigma_F^{-2}$. An electron-density difference map allowed determination of the hydrogen-atom coordinates which were varied in subsequent refinement but their temperature factors were fixed at $B=7$ Å^2. At convergence, the R value was 0·053 (0·037 for reflexions with $I\geq2{\cdot}3\sigma_I$) and wR $[wR=\sum w(|F_o|-k|F_c|)^2/\sum w|F_o|^2]$ was 0·038 (0·039). The error-of-fit was 1·93. $w\Delta^2$ was reasonably constant for ranges of F_o and $(\sin\theta)/\lambda$. A final electron-density difference map had no unusual features.* Scattering factors for the non-hydrogen atoms were from the paper of Cromer & Mann (1968), those for hydrogen from the table of Stewart, Davidson & Simpson (1965).

Results

Final atomic parameters are shown in Table 1. Table 2 contains the interatomic distances and angles, the errors in which contain contributions from both the variance–covariance matrix and the errors in the cell dimensions. Least-squares planes through selected atomic groupings are in Table 3. A diagram of the molecule is shown in Fig. 1 and explains the atomic labelling. A stereoscopic pair is in Fig. 2 while Fig. 3 shows the projection down the c axis.

Discussion

The basic structure is not very different from that found by P&J. This raises the question of why such a poor model was found in that study. Some intensities were

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. 31543 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final fractional coordinates and anisotropic thermal parameters* (Å^2), × 10^4

Sulphur x and y coordinates $\times 10^5$, hydrogen coordinates $\times 10^3$ and all other coordinates $\times 10^4$. Anisotropic thermal parameter expression of the form $\exp[-2\pi^2(h^2a^{*2}U_{11}+\ldots+2hka^*b^*U_{12}+\ldots)]$. Hydrogen atoms have a fixed isotropic temperature factor. In the hydrogen-atom labels, the first two digits denote the carbon atom to which the hydrogen atom is bonded. H00(1) and H00(2) are the enol hydrogen atoms, the former between O(11) and O(12).

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	12146 (7)	12681 (9)	2500	580 (6)	516 (6)	776 (8)	−87 (6)	−74 (7)	190 (7)
S(2)	24535 (7)	12455 (8)	1095 (2)	596 (6)	440 (5)	673 (6)	64 (5)	−97 (6)	−59 (7)
C(11)	1040 (5)	3582 (5)	4356 (13)	902 (41)	827 (44)	922 (50)	−7 (37)	7 (33)	−254 (42)
C(12)	631 (3)	3373 (4)	2433 (9)	460 (23)	695 (29)	677 (32)	−42 (22)	9 (25)	10 (28)
C(13)	670 (3)	2387 (3)	1474 (9)	434 (19)	494 (24)	622 (36)	−53 (18)	−19 (22)	43 (24)
C(14)	259 (3)	2289 (4)	−380 (8)	489 (24)	686 (29)	681 (34)	−14 (21)	−73 (24)	55 (27)
C(15)	298 (4)	1279 (6)	−1522 (10)	793 (39)	827 (38)	907 (48)	17 (38)	−299 (33)	−222 (35)
O(11)	213 (3)	4191 (3)	1684 (7)	802 (24)	678 (23)	1128 (35)	238 (20)	−11 (23)	57 (23)
O(12)	−143 (2)	3104 (3)	−1123 (6)	766 (22)	935 (25)	839 (27)	214 (20)	−238 (22)	118 (22)
C(21)	2617 (5)	3469 (6)	−1085 (10)	728 (35)	956 (41)	765 (39)	69 (32)	−195 (32)	113 (33)
C(22)	2980 (3)	3352 (4)	870 (8)	502 (25)	722 (31)	702 (34)	−24 (24)	−4 (25)	−7 (26)
C(23)	2987 (3)	2412 (3)	1965 (8)	468 (23)	455 (22)	609 (31)	−7 (17)	−14 (24)	−43 (21)
C(24)	3400 (3)	2407 (4)	3830 (9)	664 (29)	636 (28)	698 (33)	−104 (24)	165 (28)	29 (28)
C(25)	3414 (4)	1430 (5)	5058 (10)	908 (42)	797 (42)	658 (39)	−90 (32)	−11 (37)	210 (32)
O(21)	3349 (3)	4247 (3)	1533 (8)	829 (27)	898 (24)	842 (27)	−254 (21)	−127 (25)	−125 (26)
O(22)	3774 (2)	3270 (3)	4466 (7)	1213 (35)	657 (22)	968 (36)	−357 (24)	−49 (27)	69 (25)

