# Crystal and Molecular Structures of Two Thiopyranylidenedihydropyridine SS-Dioxides

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The crystal and molecular structures of 1,2-dihydro-1-methyl-2-(5-phenylthiopyran-2-ylidene)pyridine SS-dioxide (1) and 1,4-dihydro-1-methyl-4-(2-methyl-5-phenylthiopyran-4-ylidene)pyridine SS-dioxide chloroform solvate (2) have been determined from X-ray three-dimensional diffraction data. Both structures have been solved by direct methods and refined by block-diagonal least-squares to R 5·4 [(1); 2512 reflections] and 7·8% [(2); 2259 reflections]. Crystals are monoclinic space group $P2_1/c$, Z = 4; (1): $a = 8·56(1)$, $b = 7·46(1)$, $c = 22·50(1)$ Å, $\beta = 96·1$ (2)°; (2): $a = 11·58(1)$, $b = 16·13(1)$, $c = 10·82(1)$ Å, $\beta = 91·2(2)$°. The results suggest, that particularly in (2), the sulphur atom of the thiopyran ring participates in π delocalisation.

THIOPYRANYLIDENE-1,4-DIHYDROPYRIDINES (1a) and (2a) have been regarded [1] as probes for the sulphonyl conjugation possibly involved in the special stabilisation

(1a)　　　　　　　　(1b)

(2a)　　　　　　　　(2b)
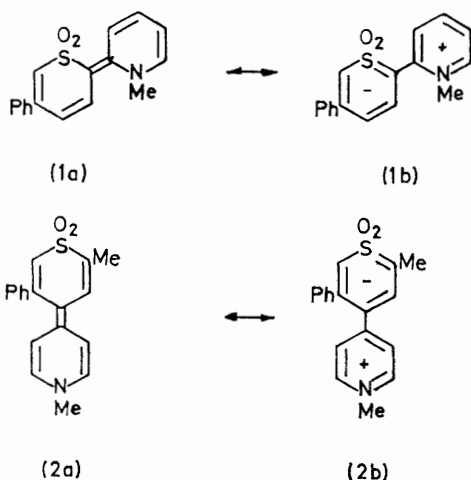
of the thiopyranyl anion.[2] Some spectroscopic properties provide evidence [1] for contributions from dipolar canonical structures (1b) and (2b). The considerable decrease of sulphonyl stretching vibrations found in

(1) relative to those for the conjugated pyridinium salt was considered to be evidence of the involvement of the sulphonyl group in the delocalisation occurring within the π frame rather than of the 1,3-π overlap between the p orbitals α,α' to the sulphonyl group. To confirm the structural model on which the spectroscopic interpretation was based, the crystal and molecular structures of 1,2-dihydro-1-methyl-2-(5-phenylthiopyran-2-ylidene)-pyridine SS-dioxide (1) and 1,4-dihydro-1-methyl-4-(2-methyl-5-phenylthiopyran-4-ylidene)pyridine SS-dioxide chloroform solvate (2) have been studied.

EXPERIMENTAL

1,2-*Dihydro*-1-*methyl*-2-(5-*phenylthiopyran*-2-*ylidene*)-*pyridine* SS-*Dioxide* (1)

Crystals are red tabular prisms, elongated on [010]. Preliminary cell-dimension and space group data were obtained from oscillation and Weissenberg photographs. Lattice parameters were then refined by least-squares by use of 16 $(\theta,\chi,\phi)_{hkl}$ measurements taken on a Siemens single-crystal diffractometer.

[1] G. Pagani, preceding paper.
[2] S. Bradamante, S. Maiorana, A. Mangia, and G. Pagani, *J. Chem. Soc.* (B), 1971, 74; S. Bradamante, A. Mangia, and G. Pagani, *ibid.,* p. 545; G. Gaviraghi and G. Pagani, *J.C.S. Perkin II,* 1973, 50.

Crystal Data.—$C_{17}H_{15}NO_2S$, $M = 299.1$. Monoclinic, $a = 8.56(1)$,* $b = 7.46(1)$, $c = 22.50(1)$ Å, $\beta = 96.1(2)°$, $U = 1428$ Å³, $D_m = 1.38$, $Z = 4$, $D_c = 1.39$, $F(000) = 624$. Cu-K_α radiation, $\lambda = 1.5418$ Å, μ(Cu-K_α) = 18.2 cm⁻¹. Absent spectra: $h0l\ l \neq 2n$, $0k0\ k \neq 2n$ define space group $P2_1/c$ (C_{2h}^5, No. 14).

Intensity data were collected up to θ 70° by use of the ω—2θ scan method and the ' five-points ' technique [3] with nickel-filtered Cu-K_α radiation on a Siemens single-crystal diffractometer. 2888 Independent reflections were measured, of which 376 were not used in the crystal analysis having intensities $<2[\sigma^2(I) + 10^{-4}I^2]^{\frac{1}{2}}$, where I is the relative intensity and $\sigma^2(I)$ its variance. The statistical factor,

TABLE 1

Basic set of reflections

		Compound (1)					Compound (2)	
	h		$|E(h)|$	$\phi(h)$		**h**		$|E(h)|$	$\phi(h)$
2	6	1	3·26	0	2	17	3	3·80	0
6	1	4	3·10	0	1	13	5	3·24	0
1	2	2	2·86	0	2	11	4	3·21	0
10	1	−8	3·11	a	2	10	5	3·76	a
6	2	−10	3·02	b	2	4	10	3·37	b
9	3	−10	2·78	c	2	4	2	2·85	c
1	2	−1	2·56	d	3	2	9	2·54	d

$\Sigma 0.7979\sigma(F_o)/\Sigma|F_o|$, taken as a measure of the precision in the data, was 1·8%. The dimensions of the crystal, roughly in the x, y, z directions, were $0.3 \times 0.6 \times 0.1$ mm; absorption was ignored.

