

2·059, 2·083 and 2·044, 2·046, 2·080 (Zalkin, Ruben & Templeton, 1964), 2·081, 2·080, 2·061 (Johnson, 1965), 2·059, 2·061, 2·065 (Sasvari & Jeffrey, 1966), 2·083, 2·073, 2·051 (Margulis & Templeton, 1962), and 2·053, 2·061, 2·063 Å (Braibanti, Tiripicchio, Manotti Lanfredi & Bigoli, 1969). The angles around the magnesium atom are again approximately octahedral. The hydrogen bonds (Table 5) play an important role in the crystal structure. They are numerous and strong. There are fourteen independent possible hydrogen bonds $O \cdots O \leq 2.86 \text{ \AA}$ (Fig. 2). An attempt has been made to distinguish between donor (of hydrogen) and acceptor atoms and a reasonable scheme consistent with the assignment of hydrogen atoms in the anion has been obtained. According to this tentative scheme two hydrogen bonds are assigned to each water molecule on the assumption that the water molecules contribute to the bond as hydrogen donors. The corresponding angles with the oxygen atoms bound through hydrogen bridges are: $O(6^{iii}) \cdots O(7) \cdots O(5^{ii}) = 127.2$, $O(2^{ii}) \cdots O(8) \cdots O(12^i) = 107.7$, $O(3^i) \cdots O(9) \cdots O(5^{iv}) = 104.7$, $O(4^{iv}) \cdots O(10) \cdots O(11^v) = 100.0$, $O(3^{iv}) \cdots O(11) \cdots O(4^{vi}) = 102.9$ and $O(1^{iii}) \cdots O(12) \cdots O(3) = 125.6^\circ$, which are reasonable values (Hamilton & Ibers, 1968). These bonds connect water molecules either with anions or with other molecules. Two more strong hydrogen bonds occur between anions $O(2) \cdots O(6^i) = 2.64 \text{ \AA}$, with $O(6)$ as donor, and $O(5) \cdots O(4^i) = 2.56 \text{ \AA}$, possibly with the hydrogen atom shared between the two. Even if limited by un-

certainities due to the experimental errors, these conclusions seem acceptable.

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The Crystal Structure of Thiopin 1,1-Dioxide and the Question of π -Electron Delocalization in the Molecule

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Thiopin 1,1-dioxide, $C_6H_6SO_2$, crystallizes in the monoclinic space group $P2_1/n$ with cell dimensions of $a = 6.788$, $b = 13.173$, $c = 7.596 \text{ \AA}$, $\beta = 109.10^\circ$, and four molecules per unit cell. Three-dimensional X-ray diffraction data were initially collected using a Weissenberg camera and $Cu K\alpha$ radiation; a second set was subsequently measured with $Mo K\alpha$ radiation on an automatic diffractometer. The structure was readily solved by location of the intermolecular S-S vectors in the Patterson function. Refinement was carried out by full matrix least-squares with anisotropic temperature factors to an R of 0.055 (weighted $R = 0.024$). Hydrogen atoms were included with isotropic temperature factors. Only the counter data were used in the final refinement cycles. There is substantial evidence for double-bond character in the two C-S bonds; no firm conclusions can be drawn regarding delocalization in the carbon atom portion of the molecule.

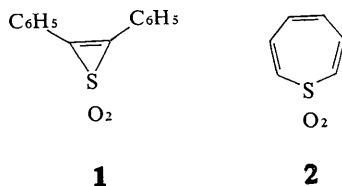
Introduction

Sulfur may expand its valence shell beyond the Lewis octet by accepting ligand electrons of π symmetry into

its unfilled $3d$ orbitals. The formation of a new chemical bond between the acceptor (sulfur) and donor (ligand) will occur if (a) the necessary donor and acceptor orbitals overlap appreciably with each other and