Table 1 (*cont.*)

	x	y	z	U_{iso}
H(111)	84 (4)	406 (4)	500 (8)	887
H(112)	114 (4)	295 (3)	467 (10)	887
H(113)	160 (3)	420 (4)	417 (8)	887
H(151)	103 (3)	99 (4)	−167 (7)	887
H(152)	18 (2)	68 (4)	−87 (9)	887
H(153)	−7 (3)	128 (4)	−220 (10)	887
H(211)	313 (3)	369 (3)	−230 (8)	887
H(212)	231 (4)	286 (4)	−155 (8)	887
H(213)	214 (3)	372 (4)	−113 (9)	887
H(251)	375 (3)	97 (4)	415 (9)	887
H(252)	378 (3)	139 (4)	625 (10)	887
H(253)	276 (3)	120 (3)	555 (8)	887
H00(1)	7 (5)	385 (4)	75 (10)	887
H00(2)	357 (4)	403 (5)	240 (11)	887

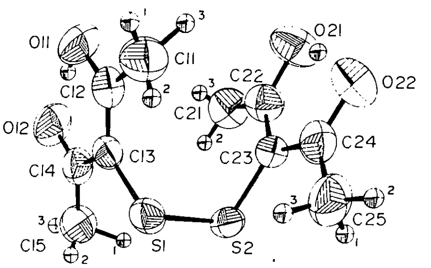

Fig. 1. A diagram of the molecule showing the atomic labelling. For clarity, atomic symbols have been omitted from the methyl H atoms and the enol H atoms are not labelled. The atoms, except the H atoms, are represented as 50% probability thermal ellipsoids.

measured from the monoclinic form and they agree well with the values used by **P&J** to solve the structure. It is now obvious that data from the monoclinic form (with reflexions of odd k index not measured) were used to determine the structure in the orthorhombic space group. Indeed, it was fortuitous that a model could be found in the first place (the agreement index,

Table 2. *Interatomic distances* (Å) *and angles* (°)

Interatomic distances

S(1)—S(2)	2·082 (2)		
S(1)—C(13)	1·744 (5)	S(2)—C(23)	1·743 (4)
C(11)–C(12)	1·487 (10)	C(21)–C(22)	1·466 (9)
	1·508*		1·484*
C(12)–O(11)	1·289 (6)	C(22)–O(21)	1·311 (7)
	1·323*		1·347*
C(12)–C(13)	1·381 (6)	C(22)–C(23)	1·380 (7)
C(13)–C(14)	1·429 (8)	C(23)–C(24)	1·432 (8)
C(14)–O(12)	1·272 (5)	C(24)–O(22)	1·274 (6)
	1·301*		1·302*
C(14)–C(15)	1·471 (8)	C(24)–C(25)	1·471 (7)
	1·497*		1·487*
O(11)···O(12)	2·418 (6)	O(21)···O(22)	2·444 (7)
C(11)–H(111)	0·79 (5)	C(21)–H(211)	1·17 (5)
C(11)–H(112)	0·82 (5)	C(21)–H(212)	0·94 (5)
C(11)–H(113)	1·13 (5)	C(21)–H(213)	0·78 (5)
C(15)–H(151)	1·14 (5)	C(25)–H(251)	0·98 (5)
C(15)–H(152)	0·88 (5)	C(25)–H(252)	0·99 (6)
C(15)–H(153)	0·72 (6)	C(25)–H(253)	1·07 (5)
O(11)–H00(1)	0·80 (7)	O(21)–H00(2)	0·73 (7)
O(12)–H00(1)	1·62 (7)	O(22)–H00(2)	1·74 (7)

* Corrected for 'riding motion'.