tion ', in which new phases are calculated as in equation (1)

$$\phi_h = \langle w(k_{ij})(\phi_{hi} + \phi_{hj} \pm k_{ij})\rangle/\langle w(k)_{ij}\rangle \qquad (1)$$

where $\phi_h + \phi_{hi} + \phi_{hj} = k_{ij}$ are the structure invariants and the weights $w(k_{ij})$ are the square root of the inverse of the variance of the k_{ij}. The basic set was split into sixteen ' starting sets ' by allocation of signs to the symbols a, b, c, and d. Table 2 reports the results for the sixteen starting sets. The figures of merit calculated in the routine, and taken as a measure of the internal consistency, are defined in equation (2) and should be a maximum. For comparison, results obtained with the usual ' tangent refinement '

$$G = \sum_h \left[\sum_{ij \neq lm} w(k_{ij})w(k_{lm}) \cos \{(\phi_{hi} + \phi_{hj}) - (\phi_{hl} + \phi_{hm})\}/\Sigma\{w^2(k_{ij}) + w^2(k_{lm})\} \right] \qquad (2)$$

are reported in which $R_F = \Sigma||E_o| - |E_c||/\Sigma|E_o|$, ($R_F$ is the Karle R factor) and $AF = (\Sigma\alpha_h - \Sigma\alpha_r)/(\Sigma\alpha_l - \Sigma\alpha_r)$ is the ' absolute figure ' of merit as defined in ref. 7: α_l are the estimated α,[8] α_r is the value of α_h assuming random phases, and α_h is $|E_h|(T_h^2 + B_h^2)^{\frac{1}{2}}$ in which T_h and B_h are the numerator and the denominator of the tangent formula respectively. Both procedures, ' weighted numerical addition ' and ' tangent refinement ' define the 14th set as being probably correct, but by use of the former procedure, the computing time of this part of calculation is reduced approximately by a factor of 50.

An E map computed by use of the most consistent set of phases clearly revealed the positions of all non-hydrogen atoms. Of 366 reflections with $|E| \geqslant 1.48$, used for phase

TABLE 2

Results for the sixteen starting sets in the phase determination procedure

					Compound (1)			Compound (2)		
Set	a	b	c	d	R	AF	G . 10²	R	AF	G . 10²
1	+	+	+	+	38·7	1·0094	0·5251	42·7	0·9048	0·5727
2	−	+	+	+	54·7	0·5478	0·1562	51·5	0·7231	0·1259
3	+	−	+	+	37·3	1·0506	0·3787	42·2	0·9481	0·2680
4	+	+	−	+	46·7	0·7284	0·1699	39·9	1·0110	0·6125
5	+	+	+	−	37·7	1·0333	0·9559	44·1	0·8965	0·4580
6	−	−	+	+	57·7	0·3692	0·0877	41·7	0·9411	0·4417
7	−	+	−	+	28·1	1·2391	1·2694	40·4	0·9758	0·3820
8	−	+	+	−	49·0	0·6948	0·6812	42·9	0·9232	0·6984
9	+	−	−	+	54·7	0·4998	0·1694	31·7	1·1537	1·0124
10	+	−	+	−	37·3	1·0588	1·1229	47·1	0·8378	0·7592
11	+	+	−	−	53·9	0·4903	0·5304	40·1	1·0012	0·7957
12	−	−	−	+	39·0	0·9826	0·7395	51·4	0·7189	0·0927
13	−	−	+	−	28·1	1·2352	0·9202	46·8	0·8395	0·3280
14	−	+	−	−	28·1	1·2483	1·4467	51·3	0·6480	0·2180
15	+	−	−	−	38·9	1·0051	0·4972	31·8	1·1595	1·3612
16	−	−	−	−	38·9	0·9985	0·8589	31·7	1·1438	0·9507

Structure Analysis and Refinement.—The data were put on an absolute scale by Wilson's statistics and normalised structure factor magnitudes $|E_{hkl}|$ were derived by use of a program written by Andreetti.[4] The structure was solved by the multisolution and phase permutation technique, with the reflections in the basic set (Table 1) choosen by ' MULTAN '.[5] The starting sets listed in Table 2 were used directly as input to a routine [6] called 'weighted numerical addi-

determination, 365 were found to be correctly phased and one, defined by only one relationship, was wrongly phased. At this stage in the tangent refinement, five phases were found to have been incorrectly assigned.

A structure-factor calculation based on the co-ordinates derived from the E map, with $\bar{B}$ 3·2 Å² for all atoms gave R 0·22. Several cycles of block-diagonal least-squares reduced R to 0·077. A difference-Fourier synthesis was then computed; it contained peaks near the positions where the hydrogen atoms were expected to occur, although

[3] W. Hoppe, *Acta Cryst.*, 1969, *A*, **25**, 67.
[4] G. D. Andreetti, personal communication.
[5] P. Main, M. M. Woolfson, and G. Germain, MULTAN, A Computer Programme for the Automatic Solution of Crystal Structures, 1971, University of York.

[6] G. D. Andreetti, to be published.
[7] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, *A*, **27**, 368.
[8] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1970, *B*, **26**, 274.

some difficulties were experienced in locating the hydrogen atoms of the C(17) methyl group. All the atom parameters were then refined (the heavy atoms anisotropically and the hydrogens isotropically) with a weighting function of the type $1/w = A + B|F_o| + C|F_o|^2$ with the parameters A, B, and C derived from a plot of $\langle \Delta F \rangle$ versus $\langle |F_o| \rangle$. The final value of R was 0·054 [goodness of fit = $\Sigma w \Delta F^2/(m - n)$) = 0·91].

The final positional and thermal parameters together with their standard deviations are given in Table 3.

1,4-Dihydro-1-methyl-4-(2-methyl-5-phenylthiopyran-4-ylidene)pyridine SS-Dioxide Chloroform Solvate (2)

Crystals were orange flattened prisms, elongated along [001]. Cell parameters and space group were determined

absolute scale by Wilson's statistics, and normalised structure factor magnitudes were derived as for (1). The structure was solved by multisolution and phase permutation methods. The basic set is reported in Table 1, and Table 2 gives the starting sets and the results of phase refinement.

