Conformational Analysis of 1,3-Dithian 1-Oxides [1]

By **Michael J. Cook** * and **Alan P. Tonge,** School of Chemical Sciences, University of East Anglia, Norwich NOR 88C

Dipole moments and n.m.r. data for 1,3-dithian 1-oxide, its 2,2-dimethyl derivative, and certain conformationally rigid 1,3-dithian 1-oxides are reported. The results, together with u.v. data for 1,3-dithian 1-oxide and its *cis*- and *trans*-2-t-butyl derivatives, demonstrate that the mobile compounds exist predominantly as the conformer with the S=O bond equatorial. The direction of the sulphoxide dipole moment is discussed.

THE axial preference of this sulphinyl oxygen atom in thian 1-oxide (1) and its derivatives has been established by equilibration [2] and n.m.r. studies.[3] The preference has been ascribed to an attractive interaction between the axial sulphinyl oxygen atom and *syn*-axial C–H bonds, a view supported by calculations of the Westheimer type.[4] Favourable attractive S=O · · · C–H interactions would seemingly contribute towards the greater thermodynamic stability of (2) over (3),[5] while adverse *syn*-axial steric interactions in 3,3-dimethylthian 1-oxide (4) account for the destabilisation of conformer (4*a*) relative to (4*e*).[6] Recently we indicated that 2,2-dimethyl-1,3-dithian 1-oxide exists predominantly with the S=O bond equatorial; [1] by contrast 1,3-oxathian 3-oxide (5) shows little preference for either conformer at 38° and exists extensively as (5*a*) at low temperatures.[7] The present paper describes our more thorough investigation of the 1,3-dithian 1-oxide ring system.

---

[1] Preliminary communication, M. J. Cook and A. P. Tonge, *Tetrahedron Letters*, 1973, 849.

[2] C. R. Johnson and D. McCants, jun., *J. Amer. Chem. Soc.*, 1964, **86**, 2935; J. C. Martin and J. J. Uebel, *ibid.*, p. 2936.

[3] J. B. Lambert and R. G. Keske, *J. Org. Chem.*, 1966, **31**, 3429.

[4] N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminski, *J. Amer. Chem. Soc.*, 1969, **91**, 337.

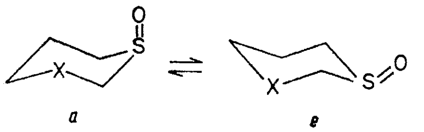
[5] C. R. Johnson, H. Diefenbach, J. E. Keiser, and J. C. Sharp, *Tetrahedron*, 1969, **25**, 5649.

[6] J. B. Lambert, D. S. Bailey, and C. E. Mixan, *J. Org. Chem.*, 1972, **37**, 377.

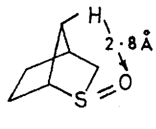
[7] K. Bergesen, M. J. Cook, and A. P. Tonge, *Org. Magnetic Resonance*, in the press.

Whereas little information is available about this series of dithian derivatives,[8] † 2-phenyl-1,3-dithian is known to exist as a chair conformation in both solid [9] and solution [10] phases, and a 2-t-butyl function has been used as a conformational holding group in a study of 2-t-butyl-4- and -5-alkyl-1,3-dithians.[11]

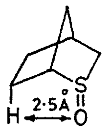
Preparation of Compounds.—1,3-Dithian (6) and the derivatives (7)—(9) were prepared by standard routes (see Experimental section). With periodate, (6) and (7) afforded the potentially mobile sulphoxides (10) and (11), while (8) and (9) gave (12)—(14) which we used as fixed models. The isomer pair (13) and (14) were formed as a 9 : 1 mixture (by n.m.r.) from which (13) was separated by chromatography. Attempted removal of the *cis*-isomer from the mixture by selective reduction using sodium bisulphite (after Johnson *et al.*[12]) unexpectedly brought about preferential reduction of the *trans*-isomer. Compound (14) was obtained by isomerisation of (13) using triethyloxonium tetrafluoroborate followed by base (*cf.* ref. 13). We were unable to invert the sulphinyl group of (12).



