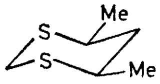
X-Ray Crystal Structure Conformational Studies on *r*-4,*c*-6-Dimethyl-1,3-dithian and its Oxides, *r*-4,*c*-6-Dimethyl-1,3-dithian *t*-1-Oxide, and *r*-4,*c*-6-Dimethyl-1,3-dithian *t*-1,*t*-3-Dioxide

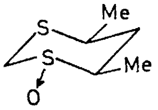
By **Andrew T. McPhail** * and **Kay D. Onan**, Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706, U.S.A.
Jorma Koskimies, W. R. Kenan Jun. Laboratories, University of North Carolina, Chapel Hill, North Carolina 27514, U.S.A.

The crystal structures of the title compounds [the 1,3-dithian (I), and its oxides (II) and (III)] have been determined from *X*-ray diffractometer data. Monoclinic crystals of (I) and (II) are isomorphous, space group *C*2/*c*, with for (I) : *a* = 20.08(1), *b* = 5.71(1), *c* = 15.69(1) Å, β = 118.4(1)°; and for (II) : *a* = 20.33(1), *b* = 5.68(1), *c* = 16.11(1) Å, β = 119.0(1)°. Crystals of (III) are also monoclinic, space group $P2_1/c$, with *a* = 5.49(1), *b* = 15.52(1), *c* = 10.81(1) Å, β = 105.9(1)°. The structures were solved by the heavy-atom method and atomic parameters were refined by full-matrix least-squares calculations to *R* 0.047 (I), 0.044 (II), and 0.072 (III) over 1 129, 1 594, and 1 241 statistically significant reflections. In all three molecules the dithian rings adopt chair conformations which are increasingly more puckered as the number of substituents increases. The C–S distances in (I) and (II) reveal interesting differences which depend upon the degree of substitution at the carbon atoms.

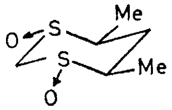
ALTHOUGH 1,4-dithian [1] and a number of its derivatives [2-5] and complexes [6-9] have been subjected to *X*-ray structural analyses, the equally interesting 1,3-dithian system has not received similar attention, the only structure determination to date being that of 2-phenyl-1,3-dithian [10] which was found to adopt a chair conformation with the phenyl group equatorially oriented. In addition, there is a general lack of accurate structural information available for organic sulphoxides. As part of our continuing interest in the structure and conformation of heterocycles we have subjected *r*-4,*c*-6-dimethyl-1,3-dithian (I) and its oxides, *r*-4,*c*-6-dimethyl-1,3-dithian *t*-1-oxide (II) and *r*-4,*c*-6-dimethyl-1,3-dithian *t*-1,*t*-3-dioxide (III), to single-crystal *X*-ray analysis.



(I)



(II)



(III)

EXPERIMENTAL

Preparations.—r-4,c-6-*Dimethyl*-1,3-*dithian* (I). This compound [11] was prepared according to the procedure of Hartmann.[12]

r-4,c-6-*Dimethyl*-1,3-*dithian* t-1-*Oxide* (II).—To a solution of (I) (11.2 g, 75.4 mmol) in acetic acid (30 ml) was added dropwise 30% aqueous hydrogen peroxide (9.0 g, 80 mmol). The solution was set aside overnight, and solvent then removed *in vacuo*. The residue was recrystallized from benzene to yield the monosulphoxide (10.3 g, 83.4%). Fractional crystallization of the mercury(II) chloride complex from ethanol according to ref. 13 gave isomerically pure (II), m.p. 158—160 °C (Found: C, 43.70; H, 7.35. $C_6H_{12}OS_2$ requires C, 43.85; H, 7.35).

r-4,c-6-*Dimethyl*-1,3-*dithian* t-1,t-3-*Dioxide* (III).—A solution of 4,6-dimethyl-1,3-dithian oxide (268 mg, 1.63 mmol) in acetic acid (15 ml) was treated with 30% hydrogen peroxide (127 mg, *ca*. 1.1 mmol). After setting aside for 14 h, solvent was removed *in vacuo*. The crude product was then chromatographed (t.l.c.; silica gel, benzene–acetic acid 4 : 1). After three developments the band with R_G 0.17 was collected and extracted with methanol. Solvent was then removed *in vacuo* and the residue sublimed at *ca*. 150° and 0.005 mmHg to give (III) (101 mg, 51%), m.p. 214 °C (Found: C, 40.1; H, 6.8. $C_6H_{12}O_2S_2$ requires C, 39.95; H, 6.7%).