The E map computed by use of the phases of the most consistent set (No. 15) clearly revealed the positions of all non hydrogen atoms. A structure-factor calculation based on the co-ordinates derived from the E map with $\bar{B}$ 4·7 Å² for all atoms gave R 19·4%. Refinement was carried out by means of cycles of block-diagonal least-squares first isotropically and then anisotropically until R was 9·8%. A ΔF synthesis was then computed and revealed significant residual peaks near the positions where the hydrogen atoms were expected to occur [around the C(17) and C(19) methyl

TABLE 3

Compound (1)

(a) Fractional co-ordinates ($\times 10^4$) and thermal parameters † (in 10^{-2} Å²), with standard deviations in parentheses

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	7191(1)	2220(1)	3771(1)	192(2)	366(2)	313(2)	56(2)	64(2)	83(2)
O(1)	6834(2)	404(3)	3935(1)	412(8)	381(8)	626(10)	140(7)	240(8)	223(7)
O(2)	8455(2)	3035(3)	4159(1)	235(7)	834(14)	425(8)	23(8)	−13(6)	−73(9)
N	2957(2)	3753(3)	4114(1)	206(7)	340(8)	321(7)	22(6)	61(6)	4(6)
C(1)	9529(3)	3132(3)	2051(1)	268(9)	385(11)	364(10)	−62(8)	72(8)	−42(8)
C(2)	10154(3)	3164(4)	1504(1)	340(11)	460(12)	420(11)	−80(10)	147(9)	−59(10)
C(3)	9269(3)	3761(4)	993(1)	506(13)	423(12)	377(11)	−62(10)	197(10)	−23(9)
C(4)	7724(3)	4331(4)	1027(1)	493(13)	340(10)	335(10)	−18(10)	72(9)	12(8)
C(5)	7092(3)	4312(3)	1571(1)	372(10)	295(9)	334(9)	−7(8)	65(8)	16(8)
C(6)	7977(3)	3725(3)	2089(1)	289(9)	263(9)	322(9)	−48(7)	86(7)	−19(7)
C(7)	7306(3)	3666(3)	2676(1)	256(8)	293(9)	307(9)	−23(7)	67(7)	−1(7)
C(8)	7673(3)	2280(3)	3048(1)	253(9)	333(10)	351(9)	34(7)	81(7)	19(8)
C(9)	6241(3)	5052(3)	2814(1)	358(10)	322(10)	367(10)	52(8)	127(8)	68(8)
C(10)	5398(3)	4922(3)	3295(1)	318(9)	322(10)	330(9)	68(8)	88(7)	48(8)
C(11)	5517(2)	3551(3)	3724(1)	206(7)	323(9)	297(8)	35(7)	58(6)	39(7)
C(12)	4541(2)	3342(3)	4201(1)	209(8)	287(9)	295(8)	1(7)	48(6)	14(7)
C(13)	5118(3)	2729(3)	4778(1)	295(9)	387(10)	291(8)	−28(8)	37(7)	38(8)
C(14)	4196(3)	2640(4)	5237(1)	404(11)	439(12)	302(9)	−75(10)	73(8)	32(8)
C(15)	2627(3)	3232(4)	5139(1)	401(12)	518(14)	366(11)	−87(11)	173(9)	−32(10)
C(16)	2052(3)	3750(4)	4582(1)	285(9)	462(12)	429(11)	−15(9)	148(8)	−55(9)
C(17)	2111(3)	3997(4)	3511(1)	276(9)	501(13)	378(11)	60(9)	−12(8)	78(9)

† Temperature factors are of the form $\exp -\frac{1}{4}(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)$, where $b_{11} = a^{*2}B_{11}$, $b_{12} = a^*b^*B_{12}$, etc.

(b) Fractional co-ordinates ($\times 10^3$) and isotropic thermal parameters ‡ (in 10^{-1} Å²) for the hydrogen atoms

	x/a	y/b	z/c	B		x/a	y/b	z/c	B
H[C(1)]	1017(3)	271(3)	245(1)	38	H[C(13)]	624(3)	220(4)	485(1)	44
H[C(2)]	1124(4)	267(4)	147(1)	58	H[C(14)]	461(3)	218(4)	565(1)	39
H[C(3)]	970(4)	380(4)	57(1)	54	H[C(15)]	194(4)	335(4)	549(1)	62
H[C(4)]	709(4)	479(4)	65(1)	40	H[C(16)]	94(3)	433(4)	447(1)	55
H[C(5)]	597(3)	478(4)	159(1)	41	H1[C(17)]	101(4)	378(5)	352(2)	76
H[C(8)]	829(3)	118(4)	294(1)	45	H2[C(17)]	253(4)	317(4)	319(1)	53
H[C(9)]	608(3)	620(4)	254(1)	50	H3[C(17)]	221(5)	522(6)	343(2)	86
H[C(10)]	466(3)	596(4)	336(1)	45					

‡ Temperature factors are of the form $\exp(-B \sin^2\theta/\lambda^2)$.

as before and lattice parameters refined from 17 measurements.

Crystal Data.—$C_{18}H_{17}NO_2S$,CHCl₃, $M = 432\cdot7$. Monoclinic, $a = 11\cdot58(1)$, $b = 16\cdot13(1)$, $c = 10\cdot82(1)$ Å, $\beta = 91\cdot2(2)°$, $U = 2021$ Å³, D_m (flotation) = 1·41, $Z = 4$, $D_c = 1\cdot42$, $F(000) = 888$, μ(Cu-K_α) = 51·6 cm⁻¹. Absent spectra: $h0l\ l \neq 2n$, $0k0$, $k \neq 2n$ define space group $P2_1/c$ (C_{2h}^5, No. 14).

Intensity data were collected similarly, and of 3269 independent reflections 1010 were not used in the crystal analysis. The statistical factor was 4·1%. The dimensions of the crystal were 0·3 × 0·1 × 0·6 mm. Absorption effects were neglected.

Structure Analysis and Refinement.—Data were placed on

carbon atoms was found a smeared residual cloud and attempts to define individual hydrogen atoms were unsuccessful]. All the atom parameters were then refined (heavy atoms anisotropically and hydrogen atoms isotropically), with the weighting function used for (1). The final value of R was 7·8% (goodness of fit 0·66). The final positional and thermal parameters together with their standard deviations are reported in Table 4.

For both compounds the observed and calculated structure factors are listed in Supplementary Publication No. SUP 20602 (27 pp., 1 microfiche).*

RESULTS

Molecular Geometry.—Tables 5 and 6 list bond distances and angles for the two compounds.

