

The Structures of 2,3-Diphenylthiirene 1-Oxide, 2,3-Diphenylthiirene 1,1-Dioxide and 2,3-Dimethylthiirene 1,1-Dioxide

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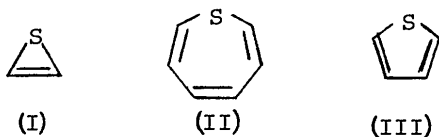
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The structures of the three title compounds, abbreviated PHSO, PHSO₂ and MESO₂, have been determined with Mo *K* α diffractometer data. The space groups and cell parameters are: for PHSO, *Pbca*, $a = 14.3933$ (7), $b = 8.9782$ (4), $c = 17.745$ (1) Å, $Z = 8$; for PHSO₂, *P* $\bar{1}$, $a = 7.354$ (1), $b = 11.578$ (1), $c = 8.7102$ (8) Å, $\alpha = 62.314$ (8), $\beta = 69.06$ (1), $\gamma = 90.00$ (2)°, $Z = 2$; for MESO₂, *A2/a*, $a = 11.661$ (3), $b = 6.243$ (2), $c = 24.23$ (1) Å, $\beta = 110.59$ (4)°, $Z = 12$. The structures were solved with direct methods and refined to *R* values of 0.049, 0.044 and 0.069. The three-ring C=C and C-S bond lengths in thiirene (from theoretical calculations), the sulfoxide and sulfones, follow a trend which suggests that π -delocalization increases from the sulfide to sulfone. The same bond-length trends were observed previously in the thiiranes. CNDO/2 calculations on thiirene models indicate that the in-plane C(p_z) orbitals are primarily responsible for the bond-length variations. π -Delocalization in thiirene dioxide may be of comparable magnitude to that in cyclopropenone. Oxygen charge densities and S-O bond orders provide an insensitive measure of S $\cdots\pi$ -electron interactions.

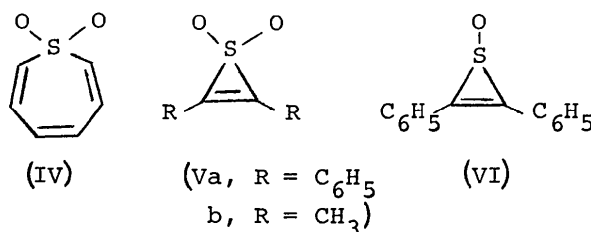
Introduction

Thiirene (I) and the planar form of thiepin (II) are expected to be unstable because of the four and eight π -electron antiaromatic Huckel arrays which are formed by the mixing of two π -electrons on sulfur with the double-bond π -electrons. The term 'antiaromatic' (Breslow, 1973) has been applied to unsaturated systems in which cyclic π -electron delocalization results in increases in the energies of the systems. The destabilizing effect of π -electron delocalization in these sulfur heterocycles is indicated by the negative REPE (resonance energy per electron) values of -0.114β for (I) and -0.029β for (II) (Hess & Schaad, 1973). The REPE of benzene, for example, is 0.065β (Hess & Schaad, 1971) and that of the benzene-like thiophene (III) is 0.032 .



Oxidation of the $4n \pi$ -electron unsaturated sulfides to the corresponding sulfoxides and sulfones should have two effects: (1) the antiaromatic properties should be diminished by a reduction in the unshared electron density on sulfur in the sulfoxide, and presumably completely erased in the sulfone; (2) the electronegative oxygens should both contract and lower the energy of the sulfur's $3d$ orbitals, increasing their potential for interaction with the $2p$ orbitals on the adjacent carbon and oxygen atoms (Jaffe & Orchin, 1962). Conjugation of the C=C π -electrons with the formally unoccupied sulfur $3d$ orbitals could give rise

to stabilized Huckel arrays with $4n+2$ (or $4n-2$ with the previous value of n) π -electrons. X-ray single crystal (Ammon, Watts & Stewart, 1970) and NMR (Williamson, Mock & Castellano, 1970) investigations of thiepin 1,1-dioxide (IV) found little evidence for delocalization in the carbon portion of the molecule [a photoelectron spectroscopic study is unpublished, reference 9 in Muller, Schweig & Vermeer (1975)], and a recently published photoelectron spectroscopic-quantum chemical investigation (Muller *et al.*, 1975) found evidence for aromatic properties in the thiirene 1,1-dioxides (V), but the effect was predicted to be small compared to the magnitude of delocalization in cyclopropenone.



We wish to report the results of our work on the crystal and molecular structures of 2,3-diphenylthiirene 1,1-dioxide (Va, PHSO₂), 2,3-dimethylthiirene 1,1-dioxide (Vb, MESO₂) (Carpino, McAdams, Rynbrandt & Spiewak, 1971) and 2,3-diphenylthiirene 1-oxide (VI, PHSO) (Carpino & Chen, 1971). It is our hope that these structural data will stimulate theoretical studies of the thiirenes, similar to those that have been recently reported for the thiiranes (*e.g.* Hoffmann, Fujimoto, Swenson & Wan, 1973; Rohmer & Roos, 1975) and thiirenes (*e.g.* Muller *et al.*, 1975; de Jong, Noorduyn, Bouwman & Janssen, 1974; Clark, 1972).

Experimental

A preliminary photographic survey was made of each compound. Final cell-parameter and intensity measurements were made with a PDP-8I-controlled Picker FACS-I diffractometer equipped with a Mo X-ray source, highly oriented graphite crystal monochromator (Mo $K\alpha$, λ 0.71069 Å), scintillation detector, pulse-height analyzer, disk for program storage, and magnetic tape for data output. Cell constants were obtained by the method of least squares with 2θ values determined at 22° from manual measurements of $\pm 2\theta$ for each reflection (the number of 2θ data measured

and average value of $|2\theta_o - 2\theta_c|$ are reported in Table 1). The intensity data were collected with the θ - 2θ scan method: background measurements made at the beginning and end of each scan, and the 2θ scan range was calculated from $A + 0.692 \tan \theta$, where A describes the basic reflection width. Three standard reflection intensities, monitored at 50–100 reflection intervals, were used to correct for intensity fluctuations and to determine a value for the 'instability factor' (Stout & Jensen, 1968, p. 420). Foil attenuators were automatically inserted during the intensity measurements to keep the maximum count rate below *ca* 15000 counts s^{-1} . The reflection intensities (I) and standard devia-