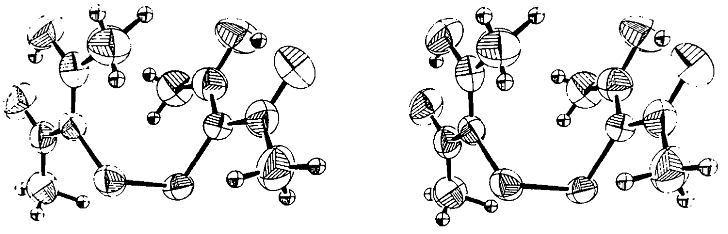

Fig. 2. A stereoscopic view of the molecule.

Table 2 (*cont.*)

Interatomic angles

S(2)—S(1)—C(13)	103·3 (2)	S(1)—S(2)—C(23)	103·2 (2)
O(11)-C(12)-C(11)	115·1 (5)	O(21)-C(22)-C(21)	113·3 (5)
O(11)-C(12)-C(13)	120·5 (5)	O(21)-C(22)-C(23)	120·2 (5)
C(11)-C(12)-C(13)	124·4 (5)	C(21)-C(22)-C(23)	126·4 (5)
S(1)—C(13)-C(12)	120·8 (4)	S(2)—C(23)-C(22)	119·4 (4)
S(1)—C(13)-C(14)	120·0 (4)	S(2)—C(23)-C(24)	120·3 (4)
C(12)-C(13)-C(14)	119·3 (5)	C(22)-C(23)-C(24)	120·3 (5)
O(12)-C(14)-C(13)	119·9 (5)	O(22)-C(24)-C(23)	119·8 (5)
O(12)-C(14)-C(15)	117·5 (5)	O(22)-C(24)-C(25)	118·1 (5)
C(13)-C(14)-C(15)	122·6 (5)	C(23)-C(24)-C(25)	122·2 (5)
C(12)—C(11)—H(111)	119 (4)	C(22)—C(21)—H(211)	117 (3)
C(12)—C(11)—H(112)	99 (5)	C(22)—C(21)—H(212)	115 (3)
C(12)—C(11)—H(113)	108 (3)	C(22)—C(21)—H(213)	114 (5)
H(111)-C(11)—H(112)	128 (7)	H(211)-C(21)—H(212)	105 (4)
H(111)-C(11)—H(113)	81 (4)	H(211)-C(21)—H(213)	119 (5)
H(112)-C(11)—H(113)	121 (5)	H(212)-C(21)—H(213)	81 (5)
C(14)—C(15)—H(151)	110 (3)	C(24)—C(25)—H(251)	96 (3)
C(14)—C(15)—H(152)	114 (4)	C(24)—C(25)—H(252)	122 (3)
C(14)—C(15)—H(153)	109 (5)	C(24)—C(25)—H(253)	113 (3)
H(151)-C(15)—H(152)	89 (4)	H(251)-C(25)—H(252)	103 (4)
H(151)-C(15)—H(153)	131 (6)	H(251)-C(25)—H(253)	121 (4)
H(152)-C(15)—H(153)	100 (6)	H(252)-C(25)—H(253)	103 (4)
C(12)—O(11)—H00(1)	93 (5)	C(22)—O(21)—H00(2)	100 (5)
C(14)—O(12)—H00(1)	92 (4)	C(24)—O(22)—H00(2)	95 (2)
O(11)—H00(1)-O(12)	174 (7)	O(21)—H00(2)-O(22)	161 (7)

Table 3. *Equations of planes through selected atomic groupings*

Planes are of the form $lX+mY+nZ+D=0$ where l, m, and n are direction cosines of the plane normal relative to orthogonal axes X, Y, Z. X is along the a axis, Y along b and Z along c. Deviations (Å), of relevant atoms, from the planes are shown in square brackets.