Crystal Data.—(I). $C_6H_{12}S_2$, $M = 148.3$. Monoclinic, $a = 20.08(1)$, $b = 5.71(1)$, $c = 15.69(1)$ Å, $\beta = 118.4(1)°$, $U = 1\,582$ Å^3, D_m (flotation) = 1.23, $Z = 8$, $D_\alpha = 1.245$ g cm^{-3}, $F(000) = 640$. Mo-K_α radiation, $\lambda = 0.710\,69$ Å; μ(Mo-K_α) = 6.1 cm^{-1}. Space group Cc (C_s^4) or $C2/c$ (C_{2h}^6) from systematic absences: hkl when $h + k \neq 2n$, $h0l$ when $l \neq 2n$; shown to be the latter by structure solution and refinement.

(II). $C_6H_{12}OS_2$, $M = 164.3$. Monoclinic, $a = 20.33(1)$, $b = 5.68(1)$, $c = 16.11(1)$ Å, $\beta = 119.0(1)°$, $U = 1\,627$ Å^3, D_m (flotation) = 1.31, $Z = 8$, $D_c = 1.343$ g cm^{-3}, $F(000) = 724$. Mo-K_α radiation, μ(Mo-K_α) = 6.1 cm^{-1}. Space group Cc (C_s^4) or $C2/c$ (C_{2h}^6) from systematic absences: hkl when $h + k \neq 2n$, $h0l$ when $l \neq 2n$; $C2/c$ verified by structure solution and refinement.

(III). $C_6H_{12}O_2S_2$, $M = 180.3$. Monoclinic, $a = 5.49(1)$, $b = 15.52(1)$, $c = 10.81(1)$ Å, $\beta = 105.9(1)°$, $U = 886$ Å^3, D_m (flotation) = 1.31, $Z = 4$, $D_c = 1.352$ g cm^{-3}, $F(000) = 384$. Cu-K_α radiation, $\lambda = 1.5418$ Å; μ(Cu-K_α) = 48.1 cm^{-1}. Space group $P2_1/c$ (C_{2h}^5) from systematic absences: $h0l$ when $l \neq 2n$, $0k0$ when $k \neq 2n$.

Crystallographic Measurements.—For each compound preliminary cell dimensions and space-group data were obtained from oscillation and Weissenberg (Cu-K_α radiation) and from precession photographs (Mo-K_α radiation).

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Single crystals of dimensions (I) *ca.* 0.2 × 0.2 × 0.8 mm and (II) *ca.* 0.2 × 0.2 × 1.0 mm were oriented on glass fibres so that the needle *b* axis was parallel to the ϕ axis of an Enraf–Nonius CAD 3 diffractometer (Zr-filtered Mo-K_α radiation, take-off angle 3°). For (III), a crystal of dimensions *ca.* 0.2 × 0.2 × 0.5 mm was oriented to rotate about a^*, and Ni-filtered Cu-K_α was used. Refined cell parameters were calculated by least-squares treatment of the θ, χ, and ϕ angles for 40 accurately centred high-order reflections widely separated in reciprocal space. Intensities for all unique reflections having $2\theta < 55°$ (I), $< 65°$ (II), $< 134°$ (III), were measured by the θ–2θ scanning technique as described previously, with scanwidths $(0.90 + 0.20 \tan \theta)°$ for (I) and (II), and $(0.90 + 0.50 \tan \theta)°$ for (III). Remeasurement of the intensity of a strong standard reflection from each crystal after each batch of 99 reflections showed no significant variation over the entire data collection period. From totals of 1 900 (I), 2 163 (II), and 1 656 (III) measurements, only those intensities for which $I > 2\sigma$ (I), where $\sigma^2 (I)$ = (scan count + total background count), were corrected for Lorentz and polarization effects to yield 1 129 (I), 1 594 (II), and 1 241 (III) observed reflections which were used in the analysis and refinement. For (III), absorption corrections were determined from the ϕ dependence of the intensity of the 300 reflection measured at χ 90° and the data appropriately corrected. Similar measurements on crystals of (I) and (II) indicated that the data required no correction.