Table 1. Crystal data and intensity measurement information

	2,3-Diphenylthiurene 1-oxide (VI) $C_{14}H_{10}OS$ 226.30	2,3-Diphenylthiurene 1,1-dioxide (Va) $C_{14}H_{10}O_2S$ 242.30	2,3-Dimethylthiurene 1,1-dioxide (Vb) $C_8H_6O_2S$ 118.15
Molecular formula			
M.W.			
Crystal size	0.4 × 0.4 × 0.3 mm*	0.5 × 0.5 × 0.4 mm	0.19 × 0.44 × 0.56 mm
Space group	<i>Pbca</i>	<i>P$\bar{1}$</i>	<i>A2/a</i>
Unit-cell parameters (e.s.d.'s)	$a = 14.3933$ (7) Å $b = 8.9782$ (4) $c = 17.745$ (1)	$a = 7.354$ (1) Å $b = 11.578$ (1) $c = 8.7102$ (8) $\alpha = 62.314$ (8)° $\beta = 69.06$ (1) $\gamma = 90.00$ (2)	$a = 11.661$ (3) Å $b = 6.243$ (2) $c = 24.232$ (11) $\beta = 110.59$ (4)°
Number of $2\theta_o$ measurements for cell parameter calculation	12	18	16
Average of $ 2\theta_o - 2\theta_c $	0.001°	0.003°	0.007°
Z	8	2	12†
V	2293.1 Å ³	600.9 Å ³	1651.3 Å ³
D_c	1.311 g cm ⁻³	1.339 g cm ⁻³	1.426 g cm ⁻³
Reciprocal lattice vector parallel to diffractometer ϕ axis	[$\bar{1}$ 10]	[010]	[010]
2θ scan rate, time for 1 background	1.0° min ⁻¹ , 20 s	0.5° min ⁻¹ , 40 s	2.0° min ⁻¹ , 20 s
Total data measured	2407	2478	2361
Total unique data excluding systematically absent reflections (observed, 3σ above background)	2020 (1287)	2126 (1705)	1907 (1342)
Maximum 2θ (sin θ/λ)	50.0° (0.595)	50.1° (0.596)	55.1° (0.651)
Reflection width, A	1.4°	2.0°	2.0°
Instability factor, D	—	0.00021	0.0017

* Crystal was mounted in a glass capillary.

† Eight molecules were located in general positions (C_2), four were located on twofold rotation axes (C_2).

Table 2. Fractional coordinates and temperature factors (Å²) for 2,3-diphenylthiurene 1-oxide (estimated standard deviations in parentheses)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O	0.5528 (2)	0.2854 (3)	0.1211 (2)	0.109 (2)	0.095 (2)	0.088 (2)	0.019 (2)	-0.024 (2)	-0.006 (2)
S	0.45118 (9)	0.2952 (1)	0.11681 (6)	0.1065 (9)	0.0661 (6)	0.0617 (6)	0.0077 (6)	-0.0097 (6)	0.0047 (5)
C(2)	0.4075 (2)	0.4643 (4)	0.0777 (2)	0.063 (2)	0.068 (2)	0.057 (2)	0.000 (2)	-0.004 (2)	0.007 (2)
C(3)	0.4068 (2)	0.3567 (4)	0.0283 (2)	0.063 (2)	0.062 (2)	0.063 (2)	0.002 (2)	-0.003 (2)	0.005 (2)
C(4)	0.3865 (2)	0.6161 (4)	0.1010 (2)	0.053 (2)	0.063 (2)	0.055 (2)	-0.001 (2)	0.002 (2)	0.005 (2)
C(5)	0.3478 (3)	0.7165 (4)	0.0503 (2)	0.063 (2)	0.075 (3)	0.051 (2)	0.002 (2)	-0.002 (2)	-0.003 (2)
C(6)	0.3262 (3)	0.8586 (4)	0.0733 (2)	0.063 (2)	0.070 (2)	0.071 (2)	0.007 (2)	0.001 (2)	0.007 (2)
C(7)	0.3424 (3)	0.9022 (5)	0.1466 (2)	0.072 (3)	0.072 (3)	0.077 (3)	0.001 (2)	0.007 (2)	-0.010 (2)
C(8)	0.3810 (3)	0.8039 (5)	0.1966 (2)	0.082 (3)	0.086 (3)	0.059 (2)	-0.010 (2)	0.001 (2)	-0.010 (2)
C(9)	0.4034 (3)	0.6623 (5)	0.1744 (2)	0.068 (2)	0.076 (3)	0.052 (2)	-0.003 (2)	-0.005 (2)	0.006 (2)
C(10)	0.3853 (2)	0.2954 (4)	-0.0451 (2)	0.051 (2)	0.058 (2)	0.059 (2)	-0.002 (2)	0.000 (2)	0.002 (2)
C(11)	0.4056 (3)	0.1483 (4)	-0.0607 (2)	0.067 (2)	0.059 (2)	0.073 (3)	0.005 (2)	-0.005 (2)	0.005 (2)
C(12)	0.3822 (3)	0.0859 (5)	-0.1289 (3)	0.074 (3)	0.061 (2)	0.092 (3)	0.006 (2)	0.000 (2)	-0.012 (2)
C(13)	0.3385 (3)	0.1707 (5)	-0.1821 (2)	0.078 (3)	0.077 (3)	0.066 (2)	0.000 (2)	-0.003 (2)	-0.015 (2)
C(14)	0.3181 (3)	0.3168 (5)	-0.1677 (2)	0.095 (3)	0.070 (3)	0.061 (2)	0.007 (2)	-0.011 (2)	0.002 (2)
C(15)	0.3424 (3)	0.3792 (4)	-0.0998 (2)	0.085 (3)	0.055 (2)	0.068 (2)	0.006 (2)	-0.005 (2)	-0.002 (2)