Plane (1): Through C(12), C(13), C(14), O(11), O(12)
$0{\cdot}8527X+0{\cdot}2898Y-0{\cdot}4347Z-1{\cdot}257=0$
[C(12) 0·008, C(13) −0·004, C(14) −0·001, O(11) −0·006, O(12) 0·004, C(11) 0·020, C(15) 0·033, S(1) −0·022]

Plane (2): Through C(22), C(23), C(24), O(21), O(22)
$0{\cdot}8675X-0{\cdot}2666Y-0{\cdot}4200Z-2{\cdot}486=0$
[C(22) 0·005, C(23) 0·002, C(24) −0·008, O(21) −0·006, O(22) 0·007, C(21) 0·067, C(25) −0·028, S(2) −0·051]

Plane (3): Through S(1), S(2), C(13)
$-0{\cdot}3837X-0{\cdot}5931Y-0{\cdot}7079Z+2{\cdot}842=0$

Plane (4): Through S(1), S(2), C(23)
$-0{\cdot}3897X+0{\cdot}5326Y-0{\cdot}7513Z+1{\cdot}177=0$

Angles between normals to planes (°)

(1)-(2)	(1)-(3)	(2)-(4)	(3)-(4)
32·3	101·0	99·5	68·6

$\sum|F_{o1}-F_{o2}|/[\sum(F_{o1}+F_{o2})/2]$, between the observed structure factors of this study and that of P&J is 0·10) and it illustrates that the least-squares refinement procedure is remarkably good in finding a set of parameters which will give acceptable agreement between F_o and F_c, even if the model is in error. Lomer & Wilson (1975) remind us, however, that refinement will adjust the parameters so that errors in the model will parallel those in the data. In the first study, the errors in the data are surely large for the space group considered. Hence, as found, the errors in the model were large also.

The molecule comprises two enolized 2,4-pentanedione (acac) residues connected by a linear disulphide bridge. The acac residues are planar and are *cis* with respect to the bridge. These planes are not parallel to each other, the normals to the planes making an angle of 32·3°. Some bond distances in the two residues are marginally different but the trends in each residue are the same.

Location of a H atom between the two O atoms, the bond length variation in the dicarbonyl moiety and the intense broad band at 1650 cm^{-1} in the infrared spectrum are strong evidence for the enol tautomer. The enol H atoms, H00(1) and H00(2), are nearest O(11) and O(21). However, they have been located too close to these O atoms. Experience with neutron diffraction studies of similar compounds has led us to believe that this H atom should be ~1·1–1·2 Å from one O atom and ~1·3–1·4 Å from the other (Power, Turner &

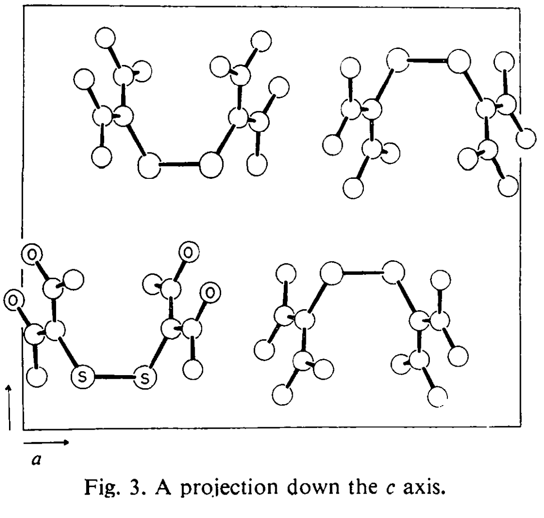

Fig. 3. A projection down the *c* axis.