(b) the energies of the orbitals are of similar magnitude (Jaffé & Orchin, 1965). In most divalent organo-sulfur compounds, the $3d$ orbitals of sulfur are quite diffuse and of sufficiently high energy for there to be no significant interaction with adjacent ligand $2p$ orbitals. (There is considerable evidence from kinetic experiments for an extra stabilization of anionic centers by divalent sulfur, an effect which has been ascribed to $3d$ orbital interactions, e.g. Oae, Tagaki, Uneyama & Minamida, 1968.) This situation, however, changes markedly if the sulfur atom forms one or two coordinate covalent bonds and thus carries formal positive charge. The $3d$ orbitals of the positively charged atom are contracted and have lower energy than the $3d$ orbitals of the neutral atom, and the above conditions necessary for the formation of π -bonds with ligand $2p$ orbitals are realized.

The ability of sulfones to stabilize adjacent carbanion centers is well known (Cram, 1965); it results in part from delocalization of the anionic charge to the sulfur atom's $3d$ orbitals (Price & Oae, 1962). If the SO_2 moiety forms a ring with an odd number of conjugated ethylenic groups, a Hückel $4n+2$ system could result from the cyclic delocalization of the carbon atoms' π electrons through the sulfone. Stable examples of the 2π electron system (1; Carpino & McAdams, 1965) and the 6π electron system (2; Mock, 1967) are known.



The structure of 2, thiepin 1,1-dioxide, and the question of π -electron delocalization in the compound are discussed in this paper. A preliminary report of our work has been published (Ammon, Watts, Stewart & Mock, 1968).

Experimental

A sample of thiepin 1,1-dioxide as striated, colorless needles was obtained from W. M. Mock (Mock, 1967). Systematic absences determined from oscillation, Weissenberg ($\text{Cu } K\alpha$) and precession ($\text{Mo } K\alpha$) photographs were consistent with the monoclinic space group $P2_1/n$. The needle axis was c . The reciprocal lattice levels $0kl-6kl$ and $hk0-hk2$ were recorded with Ni-filtered $\text{Cu } K\alpha$ radiation on equi-inclination Weissenberg photographs. It was originally planned to measure all of the diffraction spots with a Joyce-Loebl flying-spot microdensitometer. However, a troublesome instability in the CRT light source made us abandon this approach after the $0kl-4kl$ data had been measured. A further difficulty with the densitometer measurements lay in the underestimation of the weak reflection intensities (see O'Connell, 1967, for additional discussion of this kind of error).* The remaining data, $5kl-6kl$ and $hk0-hk2$, were visually estimated. Two samples were used in the collection of the a axis data because of crystal decomposition.

A set of counter data was also obtained for thiepin 1,1-dioxide. These measurements were made on a General Electric instrument equipped with a quarter-circle goniostat and four-angle programmer, using $\text{Mo } K\alpha$ radiation. One crystal of thiepin 1,1-dioxide, ca. 0.1 mm cube and mounted parallel to $[\bar{1}03]$, served for all cell parameter and intensity determinations. The 2θ values for 14 general reflections were carefully measured on the diffractometer and used as the observed data for a least-squares determination of the lattice constants, (mean $|2\theta_o - 2\theta_c|$ for these 14 data was 0.0036°). The crystal density was measured by the neutral buoyancy technique in aqueous potassium iodide solution.

* This trouble can be largely overcome by using a more powerful light source focusing objective than that supplied by the instrument manufacturer ($\times 5$). A larger objective improves the resolution of the instrument by reducing the size of the flying spot scan image on the film.