Table 2 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
H(5)	0.341 (2)	0.686 (4)	0.003 (2)	0.07 (1)
H(6)	0.292 (2)	0.926 (4)	0.038 (2)	0.07 (1)
H(7)	0.318 (3)	1.005 (5)	0.165 (3)	0.12 (2)
H(8)	0.390 (3)	0.832 (4)	0.246 (2)	0.08 (1)
H(9)	0.432 (2)	0.599 (4)	0.205 (2)	0.07 (1)
H(11)	0.434 (2)	0.095 (4)	-0.027 (2)	0.07 (1)
H(12)	0.398 (3)	-0.016 (5)	-0.140 (2)	0.10 (1)
H(13)	0.323 (2)	0.131 (4)	-0.230 (2)	0.08 (1)
H(14)	0.287 (3)	0.380 (4)	-0.206 (2)	0.09 (1)
H(15)	0.323 (2)	0.470 (4)	-0.090 (2)	0.07 (1)

tions [$\sigma(I)$] were calculated with the following equations:

$$I = SA[I_s - K(I_{B1} + I_{B2})]$$

and

$$\sigma(I) = \{S^2 A^2 [I_s + K^2(I_{B1} + I_{B2})] + DC^2\}^{1/2},$$

where I_s is the scan intensity, I_{B1} and I_{B2} are the two background values, K is the ratio (scan time)/(total background time), A is the attenuator factor, $C = I_s + I_{B1} + I_{B2}$, D is the instability factor, and S is the reflection scale factor determined from the standard intensity data.

The crystal data and the diffraction intensity information are summarized in Table 1.

Structure determination was by direct methods. PHSO was solved in an automatic way with the X-RAY System's (Stewart, Ammon, Dickinson & Hall, 1972) direct-methods subprogram *PHASE*. The solutions for PHSO2 and MESO2 were less straightforward, but were obtained with the multiple-solution direct-methods program, *PHASER* (Ammon, 1965).

Refinement was by full-matrix least squares with anisotropic temperature factors for C, O and S and

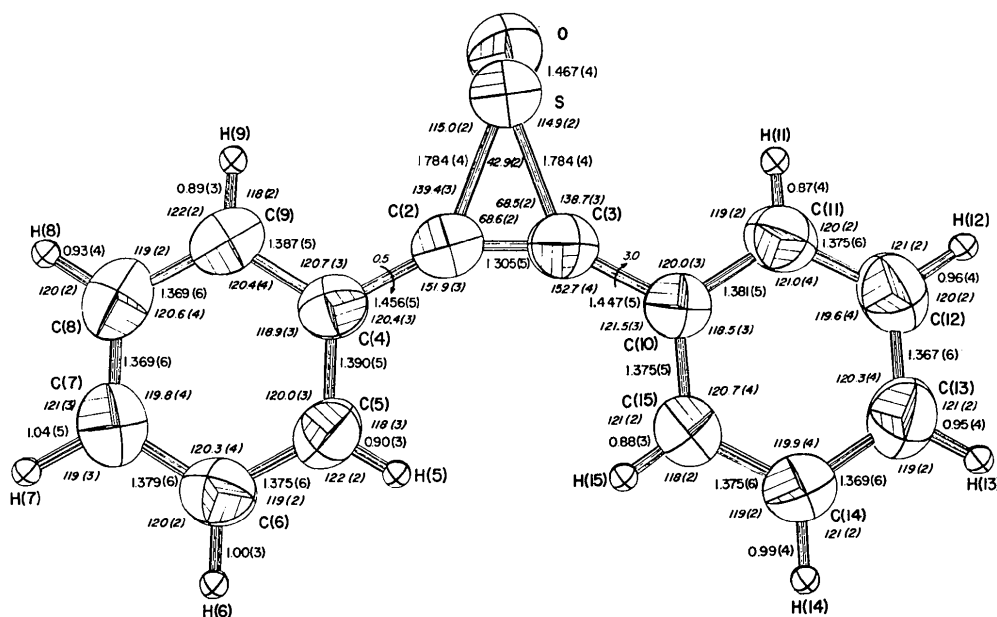


Fig. 1. Bond lengths (Å) and angles (°) for 2,3-diphenylthiirene 1-oxide. Estimated standard deviations are in parentheses.

Table 3. Fractional coordinates and temperature factors (Å^2) for 2,3-diphenylthiirene 1,1-dioxide (estimated standard deviations in parentheses)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	0.5689 (3)	0.3528 (2)	0.3694 (3)	0.052 (1)	0.125 (2)	0.148 (2)	0.008 (1)	-0.035 (1)	-0.087 (2)
O(2)	0.4463 (3)	0.1324 (2)	0.6569 (3)	0.097 (1)	0.126 (2)	0.147 (2)	0.059 (1)	-0.089 (1)	-0.089 (2)
S	0.40352 (9)	0.24349 (7)	0.5128 (1)	0.0505 (4)	0.0926 (5)	0.1103 (6)	0.0239 (3)	-0.0458 (4)	-0.0683 (4)
C(2)	0.2139 (3)	0.2162 (2)	0.4573 (3)	0.046 (1)	0.062 (1)	0.079 (1)	0.0136 (9)	-0.032 (1)	-0.042 (1)
C(3)	0.1664 (3)	0.2731 (2)	0.5678 (3)	0.051 (1)	0.066 (1)	0.078 (1)	0.013 (1)	-0.035 (1)	-0.043 (1)
C(4)	0.1559 (3)	0.1723 (2)	0.3483 (3)	0.058 (1)	0.056 (1)	0.064 (1)	0.0083 (9)	-0.026 (1)	-0.034 (1)
C(5)	0.0254 (4)	0.1897 (3)	0.3312 (4)	0.069 (1)	0.076 (2)	0.087 (2)	0.017 (1)	-0.044 (1)	-0.049 (1)
C(6)	-0.0746 (6)	0.1502 (3)	0.2225 (5)	0.110 (2)	0.087 (2)	0.100 (2)	0.011 (2)	-0.066 (2)	-0.049 (2)
C(7)	0.0537 (7)	0.0938 (3)	0.1318 (5)	0.163 (4)	0.081 (2)	0.081 (2)	-0.002 (2)	-0.058 (2)	-0.046 (2)
C(8)	0.2319 (7)	0.0752 (3)	0.1485 (5)	0.133 (3)	0.088 (2)	0.090 (2)	0.018 (2)	-0.030 (2)	-0.062 (2)
C(9)	0.2847 (4)	0.1138 (3)	0.2567 (4)	0.075 (2)	0.078 (2)	0.088 (2)	0.016 (1)	-0.026 (1)	-0.052 (2)
C(10)	0.0208 (3)	0.3253 (2)	0.6673 (3)	0.058 (1)	0.057 (1)	0.061 (1)	0.012 (1)	-0.026 (1)	-0.032 (1)
C(11)	0.0850 (5)	0.4060 (3)	0.7238 (4)	0.097 (2)	0.067 (1)	0.078 (2)	0.015 (1)	-0.043 (2)	-0.043 (1)
C(12)	-0.0504 (7)	0.4563 (3)	0.8197 (5)	0.144 (3)	0.086 (2)	0.087 (2)	0.034 (2)	-0.048 (2)	-0.059 (2)
C(13)	-0.2465 (8)	0.4289 (4)	0.8599 (5)	0.142 (4)	0.096 (2)	0.076 (2)	0.050 (2)	-0.020 (2)	-0.049 (2)
C(14)	-0.3144 (5)	0.3497 (4)	0.8043 (5)	0.068 (2)	0.111 (2)	0.087 (2)	0.029 (2)	-0.015 (2)	-0.043 (2)
C(15)	-0.1802 (4)	0.2977 (3)	0.7065 (4)	0.056 (1)	0.084 (2)	0.079 (2)	0.014 (1)	-0.024 (1)	-0.043 (1)