Compound (1).—Table 7 gives the least-squares analysis of several molecular planes. The thiopyran ring is not planar but has a boat conformation. In Figure 1(a) the projections of the ring are shown with the dihedral angles between the four atoms base plane [C(7),C(8),C(10),C(11)] and the ' bow ' [C(11),S,C(8)] and the ' stern ' [C(7),C(9),-C(10)] planes respectively. The O–S–O plane is almost perpendicular to the C–S–C plane (89·5°) and the angles

p-terphenyl.[11] The contacts H[C(13)] · · · O(1) 2·55(3), H[C(13)]–O(2) 2·65(3), and H[C(10)]–H1C[(17)] 2·19(5) Å, clearly indicate that the non-coplanarity of the groups is caused by strains due to intramolecular steric effects. The phenyl ring is planar and twisted around the C(6)–C(7) bond by 38·3°. The molecular packing is shown in Figure 2. The contacts are consistent with van der Waals interactions and packing distances <3·55 Å are reported in Table 8. The thermal motion of the molecule has been analysed in terms of rigid-body libration (Table 9). The model does not fit the whole molecule but the dihydropyridine and the

TABLE 4

Compound (2)

(*a*) Fractional co-ordinates ($\times 10^4$) and thermal parameters * (in 10^{-2} Å^2), with standard deviations in parentheses

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl(1)	6326(2)	−1035(1)	7997(2)	1031(11)	627(8)	859(10)	81(8)	−249(9)	110(7)
Cl(2)	4678(2)	−952(1)	5988(2)	906(10)	634(8)	858(10)	−114(7)	−230(8)	−99(7)
Cl(3)	4480(2)	135(1)	8066(2)	798(10)	698(9)	1322(15)	−29(7)	298(10)	−299(10)
S	1695(1)	−1128(1)	3699(1)	435(4)	280(4)	301(4)	5(3)	−62(3)	3(3)
O(1)	2838(3)	−1155(2)	3210(3)	444(14)	427(14)	538(16)	21(11)	−101(12)	−57(12)
O(2)	1621(3)	−1609(2)	4845(3)	857(20)	343(13)	331(12)	−14(13)	−85(13)	78(11)
N	−2727(3)	1398(2)	396(3)	529(17)	279(13)	388(15)	19(12)	−61(13)	54(12)
C(1)	1282(4)	−118(3)	3947(4)	509(20)	271(15)	344(17)	−26(14)	−17(15)	−61(13)
C(2)	414(4)	234(2)	3256(4)	495(20)	308(15)	313(17)	−11(14)	−76(15)	−27(14)
C(3)	−289(3)	−137(2)	2315(3)	474(19)	231(14)	301(16)	15(13)	−41(14)	−13(12)
C(4)	−146(4)	−1011(2)	2082(4)	451(18)	262(15)	283(16)	4(13)	−32(14)	−32(12)
C(5)	687(4)	−1475(2)	2645(4)	452(18)	259(15)	366(17)	−6(13)	−100(15)	−64(14)
C(6)	−1008(4)	−1491(2)	1326(4)	490(19)	210(14)	347(17)	−17(13)	−66(14)	24(13)
C(7)	−628(4)	−1952(3)	299(4)	612(24)	339(17)	467(21)	−22(17)	−44(19)	−118(17)
C(8)	−1461(5)	−2406(3)	−383(5)	732(27)	375(20)	508(23)	−16(19)	−124(20)	−159(18)
C(9)	−2601(5)	−2427(3)	−56(5)	681(26)	316(18)	618(26)	−34(18)	−214(21)	−63(18)
C(10)	−2957(4)	−1992(3)	989(5)	519(22)	376(19)	584(24)	−25(17)	−126(19)	89(18)
C(11)	−2150(4)	−1513(3)	1667(4)	447(19)	301(16)	468(20)	2(14)	−66(16)	50(16)
C(12)	−1104(4)	372(2)	1661(3)	484(19)	249(14)	292(16)	4(13)	−15(14)	23(12)
C(13)	−1572(4)	1109(2)	2210(4)	503(19)	253(14)	343(17)	27(14)	−47(15)	−12(13)
C(14)	−2374(4)	1581(3)	1588(4)	530(21)	302(16)	436(20)	17(15)	−39(17)	−41(15)
C(15)	−2294(4)	716(3)	−176(4)	539(20)	327(16)	326(18)	−14(16)	−45(15)	0(14)
C(16)	−1503(4)	210(3)	429(4)	545(21)	324(16)	265(16)	0(15)	−53(15)	7(13)
C(17)	−3593(4)	1918(3)	−244(5)	599(24)	400(20)	598(26)	81(18)	−254(21)	49(19)
C(18)	1972(4)	337(3)	4951(4)	599(25)	375(18)	468(22)	−53(17)	−118(19)	−97(17)
C(19)	5444(4)	−376(3)	7125(5)	486(22)	417(20)	717(29)	5(17)	−53(20)	40(20)

(*b*) Fractional co-ordinates ($\times 10^3$) and isotropic thermal parameters * (in 10^{-1} Å^2) for the hydrogen atoms

	x/a	y/b	z/c	B		x/a	y/b	z/c	B
H[C(2)]	16(4)	83(3)	344(5)	67	H[C(11)]	−243(4)	−117(3)	251(4)	59
H[C(5)]	75(4)	−207(3)	244(5)	65	H[C(13)]	−135(4)	127(3)	319(4)	50
H[C(7)]	27(4)	−196(3)	9(4)	57	H[C(14)]	−276(4)	209(3)	206(5)	70
H[C(8)]	−116(4)	−276(3)	−121(5)	73	H[C(15)]	−256(4)	59(3)	−113(4)	58
H[C(9)]	−323(4)	−281(3)	−49(5)	77	H[C(16)]	−105(4)	−28(3)	−12(4)	61
H[C(10)]	−385(3)	−203(2)	117(4)	38	H[C(19)]	605(5)	7(4)	669(5)	94

* Temperature factors are defined in the footnote to Table 3.

O–S–O [113·8(4)°] and C–S–C [101·9(3)°] deviate significantly from the tetrahedral value. The same situation has been observed in other sulphones with C–S–C values ranging from 101 to 107°. The dihydropyridine ring is nearly planar, the greatest deviation being 0·033 Å. The nitrogen atom is out of the C(12),C(16),C(17) plane by 0·052 Å. In the ring there is an alternation of short [C(13)–C(14) 1·366(4), C(15)–C(16) 1·353(3) Å] and long [C(12)–C(13) 1·415(3), C(14)–C(15) 1·409(4) Å] carbon–carbon bonds. The value of the C(11)–C(12) [1·437(3) Å] distance is significantly less than that (1·506 Å) for biphenyl [9] while, on the other hand, the torsion angle around the C(11)–C(12) bond is 36·6°, a rather high value, comparable with the 42° found for biphenyl,[9] 36 and 40° in *pp'*-bitolyl,[10] and 38·5° in

phenylthiopyran systems separately. Bond distances after correction for the libration motion are given in square brackets in Table 5.