Table 1. Fractional coordinates and temperature factors (\AA^2) for the carbon, oxygen, sulfur and hydrogen atoms

Estimated standard deviations are given in parentheses.
The anisotropic thermal parameters are in the form $\exp[-0.25(h^2B_{11}a^{*2} + \dots + 2klB_{23}b^*c^*)]$.

	x	y	z	B or B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	1.17040 (13)	1.11625 (06)	1.39513 (10)	4.12 (04)	3.34 (03)	2.81 (03)	0.36 (04)	1.80 (03)	0.04 (04)
O(1)	0.98221 (30)	1.15340 (14)	1.25962 (25)	4.09 (11)	5.30 (12)	4.71 (11)	1.58 (09)	1.76 (09)	0.66 (09)
O(2)	1.17563 (32)	1.10944 (17)	1.58680 (23)	7.86 (14)	5.88 (13)	3.01 (09)	0.06 (12)	3.36 (09)	0.13 (09)
C(1)	1.22887 (50)	0.99846 (22)	1.32687 (43)	4.32 (16)	3.06 (15)	4.31 (17)	0.01 (13)	2.06 (14)	0.12 (13)
C(2)	1.26295 (52)	0.98261 (26)	1.16447 (46)	4.13 (17)	3.30 (18)	5.17 (19)	-0.15 (15)	1.91 (14)	-1.25 (15)
C(3)	1.28469 (49)	1.05465 (27)	1.03133 (42)	3.83 (17)	5.42 (20)	3.06 (16)	0.14 (15)	1.49 (13)	-0.48 (15)
C(4)	1.35961 (49)	1.14884 (25)	1.06271 (43)	3.96 (17)	5.02 (20)	3.43 (17)	0.13 (14)	1.76 (14)	0.60 (14)
C(5)	1.43462 (51)	1.20206 (24)	1.23726 (43)	4.77 (19)	3.52 (16)	4.26 (17)	-0.68 (14)	1.78 (15)	0.35 (14)
C(6)	1.37619 (49)	1.19001 (23)	1.38831 (42)	4.91 (18)	3.51 (16)	3.41 (16)	-0.67 (14)	1.26 (14)	-0.63 (13)
H(1)	1.2118 (38)	0.9466 (19)	1.4089 (33)	4.67 (74)					
H(2)	1.2896 (39)	0.9149 (19)	1.1547 (35)	4.66 (80)					
H(3)	1.2611 (41)	1.0376 (21)	0.8996 (36)	5.68 (82)					
H(4)	1.3895 (39)	1.1817 (20)	0.9501 (35)	5.38 (75)					
H(5)	1.5383 (43)	1.2573 (21)	1.2423 (37)	6.32 (86)					
H(6)	1.4404 (38)	1.2232 (19)	1.4974 (32)	4.19 (74)					

The crystal data (Mo $K\alpha$, $\lambda=0.71069$ Å) for thiepin 1,1-dioxide (C₆H₆SO₂), mol.wt. 142.2 are: monoclinic, $a=6.788 \pm 0.004$, $b=13.173 \pm 0.005$, $c=7.596 \pm 0.001$ Å, $\beta=109.10 \pm 0.02^\circ$; $D_m=1.447$ g.cm⁻³, $Z=4$, $D_c=1.471$ g.cm⁻³; $V=642$ Å³; $F(000)=296$; $\mu=4.1$ cm⁻¹; absent spectra, $h0l$ for $h+l$ odd, $0k0$ for k odd; space group $P2_1/n$ (this space group corresponds to no. 14, *International Tables for X-ray Crystallography*, 1965).

The counter data were measured using Nb-filtered Mo $K\alpha$ radiation, a potassium iodide scintillation detector, pulse height discrimination and the 2θ scan technique. The 2θ scan length was precalculated using the $\tan \theta$ function described by Alexander & Smith (1964) and the 2θ scan rate was 2° min^{-1} ; a 10 sec stationary background count was made at the start and finish of each scan. Of the 1402 independent reflections examined out to $\sin \theta/\lambda=0.64$, 1092 (66.5%) had net peak intensities $\geq 1.5 \sigma$ of the measurement and were called 'observed' data. Those data having net peaks $< 1.5 \sigma$ were assigned an intensity equal to this value and designated as 'unobserved' data. The intensities of five standard reflections, monitored at 1–2 hour intervals, showed a uniform decrease during the data collection with an overall intensity loss of ca. 8% from beginning to end. A total of 2003 intensities and 51 standard groups were measured with the one crystal. The intensity sum of each standard reflection group was expressed as a function of the total number of data measured up to that point (an approximation to the amount of X-ray exposure received by the sample) and a least-squares line was fitted to these data using the program *DATA* (Ammon, 1967). The data were scaled from the least-squares line in such a manner that the