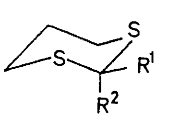
(1) X = CH_2
(4) X = CMe_2
(5) X = O



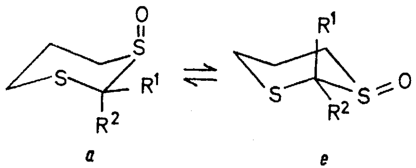
(2)



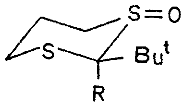
(3)



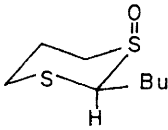
(6) $R^1 = R^2 = H$
(7) $R^1 = R^2 = Me$
(8) $R^1 = Bu^t$, $R^2 = Me$
(9) $R^1 = Bu^t$, $R^2 = H$



(10) $R^1 = R^2 = H$
(11) $R^1 = R^2 = Me$



(12) R = Me
(13) R = H



(14)

EXPERIMENTAL

Materials.—The following were prepared by literature routes: 1,3-dithian,[14] m.p. 51—53° (lit.,[14] 53—54°), 1,3-dithian 1-oxide,[8] m.p. 87—88° (lit.,[8] 87—88°).

2-Substituted 1,3-dithians were prepared by the general procedure of Eliel and Hutchins [11] involving acid catalysed condensation of propane-1,3-dithiol with an aldehyde or ketone. The corresponding sulphoxides were obtained by adding a solution (<5% w/v) of the dithian in methanol to a concentrated solution of an equivalent of sodium periodate in water and stirring for 30 min. Sodium iodate was removed by filtration and the filtrate was evaporated under reduced pressure to near dryness. The concentrate was extracted ($CHCl_3$) and the extract dried ($MgSO_4$) and evaporated to dryness. The sulphoxide residue was recrystallised or distilled as appropriate. By these general procedures, the following were prepared: 2,2-dimethyl-1,3-dithian (6·3 g, 85%) from propane-1,3-dithiol (5·4 g) and acetone (10·0 g), b.p. 86° at 20 mmHg (lit.,[15] 102° at 24 mmHg); 2,2-*dimethyl*-1,3-*dithian* 1-*oxide* (0·65 g, 20%) from 2,2-dimethyl-1,3-dithian (2·96 g) and $NaIO_4$ (4·28 g), b.p. 98—100° at 0·15 mmHg (Found: C, 43·7; H, 7·4. $C_6H_{12}OS_2$ requires C, 43·9; H, 7·3%); 2-*t-butyl*-2-*methyl*-1,3-*dithian* (13·1 g, 70%) from propane-1,3-dithiol (10·8 g) and pinacolone, m.p. 35° (from MeOH) (Found: C, 56·7; H, 9·3. $C_9H_{18}S_2$ requires C, 56·8; H, 9·5%); trans-2-*t*-*butyl*-cis-2-*methyl*-1,3-*dithian* 1-*oxide* (2·4 g, 60%) from

---

† *Added in proof*: After submission of this paper, L. Van Acker and M. Anteunis, *Tetrahedron Letters*, 1971, 225, reported n.m.r. data for compounds (5) and (10): their conclusions about the conformational equilibria are in agreement with our own.

[8] (*a*) R. M. Carlson and P. M. Helquist, *J. Org. Chem.*, 1968, **33**, 2596; (*b*) R. Kuhn and F. A. Neugebauer, *Chem. Ber.*, 1961, **94**, 2679.

[9] H. T. Kalff and C. Romers, *Acta Cryst.*, 1966, **20**, 490.

[10] H. R. Buys, *Rec. Trav. chim.*, 1970, **89**, 1244.

[11] E. L. Eliel and R. O. Hutchins, *J. Amer. Chem. Soc.*, 1969, **91**, 2703.

[12] C. R. Johnson, C. C. Bacon, and J. J. Rigau, *J. Org. Chem.*, 1972, **37**, 919.