Structure Analysis.—(II). The structure was solved by the heavy-atom method. Initial co-ordinates for the sulphur atoms were derived from the three-dimensional Patterson synthesis assuming the correct space group to be *C*2/*c*. Carbon and oxygen atom positions were obtained from a sulphur-phased (*R* 0.53) three-dimensional F_o Fourier synthesis. Full-matrix least-squares adjustment of the positional and thermal parameters, at first isotropic and then anisotropic, reduced *R* to 0.074. Hydrogen atom positions were located in a difference-Fourier synthesis and with their inclusion in the structure-factor calculation, *R* decreased to 0.057. Several further rounds of least-squares calculations during which the hydrogen atom positional and isotropic thermal parameters were adjusted in addition to the non-hydrogen atom positional and anisotropic thermal parameters brought the refinement to convergence at *R* 0.047.

(I). This compound is isomorphous with (II) and so the final atomic co-ordinates and isotropic thermal parameters from the refinement of (II), omitting those for O(9), were used as input to the first structure-factor calculation, which gave *R* 0.31. Full-matrix least-squares refinement as described for (II) proceeded smoothly to convergence at *R* 0.044.

(III). The structure was solved by the heavy-atom method as for (II). Sulphur atom positions were obtained from the three-dimensional Patterson map, and carbon and oxygen atoms located in a sulphur-phased three-dimensional F_o Fourier synthesis; hydrogen atom positions were found following full-matrix least-squares refinement of the non-hydrogen atom positional and thermal parameters to *R* 0.141. Subsequent least-squares adjustment of all atom parameters converged at *R* 0.072.

Final atomic positional and isotropic thermal parameters for (I), (II), and (III) are listed in Table 1. Tables of anisotropic thermal parameters for the non-hydrogen atoms, observed and calculated structure factors are in Supplementary Publication No. SUP 21691 (25 pp., 1 microfiche).*

TABLE 1

Fractional atomic co-ordinates (× 10^4, for H × 10^3) and isotropic thermal parameters, with estimated standard deviations in parentheses. Hydrogen atoms are labelled according to the carbon atom to which they are bonded