Moore, 1975; Power, Turner, Moore & Jones, 1975). C(12)–C(13), 1·381 (6), and C(22)–C(23), 1·380 (7) Å, tend to the C–C double bond length of 1·35 Å whereas C(13)–C(14), 1·429 (8), and C(23)–C(24), 1·432 (8) Å, are nearer the value of 1·479 Å expected for single bonds between two C(sp^2) atoms (Dewar & Schmeising, 1960). C(12)–O(11) and C(22)–O(21) are longer than C(14)–O(12) and C(24)–O(22), respectively. Hence, the enol H atom is nearer the longer C–O bond and the alternation of long and short bond lengths around the dicarbonyl moiety suggests that a unique enol tautomer is formed.

During refinement, it was noticed that the –C–CH_3 bond lengths were short and no change had occurred at convergence. When these distances were corrected for 'riding motion' (Busing & Levy, 1964), the values increased but were still shorter than the expected 1·51–1·52 Å for such bond lengths. Similar shortening was found in benzoylacetone (Semmingsen, 1972), *p*-bromobenzoylacetone (Jones, 1976*b*) and *p*-nitrobenzoylacetone (Jones, 1976*a*). However, on correction for 'riding motion', their values increased to expected values. Perhaps, in this case, the thermal parameters do not describe the methyl carbon motion correctly.

The O···O contacts are 2·418 (6) and 2·444 (7) Å, values expected for very short, intramolecular hydrogen bonds in β-diketones. The bond is asymmetric but, as mentioned previously, the enol H atoms are too close to O(11) and O(21). Similar asymmetry in the acac residues has been observed in neutron diffraction studies (Power, Turner & Moore, 1975; Power, Turner, Moore & Jones, 1975). One might expect for such derivatives that the two C–C, the two C–O and the two O–H distances in the acac moiety be equal, representing an average of the two possible enol tautomers. The asymmetry is probably due to (1) the effects of the lone pairs of the S atom, (2) the effects of near neighbours as suggested by Williams (1974) or (3) a combination of (1) and (2). The role of the lone pair is difficult to assess. O(12) and O(22) do have some non-bonded contacts shorter than those to O(11) and O(21) and the packing of the molecules may be a major factor. The shorter non-bonded contacts to the O atoms are listed in Table 4.

Table 4. *Non-bonded contacts* (Å) *less than* 3·8 Å *to oxygen atoms*

O(11)···	C(13)*	2·32	O(12)···	C(13)	2·34
	C(11)	2·35		C(15)	2·35
	O(12)	2·42		O(11)	2·42
	C(14)	2·74		C(12)	2·74
	C(25^{i})	3·60		C(25^{v})	3·46
	C(25^{ii})	3·63		C(23^{ii})	3·56
	C(24^{ii})	3·65		C(22^{ii})	3·59
	O(12^{iii})	3·65		C(11^{iv})	3·64
	C(11^{iv})	3·68		O(11^{iv})	3·65
O(21)···	C(21)	2·32	O(22)···	C(23)	2·34
	C(23)	2·33		C(25)	2·36
	O(22)	2·44		O(21)	2·44
	C(24)	2·76		C(22)	2·76
	C(15^{vii})	3·47		C(21^{ix})	3·54
	C(15^{viii})	3·64		C(13^{viii})	3·59
	C(14^{viii})	3·65		C(15^{x})	3·63
	S(1^{i})	3·79		C(12^{viii})	3·70

* Superscripts to atomic labels define transformations which relate the atomic coordinates to those in Table 1:

None	x,	y,	z	i	$\frac{1}{2}-x$,	$\frac{1}{2}+y$,	$-\frac{1}{2}+z$
ii	$-\frac{1}{2}+x$,	$\frac{1}{2}-y$,	z	iii	$-x$,	$1-y$,	$\frac{1}{2}+z$
iv	$-x$,	$1-y$,	$-\frac{1}{2}+z$	v	$-\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$-1+z$
vi	x,	y,	$-1+z$	vii	$\frac{1}{2}-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}+z$
viii	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	z	ix	x,	y,	$1+z$
x	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$1+z$				

Table 5. *Bond distances* (Å) *from sulphur to carbon in which the formal hybridized state of carbon is* sp^3 *and* sp^2