Table 3 (cont.)

	x	y	z	U
H(5)	-0.123 (4)	0.233 (3)	0.394 (4)	0.065 (9)
H(6)	-0.209 (5)	0.164 (3)	0.219 (5)	0.09 (1)
H(7)	0.027 (6)	0.066 (4)	0.057 (5)	0.10 (1)
H(8)	0.308 (6)	0.034 (4)	0.097 (6)	0.10 (1)
H(9)	0.409 (5)	0.106 (3)	0.270 (4)	0.066 (9)
H(11)	0.238 (5)	0.421 (3)	0.692 (4)	0.066 (9)
H(12)	-0.013 (5)	0.516 (4)	0.859 (5)	0.09 (1)
H(13)	-0.336 (6)	0.460 (4)	0.929 (5)	0.10 (1)
H(14)	-0.451 (5)	0.323 (3)	0.838 (5)	0.08 (1)
H(15)	-0.229 (4)	0.236 (3)	0.674 (4)	0.07 (1)

isotropic terms for H. The function minimized in the structure refinement was $\sum w(F_o - F_c)^2$, where w was a Hughes (1941)-type weighting factor: $w = 1.0$ for $F_o \leq K$

and $w = (K/F_o)^2$ for $F_o > K$. The K 's used were 60.0 for PHSO, 12.0 for PHSO₂ and for 20.0 MESO₂. The F_c 's were corrected for isotropic secondary extinction [with equation (22) given by Larson (1970)]. With the exception of the six methyl H's belonging to the MESO₂ molecule in the general position, the hydrogen atoms in the three structures were initially located from difference electron density maps and refined in the usual way. The MESO₂ H's were approximated by two appropriately positioned circles ($C-H = 1.04$ Å, $C-C-H = 109.5^\circ$) of twelve 0.25 weight atoms with isotropic temperature factors (U) of 0.09 Å². These atoms were not refined. The final R ($\sum |F_o - F_c| / \sum F_o$) and weighted R_w ($\{[\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}\}$) were 0.069 and 0.088 for MESO₂, 0.049 and 0.050 for PHSO,

Table 4. Fractional coordinates and temperature factors (Å²) for 2,3-dimethylthiirene 1,1-dioxide (estimated standard deviations in parentheses)

	x	y	z	U or U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
O	0.3593 (4)	0.8202 (6)	0.0278 (2)	0.132 (3)	0.087 (3)	0.068 (2)	-0.058 (2)	0.046 (2)	-0.026 (2)
S	0.25	0.6961 (2)	0.0	0.080 (1)	0.0416 (7)	0.0366 (6)	0.0	0.0256 (6)	0.0
C(2)	0.2385 (3)	0.4492 (6)	0.0253 (1)	0.057 (2)	0.045 (2)	0.041 (2)	0.002 (2)	0.019 (2)	0.002 (1)
C(4)	0.2167 (7)	0.3118 (8)	0.0700 (3)	0.117 (5)	0.055 (3)	0.072 (3)	0.007 (3)	0.058 (3)	0.013 (2)
H(4A)	0.264 (6)	0.35 (1)	0.111 (3)	0.08 (2)					
H(4B)	0.127 (8)	0.34 (1)	0.062 (4)	0.10 (3)					
H(4C)	0.236 (6)	0.16 (1)	0.063 (3)	0.07 (2)					
O(1')	0.5219 (3)	0.6248 (5)	0.1646 (1)	0.087 (2)	0.053 (2)	0.073 (2)	-0.007 (2)	0.025 (2)	-0.002 (1)
O(2')	0.3524 (3)	0.8523 (6)	0.1653 (2)	0.047 (2)	0.101 (3)	0.079 (2)	-0.017 (2)	0.026 (1)	0.005 (2)
S'	0.47789 (9)	0.8398 (2)	0.16736 (4)	0.0472 (6)	0.0495 (6)	0.0462 (5)	-0.0091 (4)	0.0155 (4)	-0.0013 (4)
C(2')	0.5396 (3)	1.0505 (6)	0.1438 (2)	0.043 (2)	0.044 (2)	0.047 (2)	-0.003 (1)	0.016 (1)	-0.004 (1)
C(3')	0.5777 (3)	1.0349 (6)	0.2024 (2)	0.048 (2)	0.045 (2)	0.047 (2)	-0.005 (2)	0.017 (2)	-0.004 (2)
C(4')	0.5514 (4)	1.1798 (7)	0.0951 (2)	0.061 (2)	0.059 (2)	0.058 (2)	-0.005 (2)	0.026 (2)	0.004 (2)
C(5')	0.6568 (5)	1.1345 (8)	0.2580 (2)	0.074 (3)	0.079 (3)	0.052 (2)	-0.020 (2)	0.013 (2)	-0.013 (2)