[13] C. R. Johnson and D. McCants, jun., *J. Amer. Chem. Soc.*, 1965, **87**, 5404.

[14] D. Seebach, N. R. Jones, and E. J. Corey, *J. Org. Chem.*, 1968, **33**, 300.

[15] S. Oae, W. Tagaki, and A. Ohno, *Tetrahedron*, 1964, **20**, 427.

2-t-butyl-2-methyl-1,3-dithian (3·60 g) and $NaIO_4$ (4·28 g), m.p. 81—83° (Found: C, 52·2; H, 8·5. $C_9H_{18}OS_2$ requires C, 52·5; H, 8·7%); 2-t-butyl-1,3-dithian (11·3 g, 75%) from propane-1,3-dithiol (9·5 g) and pivaldehyde (7·6 g), b.p. 76—78° at 0·4 mmHg (lit.,[15] 129° at 22 mmHg); and cis- and trans-2-*t-butyl*-1,3-*dithian* 1-*oxide* (1 : 9 by n.m.r.; 3·2 g, 60%) from 2-t-butyl-1,3-dithian (5·28 g) and $NaIO_4$ (6·44 g). Chromatographic separation over silica gel preparative t.l.c. plates ($CHCl_3$ as eluant) afforded the trans-*sulphoxide*, m.p. 91—92° (from cyclohexane) (Found: C, 50·0; H, 8·4. $C_8H_{16}OS_2$ requires C, 50·0; H, 8·3%.) The *trans*–*cis*-sulphoxide mixture (0·95 g) in dichloromethane (0·5 ml) and Et_3O,BF_4 (1·50 g) was kept at room temperature for 20 min. Ether (50 ml) was added and the oily layer separated and dissolved in 1M-NaOH in 30% aqueous ethanol (50 ml). After 24 h at room temperature, the mixture was reduced in bulk under vacuum and extracted with chloroform (2 × 50 ml). The extract was evaporated to dryness and the residue recrystallised from benzene to give the cis-*sulphoxide* (0·35 g, 40%), needles, m.p. 194—195° (Found: C, 50·0; H, 8·3%).

TABLE 1

Dipole moments of 1,3-dithian 1-oxides in benzene at 25°

Compound	$d\varepsilon/dw$	$-dv/dw$	$P_2{}^{\infty}$	P_E	μ/D
(10)	12·79 ± 0·30	0·490 ± 0·003	354·5	38·04	3·93 ± 0·05
(11)	9·40 ± 0·13	0·345 ± 0·010	333·3	47·36	3·74 ± 0·03
(12)	6·74 ± 0·05	0·287 ± 0·003	314·5	56·00	3·56 ± 0·01
(13)	7·31 ± 0·16	0·289 ± 0·005	313·6	51·45	3·58 ± 0·04
(14)	11·05 ± 0·18	0·335 ± 0·004	455·8	51·45	4·39 ± 0·04

Errors in $d\varepsilon/dw$ and dv/dw are quoted as ± standard deviations based on a least squares plot (the origin not being used as a point). The errors are combined to give the quoted error in μ. $P_{2\infty}$ Is the measured total solute polarisation at infinite dilution. P_E is the estimated electronic polarisation of the solute.

Reduction of the 9 : 1 *Sulphoxide Mixture.*—The 9 : 1 mixture (0·50 g) was added to 20% aqueous solution of sodium hydrogen sulphite (10 ml). After 15 min the mixture was extracted with cyclohexane (2 × 25 ml) to remove reduction products and then chloroform (2 × 25 ml). The $CHCl_3$ extract was dried ($MgSO_4$) and evaporated to dryness. The residue (0·05 g) consisted of a 1 : 1 mixture (by n.m.r.) of the starting sulphoxides.

Physical Measurements.—N.m.r. spectra of 10% w/v solutions were obtained at 220 MHz (20°) on a Varian spectrometer (PCMU). Spectra at 100 and 60 MHz were recorded on a Varian HA-100 spectrometer at 38° and on a Perkin-Elmer R12 spectrometer over the temperature range indicated in the later text.