Compound	Distance	Reference
(*a*) C(sp^3)–S		
S-Methyldithizone	1·790 (5)	Preuss & Gieren (1975)
Dicinnamyl disulphide	1·858	Donohue & Chesick (1975)
L-Methionyl-L-methionine	1·807*	Stenkamp & Jensen (1975)
L-Cystine dihydrochloride	1·816 (3)	Jones, Bernal, Frey & Koetzle (1974)
	1·810 (7)	Gupta, Sequeira & Chidambaram (1974)
D,L-Alanyl-L,D-methionine	1·801†	Stenkamp & Jensen (1974)
2*S*-Ethyl-2-thio-D-mannose diethyl dithioacetal	1·823‡	Ducruix & Pascard-Billy (1974)
Bis-[2-(*N*,*N*-dimethylamino)ethyl] disulphide	1·811†	Ottersen, Warner & Seff (1973)
L-Cysteine	1·811 (3)	Kerr & Ashmore (1973)
5,7-Bis(dimethylamino)-2-(methylthio)-*s*-triazolo[1,5-*a*]-*s*-triazine	1·790 (5)	Gilardi (1973)
Methyl-1-thio-α-D-ribopyranoside	1·802†	Girling & Jeffrey (1973)
2,4,5-Trichloro-6-(methylthio)isophthalonitrile	1·818 (15)	Carter, Turley & Boer (1972)
(*b*) C(sp^2)–S		
S-Methyldithizone	1·758 (3)	Preuss & Gieren (1975)
5,7-Bis(dimethylamino)-2-(methylthio)-*s*-triazolo[1,5-*a*]-*s*-triazine	1·747 (4)	Gilardi (1973)
2,4,5-Trichloro-6-(methylthio)isophthalonitrile	1·757 (13)	Carter, Turley & Boer (1972)
3,3′-Trithiobis-(2,4-pentanedione)	1·741	Power, Turner, Moore & Jones (1975)
2,2′-Dithiobis-(1-phenyl-1,3-butanedione)	1·756†	Power & Jones (1971*c*)
3,3′-Dithiobis-(2,4-pentanedione)	1·744†	This study

* Average of 4 values.
† Average of 2 values.
‡ Average of 12 values.

The S(1)–S(2) distance of 2·082 (2) Å is slightly longer than that anticipated from the plot of S–S bond length versus the –C–S–S–C– torsion angle (Hordvik, 1966). The torsion angle in this study is 68·6°. Of more interest are the C–S bond lengths of 1·744 (5) and 1·743 (4) Å. These values are considerably shorter than the accepted single bond value of 1·82 Å (Abrahams, 1956). When reporting the structure of L-cystine dihydrochloride, Jones, Bernal, Frey & Koetzle (1974) suggest that, in disulphides, the C–S bond length decreases as the –C–S–S–C– torsion angle increases. However, if in their study the four long bonds with torsion angles near 10° are ignored because non-bonded interactions probably cause severe strain in the –C–S–S–C– system, then the values for the bond lengths lie near 1·80–1·82 Å. Our distance is much shorter than would be predicted from the relationship of Jones *et al.* (1974) and we have therefore surveyed the structures of some recent organic sulphides which satisfy the following criteria: (1) the data were measured on a four-circle diffractometer, the data have been corrected for absorption if $\mu \geq 5$ cm^{-1}, no problems were encountered during refinement; (2) the S atom is divalent, is not involved in a ring system and has a formal single valence with carbon; (3) the –C–S$_n$–C (or H) system is free of strain, *e.g.* no t-butyl groups at the α-carbon, and (4) the compound only has elements from the first three periods. The values of the C–S bond lengths selected are in Table 5. It is readily seen that there are two groups, one involving C(sp^3) and the other C(sp^2). The values for S–C(sp^3) average to 1·81, those for S–C(sp^2) to 1·75 Å. The spread in values for each type is small. We propose, therefore, that 1·81 Å is the value for single bonds of type S–C(sp^3), 1·75 Å for those of type S–C(sp^2) and that the latter do not have any multiple bond character (which is often assumed).

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