first, middlemost and last data measured had scale factors of 0.96, 1.00 and 1.04. The standard deviation of fit to the line was 0.006 ($\sigma = \left[\sum_{i=1}^{51} (K_{o,i} - K_{c,i})^2 / 51 - 1 \right]^{1/2}$)

where K_i is the scale factor of the i th standard reflection group).

Work on a solution of the structure began with the film data. The intensities were reduced* in the normal way, and scale, temperature and normalized structure factor amplitudes ($|E|$'s) were calculated. A sharpened, origin-free Patterson function was then computed using values of $E^2 - 1$ for the Fourier series coefficients. An automatic search of the map for all maxima greater than 100 (this was an arbitrary choice; the largest peak was 566) to locate the intermolecular S–S vector at $2x, 2y, 2z$ produced 18 independent positions for x, y, z .

Structure factors were immediately calculated for data out to $\sin \theta/\lambda=0.4$ using the 18 x, y, z positions for sulfur coordinates. The sulfur location derived from the fourth largest Patterson peak gave the lowest R index (0.57). The two largest Patterson peaks found, which were respectively on the Harker line and plane, corresponded to the $\frac{1}{2}, \frac{1}{2} - 2y, \frac{1}{2}$ and $\frac{1}{2} - 2x, \frac{1}{2}, \frac{1}{2} - 2z$ S–S vectors arising from this sulfur atom at x, y, z . The third highest Patterson peak was ca. 1.5 Å from the Patterson origin.

The two oxygen and six carbon atoms were located from successive F_o and difference syntheses. Prior to least-squares refinement, the R index calculated with the approximate positions of all atoms except hydrogen was 0.25. Subsequent least-squares refinement with individual anisotropic temperature factors for the sulfur, oxygen and carbon atoms, and the introduction of the six hydrogen atoms (located from a difference map), gave a final R of 0.12.

The final atomic parameters obtained from the film data formed the starting point for refinement with the diffractometer data. Individual anisotropic temperature factors were used for the sulfur, oxygen and carbon atoms and individual isotropic temperature factors were applied to the hydrogen atoms. All parameters were refined simultaneously using the full matrix of the normal equations and minimizing the quantity $\sum w(|F_o| - |F_c|)^2$. The weights [$w=1/\sigma^2(F_o)$] were calculated from counting statistics; the unobserved reflections were given $w=0$ if $|F_c| \leq |F_o|$ and $w=1/\sigma^2(F_o)$ if $|F_c| > |F_o|$. Atomic scattering factors used were from the following sources: carbon and oxygen, Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955); sulfur, *International Tables for X-ray Crystallography* (1962); hydrogen, Stewart, Davidson & Simpson (1965). From the last cycle of least-squares refinement, the mean and maximum parameter shifts were respectively 0.012 σ and 0.073 σ and $|F_c|$ was

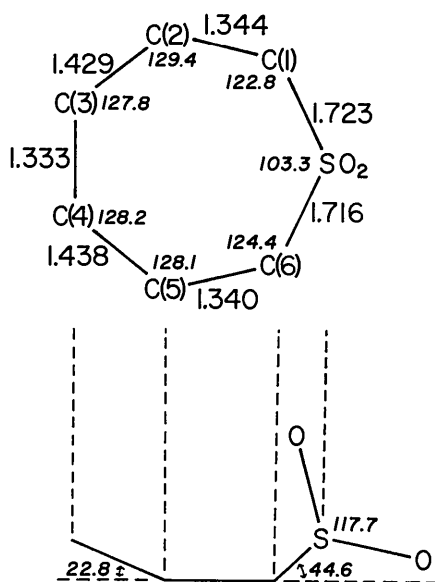


Fig. 1. Bond lengths (Å) and angles ($^\circ$) for the carbon, oxygen and sulfur atoms. S–O distances and C–S–O angles not shown may be found in Tables 2 and 3 [the upper oxygen atom is O(1)]. The lower part of the Figure shows the bow and stern angles.