Dipole moments were calculated by the method of Halverstadt and Kumler[16] from measurements of dielectric constants and specific volumes of the solvent (benzene) and four solutions. Dielectric constants at 25° were derived from measurements with a Wayne–Kerr B641 capacitance bridge by use of a glass cell as described elsewhere.[17] Specific volumes were determined from density measurements obtained using an Anton Parr DMA O2 densimeter, which recorded changes in the natural resonating frequency of a solution with density.[17] A value for the total electronic polarisation for each compound was obtained by summation of bond electronic polarisabilities.[18] Results are shown in Table 1.

U.v. spectra were recorded on a Pye–Unicam SP 800A spectrophotometer.

RESULTS AND DISCUSSION

N.m.r. Spectra.—Interpretation of the n.m.r. spectra of the 1,3-dithian 1-oxides was much simplified by obtaining spectra at 220 MHz; 100 MHz spectra merely showed complex multiplets. Representative examples of 220 MHz spectra (1000 Hz sweepwidth) illustrating their degree of first-order character, are shown in Figure 1. Parameters obtained from first-order analyses (of 250 or 500 Hz sweepwidth spectra) are reported in Table 2. Assignment of signals in the spectra of the fixed models (12)—(14) followed from the splitting patterns and the known effects of ring heteroatoms on proton chemical shifts. The appearance of large and small vicinal couplings distinguish axial from equatorial protons, and the magnitudes rule out twist conformations and favour rigid chair forms. (A rigid boat conformation which could give rise to coupling constants similar to those observed, is unlikely on the basis of studies on substituted 1,3-dithians.[9–11])

The S=O bond configurations in (12)—(14) were assigned using the following criteria. (i) Protons *syn*-axial with an S=O bond are substantially deshielded relative to the corresponding protons in the parent sulphide.[19] (ii) The difference in chemical shifts between methylene protons α to a sulphinyl group is larger, and J_{gem} is smaller, when the S=O bond is equatorial (see ref. 6).

Proton signals in the spectra of (10) and (11) are characteristic of protons in predominantly axial and equatorial environments which points to equilibria strongly biased in favour of one conformer; assignments of signals were made on the criteria used above. Partial overlap of certain signals precluded estimation of all parameters, but otherwise the spectrum of (11) is very similar to that of (12) and that of (10) more closely resembles that of (13) than that of (14). In particular, the magnitudes of the vicinal *trans*-couplings and the difference between the chemical shifts of the two C-6 protons [0·66 (10), 0·66 (13), 0·22 (14), 0·31 (11), and 0·36 p.p.m. (12)] demonstrate that (10) and (11) exist predominantly (*i.e.* at least 80%) as the conformer with

---

[16] I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.*, 1942, **64**, 2988.

[17] R. A. Y. Jones, A. R. Katritzky, P. G. Lehman, K. A. F. Record, and B. B. Shapiro, *J. Chem. Soc.* (*B*), 1971, 1302; K. A. F. Record, Ph.D. Thesis, University of East Anglia, 1970.

[18] R. J. W. Le Fèvre and K. D. Steel, *Chem. and Ind.*, 1961, 670.

[19] K. W. Buck, A. B. Foster, W. D. Pardoe, M. H. Qadir, and J. M. Webber, *Chem. Comm.*, 1966, 759.

TABLE 2

^{1}H N.m.r. parameters for 1,3-dithian 1-oxides (in $CDCl_3$) [a]