Atom	*x*	*y*	*z*	*B*/Å^2
(*a*) For (I)				
S(1)	1 576(1)	914(2)	1 698(1)	
C(2)	2 176(2)	1 156(8)	1 147(3)	
S(3)	1 703(1)	711(2)	−139(1)	
C(4)	1 389(2)	−2 298(7)	−181(2)	
C(5)	903(2)	−2 605(7)	318(2)	
C(6)	1 281(2)	−2 131(7)	1 395(2)	
C(7)	966(3)	−2 968(9)	−1 241(3)	
C(8)	760(2)	−2 685(9)	1 821(3)	
H(2A)	261(2)	0(9)	148(3)	4.5(10)
H(2B)	241(2)	268(9)	129(3)	5.7(12)
H(4)	184(2)	−328(6)	15(2)	2.9(7)
H(5A)	77(2)	−434(7)	24(3)	4.4(10)
H(5B)	46(2)	−172(7)	0(3)	3.8(9)
H(6)	171(2)	−309(7)	169(2)	3.6(8)
H(7A)	125(3)	−284(10)	−156(3)	6.0(12)
H(7B)	83(2)	−455(8)	−129(3)	4.9(11)
H(7C)	51(2)	−205(10)	−156(3)	5.9(12)
H(8A)	101(2)	−231(8)	256(3)	5.4(11)
H(8B)	62(2)	−440(8)	164(3)	5.1(11)
H(8C)	28(3)	−184(10)	148(3)	5.7(11)
(*b*) For (II)				
S(1)	1 502(0.3)	970(1)	1 572(0.4)	
C(2)	2 174(1)	1 045(4)	1 144(2)	
S(3)	1 699(0.3)	645(1)	−122(0.4)	
C(4)	1 380(1)	−2 387(4)	−191(1)	
C(5)	886(1)	−2 693(4)	270(1)	
C(6)	1 251(1)	−2 142(4)	1 327(1)	
C(7)	956(2)	−3 033(6)	−1 243(2)	
C(8)	737(1)	−2 742(6)	1 745(2)	
O(9)	1 946(1)	1 156(4)	2 639(1)	
H(2A)	254(1)	−17(6)	148(2)	3.9(6)
H(2B)	238(2)	270(6)	122(2)	4.7(7)
H(4)	184(1)	−341(5)	12(2)	2.6(5)
H(5A)	73(1)	−444(5)	20(2)	2.8(5)
H(5B)	45(1)	−179(5)	−4(2)	3.3(6)
H(6)	173(1)	−299(5)	170(2)	2.5(5)
H(7A)	124(2)	−276(7)	−155(2)	6.3(9)
H(7B)	82(2)	−477(7)	−132(2)	5.5(8)
H(7C)	46(2)	−207(9)	−161(2)	7.4(10)
H(8A)	98(2)	−224(7)	243(2)	5.4(8)
H(8B)	67(2)	−452(5)	174(2)	4.2(7)
H(8C)	28(2)	−202(7)	141(2)	5.4(8)
(*c*) For (III)				
S(1)	−3 145(2)	−540(1)	−1 500(1)	
C(2)	−2 743(9)	−1 229(3)	−104(5)	
S(3)	−3 282(2)	−2 361(1)	−532(1)	
C(4)	−6 654(8)	−2 269(3)	−1 318(4)	
C(5)	−7 044(9)	−1 669(4)	−2 472(5)	
C(6)	−6 534(9)	−718(4)	−2 152(5)	
C(7)	−7 657(11)	−3 164(4)	−1 677(7)	
C(8)	−7 413(14)	−136(5)	−3 353(6)	
O(9)	−2 824(7)	364(3)	−969(4)	
O(10)	−3 001(8)	−2 826(3)	706(4)	
H(2A)	−53(14)	−127(5)	54(7)	6.4(19)
H(2B)	−400(9)	−95(3)	47(4)	1.9(10)
H(4)	−729(7)	−204(3)	−70(4)	0.5(7)
H(5A)	−566(11)	−189(4)	−289(5)	4.2(14)
H(5B)	−888(11)	−167(4)	−307(5)	4.2(14)
H(6)	−731(7)	−57(2)	−136(4)	0.4(8)
H(7A)	−876(21)	−321(9)	−192(10)	14.9(37)
H(7B)	−680(17)	−360(6)	−72(8)	8.3(23)
H(7C)	−681(10)	−327(4)	−209(5)	3.0(12)
H(8A)	−968(15)	−29(5)	−382(7)	6.7(20)
H(8B)	−678(13)	42(5)	−306(7)	5.5(7)
H(8C)	−611(18)	−59(6)	−382(9)	10.4(29)

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

For all structure-factor calculations neutral atom scattering factors for carbon, oxygen, and sulphur were taken from ref. 14, and for hydrogen from ref. 15. In the least-squares calculations, $\Sigma w\Delta^2$ was minimized, with weights w being assigned according to the scheme $\sqrt{w} = 1$ for $|F_o| \leqslant K$, and $\sqrt{w} = K/|F_o|$ for $|F_o| > K$ [K = 13.3 (I), 13.3 (II), and 8.0 (III)], and showed no systematic dependence of $\langle w\Delta^2\rangle$ when analyzed in ranges of $|F_o|$.

DISCUSSION

Views of the molecular conformations, the atom numbering schemes for (II) and (III), and the arrangements of molecules in crystals of (II) and (III) are shown in Figures 1 and 2. (I) Is isomorphous with (II) and has the same numbering scheme but lacks O(9). In all three compounds studied the heterocyclic ring adopts a chair conformation with equatorial methyl holding groups at C(4) and C(6); the oxygen substituents of (II) and (III) are also equatorially oriented. Interatomic distances and angles for (I)—(III) are listed in Table 2. In (I) and (III) pairs of bond lengths and angles related by the non-crystallographic mirror plane of symmetry which passes through C(2) and C(5) do not differ significantly. Table 3 lists the torsion angles for the corresponding enantiomers of (I)—(III). The sum of the moduli of the endocyclic torsion angles increases through the series [(I) 365.7, (II) 381.9, (III) 400.1°], and is indicative of a greater degree of ring puckering as the number of equatorial substituents increases.