* The majority of the computations were done using the *Crystal Structure Calculations System, X-ray 63* (1964) system of programs.

greater than $|F_o|$ for 57 of the 469 unobserved data. The final R index was 0.055 and the weighted R was 0.024.

Atomic parameters are given in Table 1; bond lengths and angles are given in Tables 2 and 3 respectively; the structure factor list is shown in Table 4. Bond lengths and angles for the carbon, sulfur and oxygen atoms are also shown in Fig. 1.

Table 2. Bond lengths and estimated standard deviations

	Length	E.s.d.
S—O(1)	1.439 Å	0.002 Å
S—O(2)	1.448	0.002
S—C(1)	1.723	0.003
S—C(6)	1.716	0.003
C(1)—C(2)	1.344	0.005
C(2)—C(3)	1.429	0.005
C(3)—C(4)	1.333	0.005
C(4)—C(5)	1.438	0.004
C(5)—C(6)	1.340	0.005
C(1)—H(1)	0.96	0.03
C(2)—H(2)	0.92	0.03
C(3)—H(3)	0.99	0.03
C(4)—H(4)	1.04	0.03
C(5)—H(5)	1.00	0.03
C(6)—H(6)	0.91	0.02

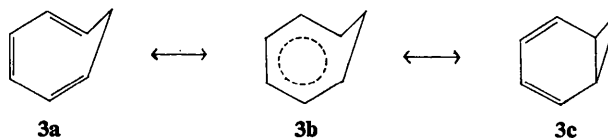
Table 3. Bond angles and estimated standard deviations

	Angle	E.s.d.
O(1)—S—O(2)	117.68°	0.14°
O(1)—S—C(1)	109.21	0.12
O(1)—S—C(6)	109.07	0.13
O(2)—S—C(1)	108.34	0.15
O(2)—S—C(6)	108.25	0.14
C(1)—S—C(6)	103.35	0.17
S—C(1)—C(2)	122.82	0.25
S—C(1)—H(1)	111.0	1.6
C(2)—C(1)—H(1)	125.5	1.6
C(1)—C(2)—C(3)	129.43	0.32
C(1)—C(2)—H(2)	108.8	1.8
C(3)—C(2)—H(2)	121.3	1.9
C(2)—C(3)—C(4)	127.83	0.30
C(2)—C(3)—H(4)	123.1	1.6
C(4)—C(3)—H(4)	108.6	1.6
C(3)—C(4)—C(5)	128.19	0.32
C(3)—C(4)—H(5)	114.1	1.4
C(5)—C(4)—H(5)	116.8	1.4
C(4)—C(5)—C(6)	128.10	0.31
C(4)—C(5)—H(5)	114.9	1.7
C(6)—C(5)—H(5)	117.0	1.7
C(5)—C(6)—S	124.37	0.23
C(5)—C(6)—H(6)	122.2	1.8
S—C(6)—H(6)	113.3	1.8

Discussion

The chemical and physical properties of thiepin 1,1-dioxide, reported by Mock (1967), are essentially those of a conjugated olefin. There is little evidence to suggest that the molecule possesses the substantial π -electron delocalization of more 'normal' aromatic compounds. This X-ray study was undertaken to determine if the details of the molecular structure would support the olefinic hypothesis or perhaps reveal some evidence for π -electron delocalization not apparent in the chemical and physical investigations.