Compound (2).—The thiopyran ring has a ' boat ' conformation as in (1), but the angles between the base atoms and the ' bow ' and the ' stern ' are significantly different. Figure 1(b) shows the projections of the ring. Bond distances and angles are not much different in the two compounds, and the molecular conformation are similar, *i.e.* boat-shaped ring. The O–S–O plane is almost perpendicular to the C–S–C plane (89·5°) and significant deviations from the tetrahedral value are observed for the angles O–S–O [111·5(5)°] and C–S–C [103·1(5)°] as in (1). Table 10 gives the least-squares analysis of several molecular planes. The dihydropyridine ring is nearly planar, the

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[10] G. Casalone, C. Mariani, A. Mugnoli, and M. Simonetta, *Acta Cryst.*, 1969, *B*, **25**, 1741.

[11] G. D. Andreetti, L. Cavalca, and P. Sgarabotto, *Gazzetta*, 1970, **100**, 697.

TABLE 5

Compound (1)

(a) Intramolecular distances (Å). Values corrected for thermal libration are given in square brackets

C(1)–C(2)	1·393(4)	[1·395]	C(7)–C(8)	1·346(3)	[1·357]
C(2)–C(3)	1·382(3)	[1·389]	S–O(2)	1·450(3)	[1·469]
C(3)–C(4)	1·399(4)	[1·407]	S–O(1)	1·445(3)	[1·461]
C(4)–C(5)	1·390(4)	[1·391]	C(11)–C(12)	1·437(3)	
C(5)–C(6)	1·392(4)	[1·399]	C(12)–C(13)	1·415(3)	[1·424]
C(1)–C(6)	1·411(4)	[1·419]	C(13)–C(14)	1·366(4)	[1·374]
C(6)–C(7)	1·496(4)	[1·498]	C(14)–C(15)	1·409(4)	[1·421]
C(7)–C(9)	1·434(4)	[1·445]	C(15)–C(16)	1·353(3)	[1·361]
C(9)–C(10)	1·367(4)	[1·375]	C(16)–N	1·372(3)	[1·379]
C(10)–C(11)	1·403(3)	[1·413]	C(12)–N	1·384(3)	[1·394]
C(11)–S	1·737(3)	[1·750]	C(17)–N	1·480(3)	[1·488]
C(8)–S	1·721(3)	[1·733]			

(b) Bond angles (deg.)

C(1)–C(2)–C(3)	120·8(0·5)	C(11)–S–O(2)	110·8(0·4)
C(2)–C(3)–C(4)	119·4(0·6)	C(8)–S–O(1)	110·1(0·4)
C(3)–C(4)–C(5)	120·3(0·6)	C(8)–S–O(2)	108·7(0·4)
C(4)–C(5)–C(6)	120·8(0·5)	O(2)–S–O(1)	113·8(0·4)
C(5)–C(6)–C(1)	118·7(0·6)	C(10)–C(11)–C(12)	126·0(0·5)
C(2)–C(1)–C(6)	120·0(0·6)	S–C(11)–C(12)	115·7(0·4)
C(5)–C(6)–C(7)	121·5(0·5)	C(11)–C(12)–N	120·6(0·5)
C(1)–C(6)–C(7)	119·8(0·6)	C(11)–C(12)–C(13)	123·1(0·5)
C(6)–C(7)–C(9)	118·9(0·5)	C(12)–C(13)–C(14)	122·4(0·5)
C(6)–C(7)–C(8)	119·0(0·5)	C(13)–C(14)–C(15)	119·0(0·6)
C(7)–C(9)–C(10)	121·4(0·6)	C(14)–C(15)–C(16)	118·8(0·6)
C(9)–C(10)–C(11)	126·2(0·6)	C(15)–C(16)–N	122·1(0·5)
C(10)–C(11)–S	117·2(0·4)	C(16)–N–C(12)	121·1(0·6)
C(8)–S–C(11)	101·9(0·3)	C(13)–C(12)–N	116·3(0·5)
C(7)–C(8)–S	123·0(0·4)	C(16)–N–C(17)	116·3(0·5)
C(9)–C(7)–C(8)	122·1(0·5)	C(12)–N–C(17)	122·3(0·6)
C(11)–S–O(1)	110·9(0·4)		

(c) Carbon–hydrogen bonds (Å)

C(1) *	1·05(2)	C(13)	1·04(3)
C(2)	1·01(3)	C(14)	1·02(2)
C(3)	1·06(3)	C(15)	1·04(3)
C(4)	1·02(3)	C(16)	1·05(3)
C(5)	1·03(2)	C(17)	0·96(3)
C(8)	1·02(3)	C(17)	1·04(3)
C(9)	1·06(3)	C(17)	0·94(5)
C(10)	1·02(3)		

* H attached to.

TABLE 6

Compound (2)

(a) Intramolecular distances (Å). Values corrected for thermal libration are given in square brackets

O(1)–S	1·436(4)	[1·441]	C(10)–C(11)	1·407(7)	[1·410]
O(2)–S	1·467(4)	[1·471]	C(6)–C(11)	1·381(7)	[1·385]
C(1)–S	1·721(5)	[1·725]	C(3)–C(12)	1·427(5)	[1·430]
C(1)–C(2)	1·364(7)	[1·366]	C(12)–C(13)	1·440(6)	[1·444]
C(2)–C(3)	1·422(6)	[1·425]	C(13)–C(14)	1·367(7)	[1·369]
C(3)–C(4)	1·442(5)	[1·446]	C(14)–N	1·377(6)	[1·380]
C(4)–C(5)	1·355(6)	[1·358]	C(15)–N	1·363(6)	[1·367]
C(5)–S	1·709(5)	[1·712]	C(15)–C(16)	1·382(7)	[1·384]
C(1)–C(18)	1·523(7)	[1·526]	C(16)–C(12)	1·426(6)	[1·429]
C(4)–C(6)	1·494(6)	[1·497]	C(17)–N	1·470(6)	[1·472]
C(6)–C(7)	1·415(6)	[1·420]	C(19)–Cl(1)	1·739(6)	
C(7)–C(8)	1·408(7)	[1·410]	C(19)–Cl(2)	1·766(6)	
C(8)–C(9)	1·374(8)	[1·378]	C(19)–Cl(3)	1·735(6)	
C(9)–C(10)	1·400(8)	[1·405]			

(b) Bond angles (deg.)