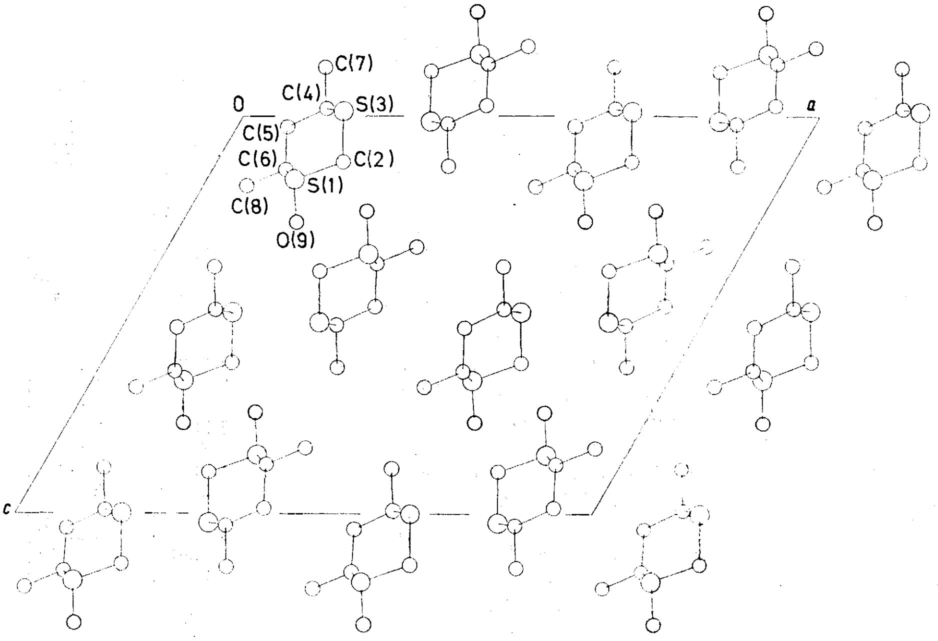

FIGURE 1 Atom numbering scheme and crystal structure of *r*-4,*c*-6-dimethyl-1,3-dithian *t*-1-oxide, (II), viewed in projection along the *b* axis

Bond lengths and angles in the CH_3–C–C–C–CH_3 moieties of (I)—(III) remain fairly constant, although the torsion angles around the C(4)–C(5) and C(5)–C(6) bonds show significant variation. The mean C–C bond lengths [(I) 1.517(5), (II) 1.526(3), (III) 1.525(8) Å] are all slightly shorter than the accepted C(sp^3)–C(sp^3) distance[16] [1.537(5) Å] and the endocyclic C(4)–C(5)–C(6) angle [(I) 116.7(3), (II) 116.3(2), (III) 115.5(4) Å] consistently assumes a value significantly greater than the normal cyclohexane value[17] [111.1(2)°]. These dimensions are similar, however, to those found in 2-phenyl-1,3-dithian[10] [1.49(3) Å, 116.5(15)°] the only other 1,3-dithian for which structural data are available. The mean exocyclic valency angles at C(4) and C(6) differ significantly with C–C–C(Me) always greater than S–C–C(Me) [111.9(3), 106.6(3) in (I); 111.7(2), 107.1(2) in (II); 112.8(5), 107.2(4)° in (III)] to minimize steric overcrowding between the methyl groups and equatorial H(5B) which is sandwiched between them. Whereas the mean endocyclic S–C–C valency angles in (I) [112.5(3)] and (II) [112.1(2)] are equal, that in (III) [109.8(3)°] is significantly smaller. These observations may be rationalized in the following way. The introduction of one *gauche* Me · · · O interaction upon oxidation of (I) to produce the less-symmetric monoxide (II) is accompanied by an increased degree of ring puckering which occurs principally in the vicinity of C(2) and S(1) where the endocyclic torsion angles around the S(1)–C(2), C(2)–S(3), and S(1)–C(6) bonds increase from 61.8, −61.8, and −57.3° in (I) to 68.0, −66.5, and −62.9° in (II); the valency angles at C(2) and S(1) correspondingly decrease from 114.5(3) and 99.2(2) in (I) to 110.0(1) and 97.1(1)° in (II). Upon further oxidation to give the