Parameters	(10) [b]	(11) [b]	(12) [c]	(13) [c]	(14) [c]
(a) Chemical shifts (δ)					
2*ax*-H or group	3·64 [d]	1·56 (Me), 1·62 (Me)	1·67 (Me)	3·53 (0·41)	3·43 (0·51)
2*eq*-H or group	4·02 [d,e]		1·20 (Bu^t)	1·25 (Bu^t)	1·17 (Bu^t)
4*ax*-H	~2·57	2·66	2·66—2·67 (0·39—0·40)	~2·63 (0·22)	2·42 (0·43)
4*eq*-H	~2·48	~2·39	2·41 (0·30)	~2·63 (0·22)	2·69 (0·16)
5*ax*-H	2·13	2·19	2·15 [f]	2·25 (−0·48)	2·62 (−0·85)
5*eq*-H	~2·48	~2·39	~2·29 [f]	2·42 (−0·43)	1·77 (0·22)
6*ax*-H	2·66	2·71	2·66—2·67 (0·39—0·40)	2·72 (0·13)	2·90 (−0·15)
6*eq*-H	3·32 [e]	3·02	3·03 (−0·32)	3·38 (−0·53)	3·12 (−0·27)
(b) Coupling constants (*J*/Hz)					
J_{4ax5ax}	~12	~12·5	~13		~13·0
J_{4ax5eq}		3·0	~3·5	~3·5	2·5
J_{5ax6ax}	12·0	~12	~13	13·0	~13
J_{5ax6eq}	~3		3·3	3·5	2·8
J_{5eq6ax}	2·8	3·0	~3·5	3·5	2·5
J_{5eq6eq}	~3		3·3	3·5	2·5
$\lvert J_{6ax6eq}\rvert$	12·0	13·0	13·0	13·0	13·5

[a] First-order analyses of spectra at 220 MHz (20°) of 10% solutions. Coupling constants to 4*eq*-H are not listed as their measurement was normally hindered by signal overlap. [b] Terms *eq*-H and *ax*-H for ' mobile ' compounds refer to the protons predominantly equatorial and axial respectively. [c] Figures in parentheses are shielding effects (p.p.m.) relative to the parent sulphide [δ (sulphide) — δ (sulphoxide)]. Parameters for (8) and (9) were obtained from spectra at 100 MHz (38°). [d] $\lvert J_{2ax2eq}\rvert$ 12·6 Hz. [e] J_{2eq6eq} 2·5 Hz. [f] Signals from 5*ax*-H and 5*eq*-H overlap with that from the 2-methyl group in 2-t-butyl-2-methyl-1,3-dithian.

the S=O bond equatorial. That the equilibrium (10*a*) $\rightleftharpoons$ (10*e*) is strongly biased is apparent also from the four-bond coupling to the lower field, but not the higher field, C-2 proton (see also ref. 8*a*). As coupling over four bonds occurs *via* a W pathway the proton absorbing at the lower field is predominantly equatorial, and therefore *trans* to the S=O bond.

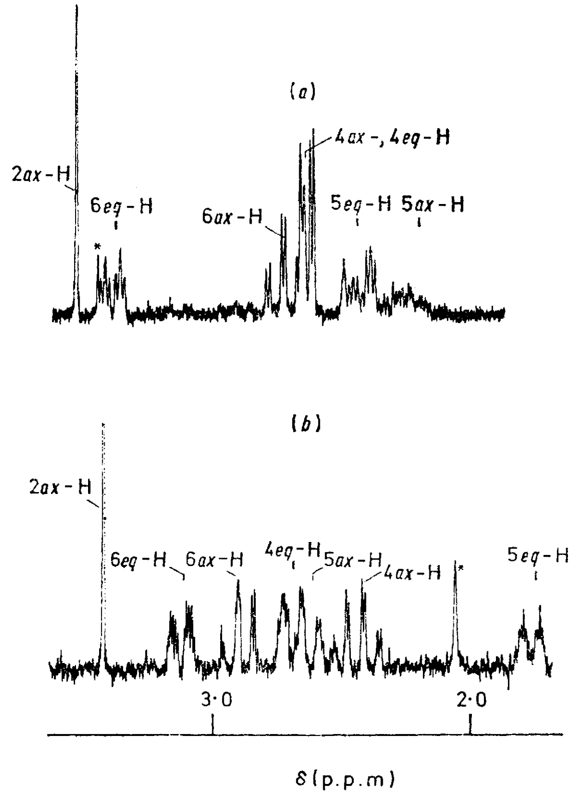


FIGURE 1 Parts of the n.m.r. spectra at 220 MHz (20°) of (*a*) a 10% solution of *trans*-2-t-butyl-1,3-dithian 1-oxide (13) in $CDCl_3$ and (*b*) a 10% solution of *cis*-2-t-butyl-1,3-dithian 1-oxide (14) in $CDCl_3$ (* = impurity)