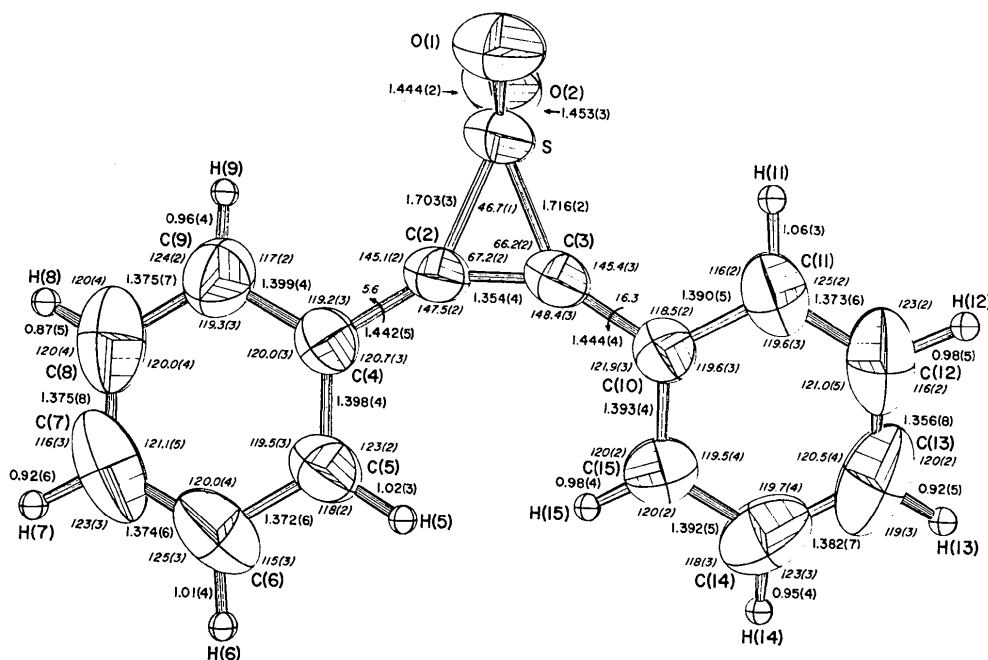


Fig. 2. Bond lengths (Å) and angles ($^\circ$) for 2,3-diphenylthiirene 1,1-dioxide. Estimated standard deviations are given in parentheses. The angles not shown are O(1)-S-O(2) 116.1 (1), O(1)-S-C(2) 118.7 (1), O(1)-S-C(3) 119.4 (1), O(2)-S-C(2) 119.4 (1) and O(2)-S-C(3) 118.9 (1).

and 0.044 and 0.051 for PHSO₂. The atomic parameters are given in Tables 2–4.*

X-ray scattering factors for C, O and S were calculated from the analytical functions reported by Cromer & Mann (1968). H scattering factors were taken from Stewart, Davidson & Simpson (1965).

Computer programs used were: (PDP-8I) Lenhart's (1975) disk control system for the Picker FACS-I diffractometer; (Univac 1108) the X-RAY System (Stewart *et al.*, 1972); PHASER, a direct-methods program (Ammon, 1965); CNINDO (QCPE No. 141) for the CNDO/2 calculations (Pople & Beveridge, 1970); ORTEP-II, a crystal structure illustration program (Johnson, 1971).

Discussion

Bond lengths and angles for the three compounds are included as part of the ORTEP drawings in Figs. 1–3. The thiirene-oxygen portions of the three compounds have the expected symmetries for sulfoxides and sulfones: C_{2v} in the case of MESO₂ and PHSO₂, and C_s for PHSO. The angles between the three-rings and the least-squares planes of the phenyl rings in PHSO₂ and PHSO are small, and presumably provide a maximum degree of phenyl to three-ring conjugation while minimizing the intramolecular phenyl...phenyl non-bonded interactions. Similar phenyl to three-ring conformations have been observed in ferrocenyldiphenylcyclopropenium tetrafluoroborate (Sime & Sime, 1974), 2,3-diphenylcyclopropenone and 2,3-diphenyl-4,4-dicyanotriafulvene (Ammon, 1973).

The 4–8° increase in the phenyl–C=C angles in PHSO and PHSO₂ over the corresponding methyl–C=C angles in MESO₂ may result from the phenyl...phenyl steric effects. Furthermore, these interactions are probably also responsible for forcing the benzene rings out of their respective thiirene planes (see Table 5) in addition to the phenyl–three-ring twist components. It is interesting that the PHSO₂ phenyl with the smallest out-of-plane bend has the largest C–C twist (16.3°). The short benzene C–C distances are presumably due to uncorrected thermal-motion effects. These lengths should be in the 1.39–1.40 Å range. There are no short intermolecular contacts in any of the compounds less than the typical van der Waals distances.

Table 5. Deviations (Å) from the thiirene planes in PHSO, PHSO₂ and MESO₂

	PHSO	PHSO ₂	MESO ₂ (C ₂)	MESO ₂ (C ₂)
O or O(1)	–1.307	1.226	1.227	1.215
O(2)	–	–1.232	–1.212	–1.215
C(4)	0.055	0.078	–0.003	–0.014
C(5)	0.084	0.246	–0.002	0.014
C(6)	0.168	0.352		
C(7)	0.228	0.291		
C(8)	0.197	0.117		
C(9)	0.101	0.006		
C(10)	0.050	0.002		
C(11)	0.032	0.350		
C(12)	0.136	0.351		
C(13)	0.254	0.023		
C(14)	0.274	–0.318		
C(15)	0.151	–0.324		

* The three structure factor lists have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31640 (34 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars Chester CH1 1NZ, England.