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TABLE 2

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

	(I)	(II)	(III)
(*a*) Bond lengths			
S(1)–C(2)	1.791(5)	1.805(3)	1.812(5)
S(1)–C(6)	1.825(4)	1.828(2)	1.821(5)
S(1)–O(9)		1.508(2)	1.509(4)
C(2)–S(3)	1.792(5)	1.797(3)	1.821(6)
S(3)–C(4)	1.822(4)	1.823(3)	1.819(5)
S(3)–O(10)			1.491(5)
C(4)–C(5)	1.523(5)	1.522(3)	1.524(7)
C(4)–C(7)	1.513(6)	1.527(4)	1.505(8)
C(5)–C(6)	1.512(5)	1.523(3)	1.524(8)
C(6)–C(8)	1.518(6)	1.531(3)	1.546(9)
C(2)–H(2A)	1.02(5)	0.97(3)	1.23(8)
C(2)–H(2B)	0.96(5)	1.02(4)	1.13(5)
C(4)–H(4)	0.98(4)	1.01(3)	0.91(4)
C(5)–H(5A)	1.02(4)	1.03(3)	1.04(6)
C(5)–H(5B)	0.94(4)	0.93(3)	1.04(6)
C(6)–H(6)	0.93(4)	0.99(3)	1.08(4)
C(7)–H(7A)	0.92(5)	0.94(4)	0.60(12)
C(7)–H(7B)	0.94(5)	1.02(4)	1.21(9)
C(7)–H(7C)	0.96(5)	1.05(4)	0.75(5)
C(8)–H(8A)	1.04(5)	1.01(3)	1.23(8)
C(8)–H(8B)	1.02(4)	1.02(3)	0.95(7)
C(8)–H(8C)	0.98(5)	0.91(4)	1.21(10)
(*b*) Valency angles			
C(2)–S(1)–C(6)	99.0(2)	97.1(1)	96.4(2)
C(2)–S(1)–O(9)		106.8(1)	104.9(2)
C(6)–S(1)–O(9)		105.3(1)	106.8(2)
S(1)–C(2)–S(3)	114.5(3)	110.0(1)	112.5(3)
C(2)–S(3)–C(4)	99.4(2)	99.7(1)	96.7(2)
C(2)–S(3)–O(10)			105.6(2)
C(4)–S(3)–O(10)			107.4(2)
S(3)–C(4)–C(5)	112.7(3)	112.2(2)	109.1(3)
S(3)–C(4)–C(7)	106.4(3)	106.7(2)	107.6(4)
C(5)–C(4)–C(7)	112.0(3)	111.3(2)	113.2(4)
C(4)–C(5)–C(6)	116.7(3)	116.3(2)	115.5(4)
S(1)–C(6)–C(5)	112.9(3)	111.9(2)	109.8(3)
S(1)–C(6)–C(8)	106.8(3)	107.4(2)	106.7(4)
C(5)–C(6)–C(8)	111.7(3)	112.3(2)	112.3(5)
S(1)–C(2)–H(2A)	109(3)	107(2)	112(4)
S(1)–C(2)–H(2B)	108(3)	109(2)	106(2)
S(3)–C(2)–H(2A)	110(3)	113(2)	100(4)
S(3)–C(2)–H(2B)	110(3)	103(2)	115(2)
H(2A)–C(2)–H(2B)	105(4)	115(3)	112(3)
S(3)–C(4)–H(4)	107(2)	107(1)	104(3)
C(5)–C(4)–H(4)	109(2)	111(1)	111(3)
C(7)–C(4)–H(4)	109(2)	108(1)	112(2)
C(4)–C(5)–H(5A)	104(3)	107(2)	101(3)
C(4)–C(5)–H(5B)	111(2)	111(2)	114(4)
C(6)–C(5)–H(5A)	106(3)	106(2)	108(4)
C(6)–C(5)–H(5B)	110(2)	108(2)	103(4)
H(5A)–C(5)–H(5B)	109(4)	108(2)	116(5)
S(1)–C(6)–H(6)	109(3)	104(2)	104(2)
C(5)–C(6)–H(6)	107(2)	112(1)	108(2)
C(8)–C(6)–H(6)	109(2)	108(1)	116(2)
C(4)–C(7)–H(7A)	114(3)	113(2)	119(14)
C(4)–C(7)–H(7B)	109(3)	110(2)	105(4)
C(4)–C(7)–H(7C)	109(3)	111(2)	96(5)
H(7A)–C(7)–H(7B)	105(5)	107(3)	114(13)
H(7A)–C(7)–H(7C)	111(4)	108(3)	116(12)
H(7B)–C(7)–H(7C)	109(4)	107(3)	103(6)
C(6)–C(8)–H(8A)	112(3)	110(2)	106(4)
C(6)–C(8)–H(8B)	104(3)	109(2)	104(4)
C(6)–C(8)–H(8C)	111(3)	111(2)	86(5)
H(8A)–C(8)–H(8B)	115(4)	106(3)	123(6)
H(8A)–C(8)–H(8C)	110(4)	110(3)	111(6)
H(8B)–C(8)–H(8C)	105(4)	111(3)	118(6)