Spectra of (10) in [$^2H_6$]benzene (100 MHz) at 38°, [$^2H_6$]acetone (60 MHz) at −40 to 40°, and in [$^2H_6$]dimethyl sulphoxide (60 MHz) at 40—160° were also recorded. Four-bond coupling to the lower field C-2 proton and spectral features characteristic of conformer (10*e*) persisted over the range of solvent and temperature investigated, although at higher temperatures, broadening of the higher field C-2 proton doublet became apparent indicating increasing population of (10*a*) under these conditions (Figure 2).

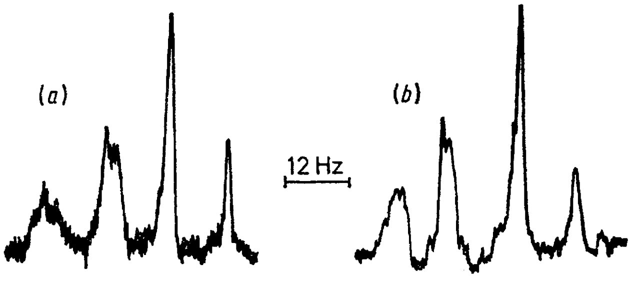
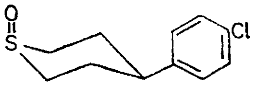


FIGURE 2 The C-2 protons of 1,3-dithian 1-oxide (60 MHz): (*a*) at −40° in [$^2H_6$]acetone and (*b*) at 160° in [$^2H_6$]dimethyl sulphoxide

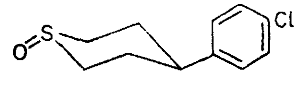
Dipole Moments.—Inspection of molecular models of the two chair conformations of 1,3-dithian 1-oxide reveals that the dipole moment should be smaller when the S=O bond is equatorial. Thus the results in Table 1 confirm, qualitatively, the configurational assignments of the S=O groups in (12)—(14).

Calculation of the conformational equilibrium constants for (10) and (11) requires estimates of the dipole moments of the individual conformers. Such estimates are potentially available from model compounds or calculations. Unfortunately (12) or (13), and (14) are probably unacceptable models for (10*e*) and (10*a*) in view of the recent report [20] of a substantial difference between the dipole moment of 2-t-butyl-1,3-dithian (9) (1·82 D) and the parent (6) (2·14 D), a difference attributed to a modified inductive effect of the 2-alkyl group and/or a slight deformation of ring geometry.[20,*] On the other hand (12)/(13) and (14) are expected to be more satisfactory as models for (11*e*) and (11*a*) where a modified inductive effect may again be important. From the dipole moments of (11) and (12)—(14) we calculate (11*e*) to be favoured over (11*a*) by 81 : 19.

In the absence of suitable models for (10*e*) and (10*a*) the calculation of the expected dipole moments of the two conformers was explored. Calculations of this type require a knowledge of the direction of the dipole moment of the sulphoxide group, and the geometry of the ring. On the basis of studies by Cumper and his co-workers,[23] Leonard and Johnson [24] derived a value of 40° for the angle θ of the sulphoxide moment to the C–S–C plane. However, this value gave a rather poor quantitative agreement between the calculated and experimental values for the isomeric thian 1-oxides (15) and (16), *viz.* 4·30 and 2·24 D compared with 3·98 and 2·60 D.[25] We deemed it desirable to recalculate the direction of the S=O moment using criteria (i), the experimental dipole moments of (15), (16), *p*-chlorophenylcyclohexane (2·18 D) acting at an angle of 130·5° to the C-2–C-1–C-6 plane,[26] and that of thian 1-oxide equalling 4·19 D,[23] and (ii), the geometry for the thian 1-oxide ring corresponding to angles of 127·9° between the C-2–S-1–C-6 and C-2–C-3–C-5–C-6 planes and 127·4° between the C-3–C-4–C-5 and C-2–C-3–C-4–C-5 planes (the angles are those calculated for thian [27] using the 'strain-energy minimised geometry' approach recently developed in these laboratories [28]). Calculations [29] using the above parameters give values for θ of 21·3°, from the data for (15), and 17·4°, from that for (16).