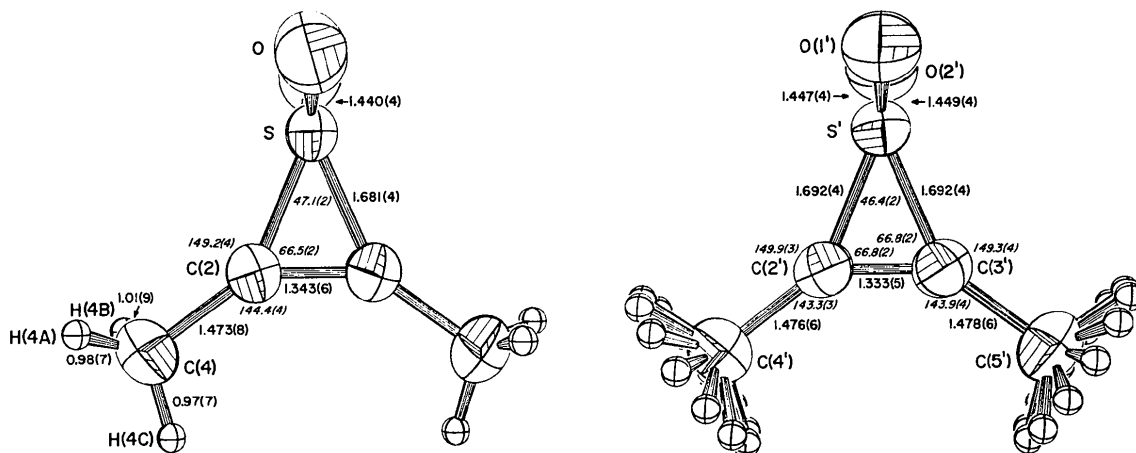

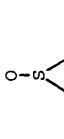
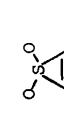

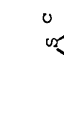
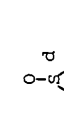



Fig. 3. Bond lengths (Å) and angles (°) for 2,3-dimethylthiirene 1,1-dioxide. Estimated standard deviations are given in parentheses. The C_2 molecule is on the left. The angles not shown are O–S–O 114.9 (2), O–S–C(2) 119.6 (2), O(1')–S'–O(2') 114.8 (2), O(1')–S'–C(2') 120.4 (2), O(1')–S'–C(3') 119.9 (2), O(2')–S'–C(2') 119.4 (2) and O(2')–S'–C(3') 119.1 (2).

The three-ring thiirene and corresponding thiirane data have been collected in Table 6 to facilitate comparison of the structural parameters; bond lengths for the unknown thiirene have been estimated as the average values from three geometry-optimized molecular orbital studies. Qualitatively, an increase in

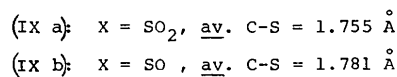
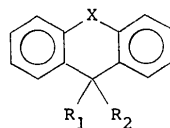
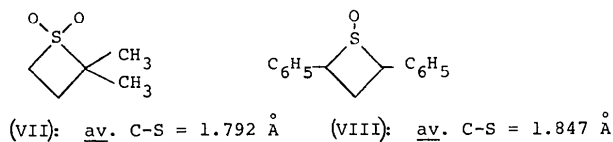
Table 6. Bond length (Å) and angle (°) data for the thiirenes and thiiranes

	CNDO/2 ^a	ab initio ^a	MINDO/3 ^b							
C-C	1.304 Å	1.290 Å 1.288 Å av. 1.288 Å	1.270 Å	1.305 Å	1.333 Å 1.343 Å	1.354 Å	1.492 Å	1.504 Å	1.590 Å	1.60 Å
C-S	1.767	1.803 1.808 1.793 av. 1.790 Å		1.784, 1.784	1.692 1.681 1.692	1.716, 1.703	1.819	1.822	1.731	1.72, 1.74
S-O		1.467		1.447, 1.449	1.440	1.444, 1.453	1.483	1.439	1.41, 1.44	55.4°
∠ C-S-C		42.9°		46.4°	47.1°	46.7°	65.8°	48.8°	54.7°	
∠ O-S-O		126.0° ^c		114.8	114.9	116.1	1.33.6 g	121.4	120.4	

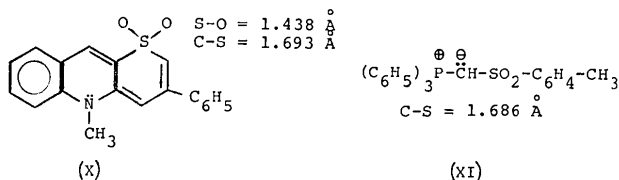
^a Clark (1972); ^b Dewar & Ramsden (1973); ^c Cunningham, Boyd, Myers, Gwinn & Le Van (1951); ^d Saito (1969); ^e Nakano, Saito & Morino (1970); ^f Desiderato & Sass (1967); ^g twice the angle between the S-O bond and the three-ring.

cyclic π -delocalization from thiirene to thiirene oxide to thiirene dioxide would be expected to result in a loss of C=C π -character (the C=C distance should increase) and an increase in C-S π -character (the C-S distance should decrease). These trends are found in both the C=C and C-S lengths: for example, C=C is 1.288 in thiirene, 1.305 in PHSO and 1.354 Å in PHSO₂; C-S is 1.790 in thiirene, 1.784 in PHSO and 1.709 Å in PHSO₂. The changes from 1.305 to 1.354 Å, and from 1.784 to 1.709 Å, are quite remarkable and suggestive of substantial delocalization in the sulfone. However, the interpretation of these differences as evidence for π -delocalization is not straightforward since parallel trends, which are perhaps even more dramatic, have been found in the thiirane distances: for example C-C is 1.504 in thiirane oxide and 1.590 Å in thiirane dioxide; C-S is 1.822 and 1.731 Å, respectively.

The C-S distances in other sulfoxides and sulfones show the same relative magnitudes found in the thiirenes and thiiranes. That is, the sulfones have shorter C-S lengths than the sulfoxides. Examples of this can be found in (VII) (Ziegler, Weiss, Schildknecht, Grund & Sasse, 1973) and (VIII) (Hardgrove, Bratholdt & Lein, 1974), and in the thioxanthene (IX) parameters compiled by Chu (1975*a, b*).

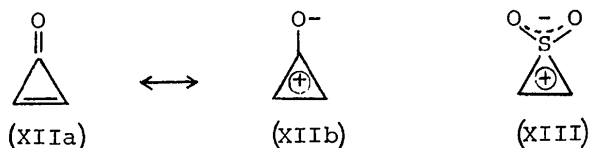


The decrease in the C=C distances in MESO₂ (1.333, 1.433 Å) from the PHSO₂ 1.354 Å value is most probably associated with the ring substituent change of methyl to phenyl. A similar variation has been observed in the 2,3-diS-4,4-dicyanotriafulvenes: C=C is 1.344 Å for S=phenyl (Ammon, 1973), and 1.327 Å for S=methyl (Ammon, Sherrer & Eicher, 1975, unpublished). The three C-S distances in the MESO₂ molecules (av. 1.686 Å) are shorter than the corresponding PHSO₂ distances (av. 1.709 Å), and although the difference is significant at a probability level of 0.0001 (Stout & Jensen, 1968, p. 456), there is no obvious rationale for the difference other than the ring substituent change. The MESO₂ C-S average of 1.686 Å is one of the shortest C(sp²)-SO₂ distances reported. Other short C-S bonds have been found in (X) (Pagani, 1974) and (XI) (Wheatley, 1965).