symmetric dioxide (III), the heterocyclic ring must pucker even more in order to minimize steric effects which result from the presence of two symmetrically disposed *gauche* Me···O interactions in addition to the Me···H(5B) interactions already discussed. Repulsion between the $\overset{+}{\text{S}}$–$\overset{-}{\text{O}}$ dipoles (*vide infra*) prevents further puckering taking place around C(2), and consequently it must occur around the other ring bonds, thereby leading

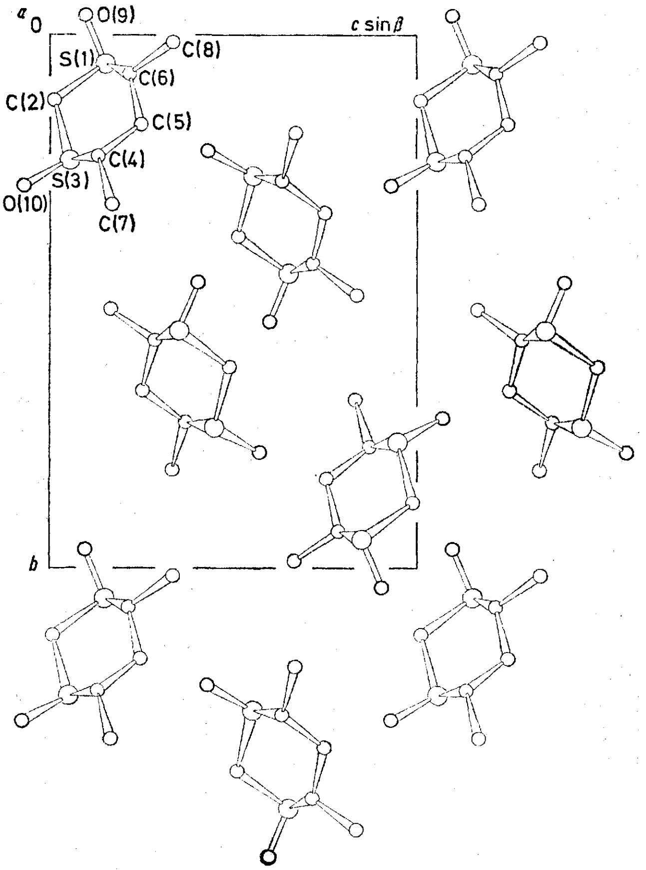

FIGURE 2 Atom numbering scheme and crystal structure of *r*-4,*c*-6-dimethyl-1,3-dithian *t*-1,*t*-3-dioxide, (III), viewed in projection along the *a* axis

TABLE 3

Torsion angles (°); the angle A–B–C–D is defined as positive if, when viewed along the B–C, atom A must be rotated clockwise to eclipse atom D

	(I)	(II)	(III)
C(6)–S(1)–C(2)–C(3)	61.8	68.0	66.6
O(9)–S(1)–C(2)–C(3)		176.4	175.9
C(2)–S(1)–C(6)–C(5)	−57.3	−62.9	−61.5
C(2)–S(1)–C(6)–C(8)	179.5	173.5	176.6
O(9)–S(1)–C(6)–C(5)		−172.5	−169.2
O(9)–S(1)–C(6)–C(8)		63.9	68.9
S(1)–C(2)–S(3)–C(4)	−61.8	−66.5	−67.2
S(1)–C(2)–S(3)–O(10)			−177.4
C(2)–S(3)–C(4)–C(5)	56.8	57.9	61.8
C(2)–S(3)–C(4)–C(7)	179.8	−179.9	−175.1
O(10)–S(3)–C(4)–C(5)			170.5
O(10)–S(3)–C(4)–C(7)			−66.4
S(3)–C(4)–C(5)–C(6)	−63.8	−61.6	−71.5
C(7)–C(4)–C(5)–C(6)	176.3	179.0	168.8
C(4)–C(5)–C(6)–S(1)	64.2	65.0	71.5
C(4)–C(5)=C(6)–C(8)	−175.4	−174.2	−170.0

to a decrease of the endocyclic valency angles at C(4) and C(6).