O(1)–S–O(2)	111·5(0·5)	C(10)–C(11)–C(6)	120·3(0·9)
S–C(1)–C(2)	120·9(0·7)	C(7)–C(6)–C(11)	120·8(0·9)
C(1)–C(2)–C(3)	128·4(1·0)	C(2)–C(3)–C(12)	118·4(0·8)
C(2)–C(3)–C(4)	118·1(0·7)	C(4)–C(3)–C(12)	123·6(0·7)
C(3)–C(4)–C(5)	123·0(0·7)	C(3)–C(12)–C(13)	121·4(0·7)
C(4)–C(5)–S	126·1(0·8)	C(3)–C(12)–C(16)	123·8(0·9)
C(1)–S–C(5)	103·1(0·5)	C(12)–C(13)–C(14)	121·0(0·8)
S–C(1)–C(18)	115·1(0·6)	C(13)–C(14)–N	121·8(0·9)
C(2)–C(1)–C(18)	124·1(1·0)	C(14)–N–C(15)	119·6(0·8)
C(3)–C(4)–C(6)	121·6(0·7)	N–C(15)–C(16)	120·6(0·8)
C(5)–C(4)–C(6)	114·9(0·8)	C(15)–C(16)–C(12)	122·2(0·9)
C(4)–C(6)–C(7)	119·2(0·8)	C(13)–C(12)–C(16)	114·8(0·7)
C(4)–C(6)–C(11)	120·0(0·8)	C(14)–N–C(17)	120·4(0·9)
C(6)–C(7)–C(8)	117·7(0·9)	C(15)–N–C(17)	120·0(0·8)
C(7)–C(8)–C(9)	122·0(1·1)	Cl(1)–C(19)–Cl(2)	109·7(0·5)
C(8)–C(9)–C(10)	120·0(1·1)	Cl(1)–C(19)–Cl(3)	110·5(0·4)
C(9)–C(10)–C(11)	119·5(0·9)	Cl(2)–C(19)–Cl(3)	109·8(0·4)

(c) Carbon–hydrogen bonds (Å)

C(2) *	1·03(5)	C(11)	1·12(5)
C(5)	0·99(5)	C(13)	1·12(4)
C(7)	1·07(5)	C(14)	1·07(5)
C(8)	1·12(5)	C(15)	1·09(4)
C(9)	1·06(5)	C(16)	1·13(5)
C(10)	1·06(4)	C(19)	1·12(6)

* H attached to.

TABLE 7

Compound (1)

(a) Distances (Å) of relevant atoms from mean planes through the molecule

Plane (1): C(1)—(6)

  C(1) −0·004, C(2) 0·001, C(3) 0·004, C(4) −0·003, C(5) −0·002, C(6) 0·004, C(7) −0·018

Plane (2): C(7)—(11), S

  C(7) −0·006, C(8) −0·190, C(9) 0·210, C(10) 0·077, C(11) −0·188, S 0·097, O(1) −0·852, O(2) 1·481

Plane (3): C(12)—(16), N

  C(12) 0·031, C(13) −0·008, C(14) −0·031, C(15) 0·029, C(16) 0·012, N −0·033, C(17) −0·319, C(11) 0·140

Plane (4): C(7),C(8),C(10),C(11)

  C(7) −0·024, C(8) 0·019, C(10) 0·020, C(11) −0·015, S 0·460, O(1) −0·292, O(2) 1·897, C(9) 0·059

(b) Normal equations of planes in the form $lX + mY + nZ = p$, where X, Y, and Z are in Å, referred to orthogonal axes x, y, and z *

Plane	l	m	n	p
(1)	0·3137	0·9313	0·1853	5·4352
(2)	0·6266	0·6551	0·4222	7·8425
(3)	0·2299	0·9431	0·2401	5·2401
(4)	0·6644	0·5290	0·5280	8·3611

(c) Angles (deg.) between planes

      (1)–(2) 27·8   (2)–(3) 30·3

greatest deviation being 0·015 Å. The nitrogen atom is out of the C(14),C(15),C(17) mean plane by 0·014 Å. The dihedral angle formed by the four atoms C(1),C(2),C(4),C(5), base plane, and the dihydropyridine rings is 27·5°, while the distance C(3)–C(12) is 1·427(5) Å, a situation very similar to that observed for (1). The phenyl ring is twisted with respect to the thiopyran system by 58·6°. The mode of
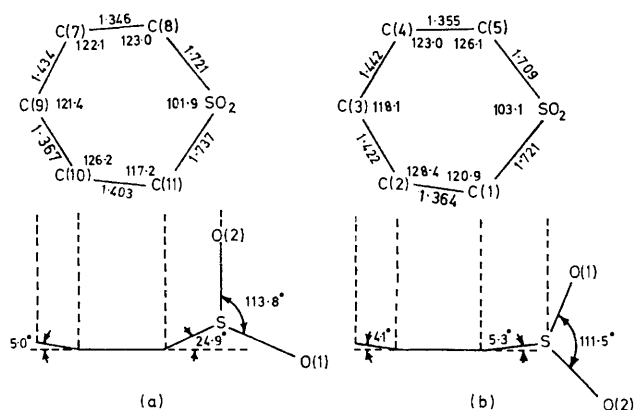

FIGURE 1   Projections of the thiopyran rings:

(a) compound (1), (b) compound (2)

FIGURE 2 Compound (1): Projection of the structure along [010]

TABLE 8

Compound (1): contacts <3.55 Å

C(16) $\cdots$ O(2^{I})	3·17		C(15) $\cdots$ O(2^{VI})	3·38
N $\cdots$ C(4^{II})	3·36		C(14) $\cdots$ C(12^{VI})	3·39
C(5) $\cdots$ O(1^{III})	3·53		C(13) $\cdots$ C(13^{VI})	3·54
O(1) $\cdots$ C(2^{IV})	3·31		C(14) $\cdots$ C(13^{VI})	3·51
C(14) $\cdots$ O(1^{V})	3·12		O(1) $\cdots$ C(3^{IV})	3·54
C(15) $\cdots$ O(1^{V})	3·42			

Roman numerals as superscripts denote the following equivalent positions relative to the reference molecule at x, y, z:

I	$x - 1, y, z$	IV	$2 - x, y - \frac{1}{2}, \frac{1}{2} - z$
II	$1 - x, y - \frac{1}{2}, \frac{1}{2} - z$	V	$1 - x, -y, 1 - z$
III	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$	VI	$1 - x, 1 - y, 1 - z$

TABLE 9

Compound (1): results of rigid-body analysis of thermal parameters

(a) Dihydropyridine group

	Eigen-values	Direction cosines of eigenvectors *		
Librational tensor	27·89	0·4704	0·6425	0·6049
L/deg.^{2}	21·54	−0·5844	−0·2868	0·7592
	4·26	0·6612	−0·7106	0·2405
Translational	0·0434	0·9733	0·1818	0·1403
tensor T/Å^2	0·0324	0·1888	−0·2854	−0·9396
	0·0110	−0·1308	0·9410	−0·3121

(b) Phenylthiopyrane

	Eigen-values	Direction cosines of eigenvectors *		
Librational tensor	35·78	−0·5297	0·0448	0·8470
L/deg.^{2}	5·92	0·6052	0·6797	0·4145
	1·46	0·5943	0·7321	0·3329
Translational	0·0365	0·8370	0·2835	0·4681
tensor T/Å^2	0·0215	0·2468	0·5678	−0·7853
	0·0068	−0·4884	0·7728	0·4052

* Direction cosines relative to orthogonal axes x, y, z^*. The origin is at the baricentre. $\sigma(\Delta U_{ij}) = 0.0017$.