(15)



(16)

TABLE 3

Cartesian co-ordinates of vectors and calculated dipole moments for 1,3-dithian 1-oxide

			Sulphoxide moment at 21° to C-2–S-1–C-6 plane						Sulphoxide moment at 40° to C-2–S-1–C-6 plane					
$\hat{P}_3$ [a]	$\hat{P}_1$ [a]	$\hat{N}_1$ [a]	$\hat{P}_1 \cos 21°$	$\hat{N}_1 \sin 21°$	S=O(*ax*) vector	S=O(*eq*) vector	$\mu(10a)$/D	$\mu(10e)$/D	$\hat{P}_1 \cos 40°$	$\hat{N}_1 \sin 40°$	S=O(*ax*) vector	S=O(*eq*) vector	$\mu(10a)$ D	$\mu(10e)$ D
−0·4473	0·8961	−0·2125	0·8365	−0·0762	0·7603	0·9127	4·79 [b]	4·01 [b]	0·6834	−0·1366	0·5468	0·8200	5·08 [b]	3·66 [b]
−0·2882	−0·2890	0·3867	−0·2701	0·1386	−0·1315	−0·4087	4·89 [c]	4·03 [c]	−0·2216	0·2486	0·0270	−0·4702	5·20 [c]	3·64 [c]
−0·8467	−0·3369	−0·8974	−0·3145	−0·3216	−0·661	0·0071			−0·2550	−0·5678	−0·8348	0·3188		

[a] Data for 1,3-dithian (refs. 20 and 27). $\hat{P}_3$ is normalised vector in C-2–S-3–C-4 plane; $\hat{P}_1$ is normalised vector in C-2–S-1–C_6 plane; $\hat{N}_1$ is normalised vector normal to the C-2–S-1–C-6 plane. [b] Calculated using a value of 4·19 D [23] for the sulphoxide dipole moment and 1·54 D [20] for the dipole moment at S-3. [c] As *b* but using a value of 1·7 D [27] for the dipole moment at S-3.

The dipole moments for (10*a*) and (10*e*), calculated assuming the 'strain-energy minimised geometry' calculated for 1,3-dithian [20] and values for θ of 21 and 40° are reported in Table 3. Each set of calculations predicts a lower dipole moment for (10*e*) relative to (10*a*). Comparison of these data with the measured dipole moments of the corresponding rigid compounds (12)—(14) is instructive; thus assuming that (10*e*) and (10*a*) have marginally larger dipole moments than those of their 2-t-butyl analogues because of inductive effects within the latter, the data obtained using θ = 21° seem more satisfactory.† Consideration of the experimental dipole moment of (10) in the light of either set of calculated values, however, leads to the same qualitative conclusion, *i.e.* that conformer (10*e*) is heavily populated, a conclusion in accord with that reached from the n.m.r. data.

U.v. Spectra.—Although cross ring sulphur orbital interactions in 1,3-dithian may be small,[30] Iwamura *et al.*,[31] from *X*-ray photoelectron spectroscopy studies, have reported positive charge delocalisation over the sulphur atoms of 1,3,5-trithian 1-oxide and 1,1-dioxide. We find (Table 4) that the absorption in the u.v. spectrum of (14) shows a bathochromic shift of *ca.* 10 nm relative to that of (13) suggesting the electronic interactions, whatever their nature, are dependent upon sulphoxide environment. The u.v. spectrum of (10)

---

[*] The effect of a t-butyl group on ring geometry is a matter of some uncertainty.[21] While ring distortion cannot be ruled out in the present case, it should be noted that there is no evidence of distortion in 2-t-butyl-1,3-dioxan.[22]

[†] One of the referees has pointed out that θ may in fact vary with the molecular system studied.