The mean C–S distances [1.808 (I), 1.818 (II), 1.824 (III) Å] show a small increase with increasing degree of substitution of the 1,3-dithian ring, and small, but significant, differences between the individual C–S bonds are evident. In (I) and (II) the S(1)–C(6) and S(3)–C(4) bonds [1.825(4) and 1.822(4) in (I), 1.828(2) and 1.823(3) Å in (II)] are distinctly longer than S(1)–C(2) and C(2)–S(3) [1.791(5) and 1.792(5) in (I), 1.805(3) and 1.797(3) Å in (II)]. On the other hand, the S–C bond lengths of dioxide (III) range from 1.812(5) to 1.821(5) Å and all are equal. Thus, oxidation of one sulphur does not produce any marked change in bond-length pattern, and so it may be concluded that the differences in degree of substitution at the carbon atoms involved in these bonds must be primarily responsible for the observed variations, *i.e.* the shorter bonds always involve the methylene carbon atom. Studies on other related systems are clearly desirable in order to try to obtain further clarification of this point. The uniformity of S–C distances in (III) contrasts with the situation in (I) and (II), and may be ascribed to the involvement of intramolecular repulsion between the $\overset{+}{S}$–$\overset{-}{O}$ dipoles in (III), where they would be expected to increase the S $\cdots$ S separation, the C(2)–S bond lengths, and the S–C–S valency angles. In addition to the C–S distances already discussed, the other features are also observed: the S $\cdots$ S separation decreases from 3.013(2) in (I) to 2.951(1) in oxide (II), increasing again in dioxide (III) [3.022(2) Å], and the variation in S–C–S angle follows a similar pattern [114.5(3) (I), 110.0 (II), and 114.5(3)° (III)].

The valency angles at the sulphur atoms show small variations which may be attributed to differences in oxidation state and to steric effects. At bivalent sulphur the C–S–C angles [99.4(2) and 99.0(2) in (I), 99.7(1)° in (II)] are similar to those in 2-phenyl-1,3-dithian [99.2(15) and 100.9(15)°],[10] 1,4-dithian [99.0(6)°],[1] and 2,5-diphenyl-1,4-dithian 1-oxide [98.2(4)°].[18] As expected, the corresponding angles at the sulphoxides [97.1(1) in (II), 96.4(2) and 97.7(2)° in (III)] are smaller. The mean C–S–O angle (106.1°) in (II) and (III) is typical for sulphoxides.[2,18–20] Significant differences between the pairs of C–S–O angles in (III) may be ascribed to *gauche* interactions between the equatorial oxygen and methyl groups which result in enlarged values for the C(6)–S(1)–O(9) and C(4)–S(3)–O(10) angles [106.8(2) and 107.4(2)°] and decreased values for C(2)–S(1)–O(9) and C(2)–S(3)–O(10) [104.9(2) and 105.6(2)°]. The smaller difference between the corresponding angles in the less-symmetric oxide (II) occurs in a direction opposite to that found in (III) and, although the reason for this cannot be unequivocally established on the basis of a single observation, a likely explanation appears to be that the *gauche* Me $\cdots$ O interaction in (II) is relieved through ring puckering rather than through valency-angle deformation at sulphur.

A survey of all intermolecular distances <4.0 Å in crystals of (I), (II), and (III) revealed that only normal van der Waals separations were present in (I) and (II). In crystals of (III), however, the hydrogen atoms of C(2) which is flanked by two $\overset{+}{S}$–$\overset{-}{O}$ groups are involved in two short C–H $\cdots$ O hydrogen-bonded interactions about centres of symmetry [O(9) $\cdots$ H(2A) (at $-x, -y, -z$), 2.26, and O(9) $\cdots$ H(2B) (at $1 - x, -y, -z$) 2.17 Å.]

We thank Professor E. L. Eliel (University of North Carolina, Chapel Hill) for drawing our attention to these problems and for informative discussions, the U.S. National Science Foundation for funds towards the purchase of the diffractometer and for financial support (to J. K.), and Duke University for financial support through the award of a James B. Duke Fellowship (to K. D. O.). Crystallographic calculations were performed on an IBM 370/165 computer located at the Triangle Universities Computation Centre, Research Triangle Park, North Carolina, and supported by a grant of computer time from Duke University.

[5/2221 *Received, November* 14*th*, 1975]

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