In both cases, the shortening is presumably due to conjugation of the SO_2 with a formally unshared π -electron pair [on N in (X) and on C in (XI)].

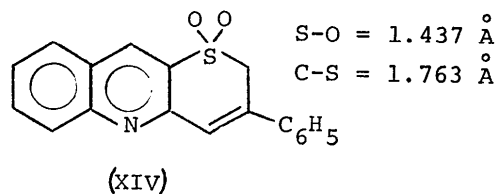
The magnitudes of the S-O distances, 1.467 Å in the sulfoxide and an average of 1.445 Å in the sulfones, are similar to lengths found in other SO and SO_2 compounds. In all cases the sulfone distances are significantly smaller than the sulfoxide values [e.g. (IXa) = 1.439 Å, (IXb) = 1.497 Å (Chu, 1975a,b)]. The S-O to three-ring angles are larger in the sulfoxides than sulfones in both the thiirenes and thiiranes, which could be an indication that an electron pair on sulfur is effectively larger than an oxygen atom.



Huckel-type π -delocalization in the thiirenes would involve a two π -electron thiirenium structure which is formally analogous to the cyclopropenium oxide (XIIb) resonance form of cyclopropanone (XIIa). Such a thiirenium form, illustrated by structure (XIII) for the dioxide, would presumably contain a highly polarized SO_2 moiety, and the S-O distance and oxygen atom charge densities would be expected to differ substantially from these quantities in normal sulfones. Muller *et al.* (1975) used CNDO/S calculations to obtain oxygen charge densities for pairs of compounds such as thiirane/thiirene dioxide, cyclopropanone/cyclopropanone and cycloheptanone/cycloheptatrienone (tropone), and to calculate the π -charge transfer due to conjugation between the hydrocarbon units and the SO_2 or C=O 's. The magnitudes of π -charge transfer (0.30 e in cyclopropanone, 0.18 e in tropone, 0.09 e in thiirene dioxide) were used as a measure of the tendency of these compounds to exhibit aromatic properties: that is, cyclopropanone > tropone > thiirene dioxide. The total charge densities also show that there is substantially more negative charge on oxygen in cyclopropanone than in cyclopropanone, whereas the oxygen charges are about the same in thiirene dioxide and thiirane dioxide. Examples of these oxygen charges are: from CNDO/S calculations (Muller *et al.*, 1975), cyclopropanone = -0.298 and cyclopropanone = -0.446, thiirane dioxide = -0.421 and thiirene dioxide = -0.417; from CNDO/2 calculations (de Jong *et al.*, 1974), -0.256, -0.365, -0.220 and -0.225, respectively. Infrared frequency shifts of *p*-nitrophenol in the presence of several sulfones and ketones

(de Jong *et al.*, 1974), which provide a measure of hydrogen-bonding ability and presumably are related to the oxygen charge densities in the donor molecules, were in good agreement with the CNDO/2 charge densities for both series of compounds.

Bond indices calculated for several sulfones and ketones (de Jong *et al.*, 1974) provided the same kind of information about the importance of dipolar resonance forms as was obtained from the oxygen charge densities. The change in the oxygen charge density of -0.256 in cyclopropanone to -0.365 in cyclopropanone is paralleled by an appreciable decrease in the C-O bond index (from 1.880 to 1.689); the S-O bond index change is from 2.191 in thiirane dioxide to 2.112 in thiirene dioxide. Thus both the oxygen charge densities and associated bond index changes are appreciably larger for the three-ring ketones than for the three-ring sulfones, which have been taken as an indication that there is relatively less π -delocalization in the latter compound. However, it is not entirely clear that the bond index-charge density logic which works so nicely for cyclopropanone/cyclopropanone is equally applicable to the sulfones. Sulfone S-O distances are remarkably constant at 1.43-1.45 Å for a wide variety of different molecules: e.g. dimethyl sulfone, 1.431 Å (Saito & Makino, 1972); thioxanthene dioxides, 1.439 Å (Chu, 1975a,b), thiopin dioxide, 1.443 Å (Ammon *et al.* 1970), thiirane dioxide, 1.439 Å (Nakano, Saito & Morino, 1970), PHSO₂, 1.448 Å, and MESO₂, 1.444 Å. The oxygen charge densities in sulfones, either obtained from calculations or estimated from hydrogen-bonding frequency shifts, also show a relatively small variation. The apparent insensitivity of the SO_2 bond lengths and oxygen charge densities to structural variations in the carbon portions of the molecules might well be due to an insulating effect of the formally unoccupied sulfur 3d orbitals: that is, electronic interactions between the carbon framework and sulfur can occur without any appreciable change in the oxygen-sulfur interactions. This hypothesis is nicely illustrated by the virtual identity of the S-O distances in compounds (X) and (XIV) (Pagani, 1974); N...S conjugative effects in (X) have shortened the C-S distance by 0.07 Å from the (XIV) value. The insensitivity of the S-O bond to the neighboring π -electron environment has also been suggested by de Jong & Janssen (1972).



We have performed a series of CNDO/2 calculations on identical structural models of thiirene, thiirene oxide and thiirene dioxide to provide a picture

of bonding in these compounds. The standard CNDO/2 parameterization was used along with model parameters of C-C 1.329, C-S 1.740, S-O 1.457, C-H 1.07 Å, C-S-O 115 and H-C-C 149°; the calculated atomic charge densities and bond indices (Wiberg, 1968) are listed in Table 7. The trends in the C-C and C-S bond indices qualitatively agree with the trends observed in the experimental bond lengths, whereas the S-O indices predict that the sulfoxide distance should be smaller than the sulfone distance. This discrepancy is presumably associated with the CNDO/2 parameterization since similar trends in the S-O bond indices were found for the thiiranes and for dimethyl sulfoxide/dimethyl sulfone. The discrepancy between the S-O distance and oxygen charge reported by de Jong *et al.* (1974) for sulfones, *viz.* that a smaller oxygen charge is accompanied by a decrease in the S-O bond index, also was found in the thiirene oxide calculations. This anomaly was also observed in the thiiranes, but not in the dimethyl sulfide derivatives. We further note that in the thiirene, thiirane and dimethyl sulfide sulfones, the lowest unoccupied molecular orbital (LUMO) was very slightly bonding (almost nonbonding).