TABLE 10

Compound (2)

(a) Distances (Å) of relevant atoms from mean planes through the molecule

Plane (1): C(6)—(11)

C(6) 0·008, C(7) −0·015, C(8) 0·007, C(9) 0·012, C(10) −0·015, C(11) 0·003, C(4) −0·033

Plane (2): S, C(1)—(5)

S 0·011, C(1) −0·055, C(2) 0·009, C(3) 0·081, C(4) −0·005, C(5) −0·041, C(19) −0·047, O(1) −1·231, O(2) −1·165

Plane (3): C(12)—(16), N

C(12) −0·008, C(13) 0·015, C(14) −0·013, C(15) 0·005, C(16) 0·000, N 0·001, C(17) −0·033, C(3) −0·015

Plane (4): C(1),C(2),C(4),C(5)

C(1) −0·007, C(2) 0·007, C(4) −0·007, C(5) 0·007, C(3) 0·053, C(18) −0·077, S 0·098, O(1) 1·345, O(2) −1·045

(b) Normal equations of planes in the form $lX + mY + nZ = p$, where X, Y, and Z are in Å, referred to orthogonal axes x, y, and z^*

Plane	l	m	n	p
(1)	−0·1796	0·7915	−0·5842	−2·5343
(2)	0·6360	0·2677	−0·7237	−2·1989
(3)	0·7533	0·5505	−0·3598	−1·2993
(4)	0·6624	0·2489	−0·7066	−2·1335

(c) Angles (deg.) between planes

(1)–(2) 58·6   (2)–(3) 27·5

TABLE 11

Compound (2): contacts <3.55 Å

N $\cdots$ O(2^{I})	3·47		H[C(19)] $\cdots$ O(1^{V})	2·17
C(14) $\cdots$ O(2^{I})	3·43		C(2) $\cdots$ C(18^{IV})	3·53
C(9) $\cdots$ Cl(1^{II})	3·30		Cl(3) $\cdots$ C(11^{IV})	3·51
C(15) $\cdots$ O(1^{III})	3·40		C(5) $\cdots$ C(15^{III})	3·51
C(13) $\cdots$ O(2^{IV})	3·29		C(17) $\cdots$ O(2^{I})	3·32
C(19) $\cdots$ O(1^{V})	3·20		C(7) $\cdots$ O(2^{VI})	3·53

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I	$-x, \frac{1}{2} + y, \frac{1}{2} - z$	IV	$-x, -y, 1 - z$
II	$x - 1, y, z - 1$	V	$1 - x, -y, 1 - z$
III	$-x, -y, -z$	VI	$x, -\frac{1}{2} - y, z - \frac{1}{2}$

TABLE 12

Compound (2): results of rigid-body analysis of thermal parameters

	Eigen-values	Direction cosines of eigenvectors *		
Librational tensor	14·04	0·8041	−0·1964	0·5612
L/deg.^{2}	7·36	0·1129	0·9771	0·1803
	2·82	−0·5838	−0·0816	0·8078
Translational	0·0560	−0·6515	0·0244	0·7582
tensor T/Å^2	0·0321	0·4586	−0·7835	0·4193
	0·0240	0·6043	0·6209	0·4993

* Direction cosines relative to orthogonal axes x, y, z^*. The origin is at the baricentre. $\sigma(\Delta U_{ij}) = 0.0013$.

packing in Figure 3 shows a projection on the (001) plane. The molecules are arranged to form layers separated by chloroform molecules. Chloroform is involved in some interactions with a dioxide oxygen atom. In fact the contact O(1) $\cdots$ H[C(19)] 2·2 Å is significantly shorter

than the sum of van der Waals radii for oxygen[12] and hydrogen[13] ($1.4 + 1.0 = 2.4$ Å). Other contacts are consistent with van der Waals interactions and packing distances < 3.55 Å are reported in Table 11. The thermal motion has been analysed in terms of rigid-body libration.