[20] L. Angiolini, I. D. Blackburne, R. A. Y. Jones, and A. R. Katritzky, *Gazzetta*, in the press.

[21] V. R. Haddon and L. M. Jackman, *Org. Magnetic Resonance*, 1973, **5**, 333; R. Parthasarathy, J. Ohrt, H. B. Kagan, and J. C. Fiaud, *Tetrahedron*, 1972, **28**, 1529; P. L. Johnson, J. P. Schaeffer, V. J. James, and J. F. McConnell, *ibid.*, p. 2901.

[22] A. J. Jones, E. L. Eliel, D. M. Grant, M. C. Knoeber, and W. F. Bailey, *J. Amer. Chem. Soc.*, 1971, **93**, 4772; H. R. Buys and E. L. Eliel, *Tetrahedron Letters*, 1970, 2779.

[23] C. W. N. Cumper and A. I. Vogel, *J. Chem. Soc.*, 1959, 3521; C. W. N. Cumper and S. Walker, *Trans. Faraday Soc.*, 1956, **52**, 193.

[24] N. L. Leonard and C. R. Johnson, *J. Am.r. Chem. Soc.*, 1962, **84**, 3701.

[25] C. R. Johnson, *J. Amer. Chem. Soc.*, 1963, **85**, 1020.

[26] R. J. Bishop, L. E. Sutton, D. Dineen, R. A. Y. Jones, A. R. Katritzky, and R. J. Wyatt, *J. Chem. Soc.* (*B*), 1967, 493.

[27] I. D. Blackburne and D. M. Read, personal communication.

[28] I. D. Blackburne, R. P. Duke, R. A. Y. Jones, A. R. Katritzky, and K. A. F. Record, *J.C.S. Perkin II*, 1973, 332.

[29] For details see A. P. Tonge, Ph.D. Thesis, University of East Anglia, 1973.

[30] D. R. Williams and L. T. Kontnik, *J. Chem. Soc.* (*B*), 1971, 312.

[31] H. Iwamura, M. Fukunaga, and K. Kushida, *J.C.S. Chem. Comm.*, 1972, 450.

closely resembles that of (13) in both ethanol and cyclohexane and thus provides further qualitative evidence for the predominance of (10*e*) in both polar and nonpolar media.

TABLE 4

U.v. spectral data for 1,3-dithian 1-oxides

	Ethanol solvent		Cyclohexane solvent	
Compound	$\nu_{max.}$/nm	ε	$\lambda_{max.}$/nm	ε
(10)	231	750	*ca.* 230	*a*
(13)	232	1060	230	1100
(14)	242	1030	243	1300

[a] Appears as a shoulder superimposed on end absorption.

Conclusions.—N.m.r. spectral data show that the present series of 1,3-dithian 1-oxides exist in chair conformations. From dipole moment, n.m.r., and u.v. spectral data it is concluded that the parent, (10), and 2,2-dimethyl-1,3-dithian 1-oxide (11) exist predominantly (at least 80%) as the conformer with the S=O bond equatorial. The difference in the preference of the S=O bond in (10) and (11) and that found in thian 1-oxide [2-4] appears, at first sight, to result from the introduction of a polar function at the 3-position in the ring. However, the further contrast between the S=O bond preference in 1,3-dithian 1-oxides and in 1,3-oxathian 3-oxide [7] indicates the inadequacies of such an argument and underlines the complex nature of interactions between polar functions. Further studies of factors influencing the conformational preferences of polar bonds are currently under way.

We thank the S.R.C. for a research studentship (to A. P. T.), and Dr. I. D. Blackburne and Mr. D. M. Read for helpful discussions and calculations of the theoretical dipole moments.

[3/2342 *Received, 15th November,* 1973]