An examination of the separate atomic orbital-orbital interactions provides some information on the extent of π -delocalization in the thiirenes. The contri-

butions to the C-C bond indices have been reported as p_y - p_y (out-of-plane π -bonding), p_z - p_z (in-plane π -bonding) and other terms in Table 8. The out-of-plane p_y - p_y interaction is predicted to decrease from thiirene to thiirene oxide, and then to increase from the oxide to the dioxide. Although the in-plane p_z - p_z interaction decreases from thiirene to the oxide, the decrease from the oxide to dioxide is substantial, and this latter change more than compensates for the aforementioned increase in the p_y - p_y interaction and leads to an overall decrease in the C-C bond index. Hoffmann *et al.* (1973) had previously observed that the in-plane p_z - p_z interaction was the most important factor in leading to an increase in the C-C bond lengths in the thiirane series.

Table 8. Bond index contributions to the C=C bond

These are the individual P_{jk}^2 contributions to the total bond index. (See Table 7 for definition of bond index.)

	Thiirene	Thiirene 1-oxide	Thiirene 1,1-dioxide
$C(p_y)$ - $C(p_y)$	0.8158	0.7379	0.7790
$C(p_z)$ - $C(p_z)$	0.2123	0.1954	0.1130
Σ (other terms)	0.8768	0.8745	0.8792
C=C index	1.9049	1.8077	1.7712

The data presented in Table 9 provide a partial breakdown of the contributions to the C-S bond index. The total out-of-plane p_y contribution increases from thiirene to the sulfoxide, and then decreases from the sulfoxide to the sulfone. The p_y contributions in both the oxide and dioxide are larger than in thiirene itself, a circumstance which is primarily due to a significant increase in the $C(p_y)$ - $S(p_y)$ contribution in the two thiirene derivatives over that in the thiirene. The $C(p_y)$ - $S(d_{yz})$ contribution decreases slightly from the sulfide to oxide to dioxide, and the $C(p_y)$ - $S(d_{xy})$ contribution is insignificant. The C-S bond orders (middle of Table 9) from the out-of-plane $C(p_y)$ interactions in thiirene oxide and dioxide are larger than the thiirene contribution, and all three of these bond orders are larger than the corresponding out-of-plane p_y bond order of 0.405 for cyclopropenone [from a

Table 7. CNDO/2 charge densities (q) and bond indices (i)

The bond index (Wiberg, 1968) is defined as: $i = \sum_{jk} P_{jk}^2$, where j and k refer to the atomic orbitals located on the atoms between which the bond index is evaluated, and P is the j, k th density matrix element.

	Thiirene	Thiirene 1-oxide	Thiirene 1,1-dioxide
$q(O)$		-0.271	-0.223
$q(S)$	-0.145	0.158	0.308
$q(C)$	0.021	0.000	0.006
$q(H)$	0.051	0.056	0.062
$i(C-S)$	1.079	1.122	1.134
$i(C=C)$	1.905	1.808	1.771
$i(S-O)$		2.303	2.068

Table 9. Bond index contributions to the C-S bond

These are the individual P_{jk}^2 contributions to the total bond index. (See Table 7 for definition of bond index.)

	Thiirene	Thiirene 1-oxide	Thiirene 1,1-dioxide
$C(p_y)$ - $S(p_y)$	0.004	0.067	0.055
$C(p_y)$ - $S(d_{yz})$	0.171	0.152	0.126
$C(p_y)$ - $S(d_{xy})$	0.000	0.001	0.002
$\Sigma C(p_y)$ - S^*	0.175	0.229	0.182
$C(p_y)$ - $S(p_y)$ + $C(p_y)$ - $S(d_{yz})$ bond order†	0.476	0.649	0.589
$C(p_z)$ - $S(s)$	0.032	0.029	0.117
$C(p_z)$ - $S(p_x)$	0.294	0.250	0.225
$C(p_z)$ - $S(p_z)$	0.242	0.195	0.160
$C(p_z)$ - $S(d_{xz})$	0.031	0.065	0.104
$\Sigma C(p_z)$ - S^*	0.599	0.539	0.606

* The total $C(p_y)$ - S and $C(p_z)$ - S contributions to the C-S bond index.

† Bond order = $\sum P_{jk} S_{jk} / |S_{jk}|$, where S is the j, k th overlap integral. The $S_{jk} / |S_{jk}|$ term multiplies each P_{jk} element by the sign of the overlap integral.

CNDO/2 calculation based on the molecular parameters reported by Benson, Flygare, Oda & Breslow (1973)].

The overall in-plane p_z contribution decreases from thiirene to the sulfoxide, and then increases to the sulfone, which tends to compensate for the increase-then-decrease trend in the out-of-plane p_y contribution. The most important of the $C(p_z)$ interactions for C-S shortening are the $C(p_z)$ -S(s) and $C(p_z)$ -S(d_{xz}) terms.

Summary

The C=C and C-S bond lengths in thiirene, PHSO, PHSO₂ and MESO₂ follow a trend which suggests that out-of-plane π -delocalization increases in the order sulfide < sulfoxide < sulfone. These same bond-length trends are found in the thiiranes, and CNDO/2 calculations indicate that in both the thiiranes and thiirenes the in-plane $C(p_z)$ orbitals are primarily responsible for the bond-length variations. However, the contributions of the out-of-plane $C(p_y)$ -S interactions to the C-S bond orders in the thiirene series are larger than in cyclopropenone, suggesting that π -delocalization may be of comparable magnitudes in the two systems. Arguments were presented to suggest that the oxygen charge densities and S-O bond distances provide an unsatisfactory measure of S- π -electron interactions.

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