ruling out any feasible interaction between the corresponding π orbitals as a stabilisation mechanism in the molecules and, by analogy, in the thiopyran SS-dioxide anion. The conjugative abilities of the sulphonyl group have been studied theoretically,[14,15] and empirically,[16-18]
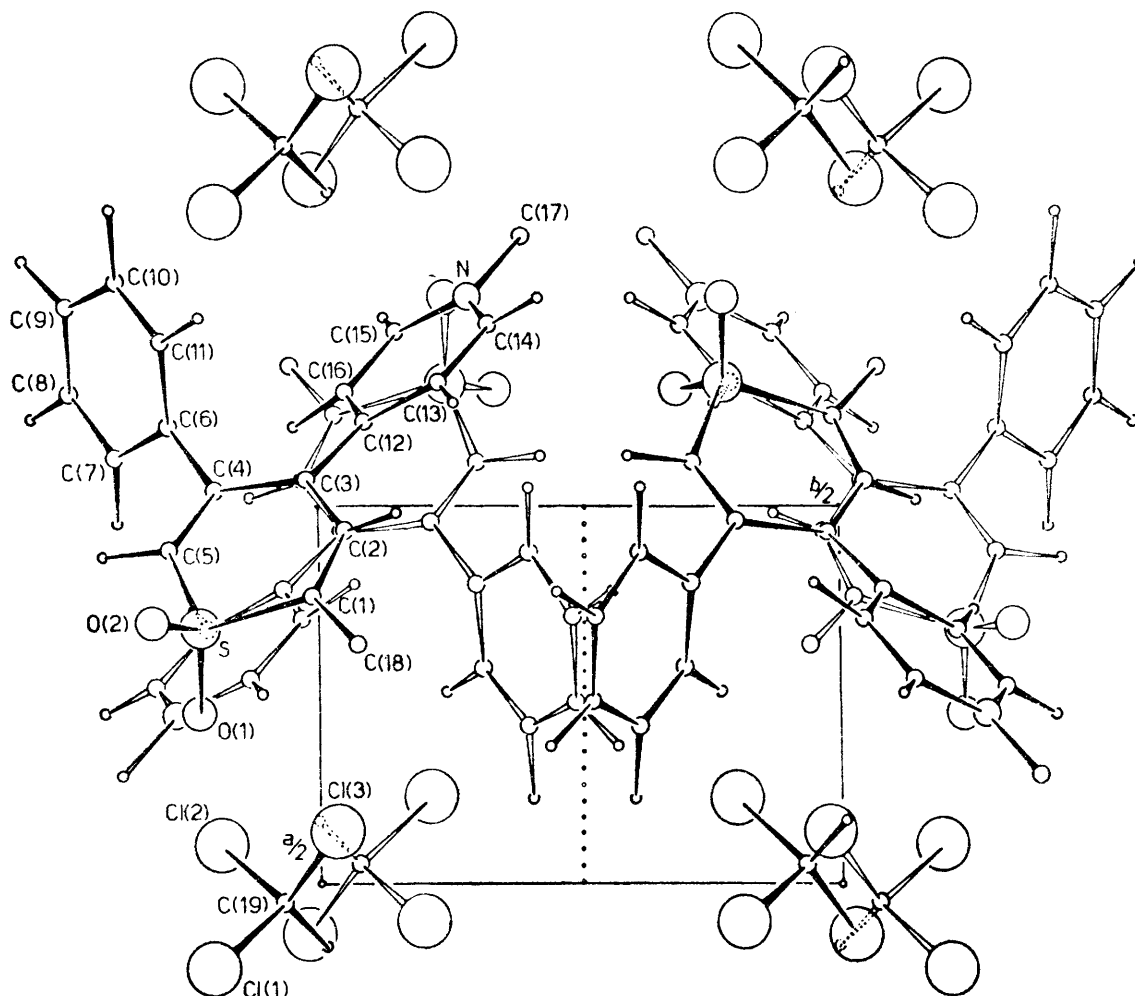
FIGURE 3   Compound (2): projection of the structure on (001)

(Table 12); bond distances after correction are listed in square brackets in Table 6. The model fits the whole molecule well.

and there are also comprehensive reviews.[19] Recently the problem has been discussed[20] in connection with thiepin SS-dioxide. According to the Koch and Moffitt scheme,[14] the thiopyran SS-dioxide anion and hence (1) and (2), all assumed as being planar, fall into the case (I) category for which strong conjugation with weakening of sulphur–oxygen bonds is expected.

DISCUSSION

The distances between carbon atoms α and α' to the sulphonyl group are 2.686 in (1) and 2.685 Å in (2), thus

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Pertinent molecular features to be discussed are: (i) carbon–carbon bond lengths, (ii) carbon–sulphur bond lengths, and (iii) sulphur–oxygen bond lengths.

(i) Compound (2) apparently better satisfies steric requirements for adopting a more planar thiopyran ring than does (1) and thus falls better into the case (I) category. Twist angles $\neq 0$ of the pyridine ring relative to the thiopyran ring are expected to reduce normal olefinic conjugation: in (1) and (2) evidence for this is given by the values of bond lengths between carbons joining the two rings (1·437 and 1·427 Å respectively), which are between 1·482 Å (accepted as single $C_{sp^2}-C_{sp^2}$ [21] bond) and 1·33 Å (accepted as double $C_{sp^2}=C_{sp^2}$ [22] bond). It follows that there is an appreciable contribution of dipolar structures to these molecules. Bond alternation is evident in both (1) and (2), in the sulphur and in the nitrogen heterocycle. It appears however that this is less than expected: in the sulphur heterocycles double bonds [means 1·357 for (1) and 1·360 Å for (2)] are apparently longer, and single bonds (1·419 and 1·432 Å) are shorter than in thiepin SS-dioxide [20] (1·340 and 1·433 Å). While these values should not be given undue emphasis, it is relevant however that in (1) and (2) the divinyl sulphone framework shows olefinic bond lengths of the same order or longer than in thiepin dioxide rather than comparable with those of 4,5-dihydrothiepin dioxide [23] (1·312 Å mean double, and 1·490 Å mean single bond).

(ii) In (1) and (2) carbon–sulphur bonds are of the same order or shorter (1·729 and 1·715 Å) than in thiepin dioxide (1·720 Å) and in thiopyran dioxide (1·730 Å).[24] These are appreciably short $C_{sp^2}-S^{IV}$ lengths, intermediate between the values for 4,5-dihydrothiepin dioxide (1·753 Å) and for the sulphonyl stabilised ylide tosyltriphenylphosphorane (1·69 Å).[25]

(iii) Sulphur–oxygen bonds in (1) and (2) have mean

values 1·448 and 1·452 Å: usual values are in the range 1·42—1·44 Å (*trans*-2-chloro-2,4,4-trimethyl-3-morpholinothietan 1,1-dioxide 1·422,[26] 2,2-dimethylthiochroman-4-one dioxide 1·437,[27] thiepin dioxide 1·442,[20] 4,5-dihydrothiepin dioxide 1·436,[23] and thiopyran dioxide 1·441 Å [24]) the unique exception recorded being benzothiophen dioxide (1·49 Å).[28] Conversely long S–O bond lengths have been reported for tosyltriphenylphosphorane (1·458 Å).[25] It does not seem to be accidental that values for (1) and (2) are appreciably longer than normal values, approaching that found for the sulphonyl stabilised ylide. The bond length increase is very small, but it is known that considerable variations in S–O bond-orders generally cause small variations in S–O bond lengths: in some sulphonyl stabilised sulphonium nitrogen ylides,[29] a decrease of 0·1 Å in the $N-S(O_2)$ bond relative to the closely related sulphonium salt has been found while the corresponding variation in the S–O bond is only 0·02 Å.

It would be relevant that, particularly in (2) where the best requirements for the case (I) category are met, appreciably long S–O bonds are accompanied by considerably short $C_{sp^2}-S$ bonds with less bond alternation than expected: the sulphonyl group is thus somehow involved in the delocalisation. Owing to the uncertainty connected with small bond length variations, this point needs further investigation before it can be firmly accepted.

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