The thiepin ring is in a boat conformation with angles of 44.6 and 22.8° between the four-atom base plane [C(1)—C(2)—C(5)—C(6)] and the 'bow' [C(1)—S—C(6)] and 'stern' [C(2)—C(3)—C(4)—C(5)] planes respectively. This conformation was predicted by Mock (1967) from an examination of molecular models and is typical of cycloheptatrienes in which the bow atom is tetrahedral. The bow and stern angles found in cycloheptatriene (Traetteberg, 1964) are 36.5 and 40.5° respectively and those observed in the cycloheptatriene moiety of a thujic acid derivative (Davis & Tulinsky, 1966) are 47.9* and 24.4°. Davis & Tulinsky calculated the overlap integral S for interaction of the $2p$ orbitals on C(1) and C(6) and concluded that there was evidence for norcaradiene character (e.g. 3b-3c) in the seven-membered ring of thujic acid. An excellent example of a



norcaradiene structure was reported by Fritchie (1966) who found bow and stern angles of 71.9 and 4.2° in 2,5-dimethyl-7,7-dicyanonorcaradiene. Using this structure to represent a molecule with full norcaradiene character, and cycloheptatriene to represent a molecule with little norcaradiene character, it can be seen that one effect of a C(1)—C(6) interaction is to increase the bow angle and decrease the stern angle. The bow and stern angles in the 7-membered rings of thujic acid and thiepin 1,1-dioxide are remarkably similar and fall between these extremes.

To investigate the possibility of norcaradiene character in thiepin 1,1-dioxide, we computed the overlap integral S for interaction of the $2p$ orbitals of C(1) and C(6), using the tables published by Mulliken, Rieke, Orloff & Orloff (1949). The $2p$ orbitals were assumed to be normal to their respective S—C—C planes; the C(1)—C(6) distance is 2.7 Å. The value of 0.039 calculated for S_{16} is essentially the same as that obtained for C(1)—C(3) overlap in *trans*-1,3-butadiene. Davis & Tulinsky (1966) reported an S_{16} of 0.072 [C(1)—C(6) = 2.42 Å] for the cycloheptatriene ring of thujic acid. On the basis of these computations, we conclude that there is no evidence for norcaradiene character in thiepin 1,1-dioxide.

Any mechanism which permits conjugation between C(1) and C(6) in these cyclic triene systems should influence the properties of the carbon-carbon bonds in the remainder of the system. The effect on bond lengths would be to lengthen the double bonds and shorten the single bonds. Table 5 contains some bond-length data

* In heptafulvalene, a molecule with a trigonal bow atom, the bow and stern angles are 24.7 and 15.7° (Coppens, 1969). Bow and stern angles of 45.2 and 19.8° have been recently reported (Sakore, Schlessinger & Sobell, 1969) for thieno[3,4-*d*]thiepin 6,6-dioxide (compound (b), Table 6).

Table 4. Structure factor data for thiepin 1,1-dioxide

The data are given in blocks of constant k and l. Within each block the data are listed as h, 10F_o and 10F_c. Those data marked with an asterisk were unobserved.

Table with multiple columns containing numerical data for structure factors. The data is organized into blocks based on k and l values. Each block contains columns for h, 10F_o, and 10F_c. Some values are marked with an asterisk (*). The table is dense and spans the entire page.

sulfur linkages in (*g*) (1.706, 1.696 Å), since the thiabenzene nucleus is a heterocyclic analog of benzene with the CH₃-S-O moiety in place of the usual benzene C-H group. Compound (*h*) is an ylide with the negative charge on carbon delocalized between a S(III) and two cyano substituents.

The Csp^2 -S distance of 1.730 Å in 2*H*-thiapyran 1,1-dioxide (*c*) is anomalously short, compared with the many examples of 1.75–1.80 Å aromatic Csp^2 -S distances. In the aromatic sulfones, appreciable interaction of the SO₂ moiety with the carbon π -orbitals would probably lead to a loss of stability in the aromatic nucleus, and hence an overall decrease in molecular stability, compared with a molecule with relatively little Csp^2 -SO₂ interaction. Since the delocalization energy of butadiene is considerably less than that of benzene, a conjugative interaction of the SO₂ group

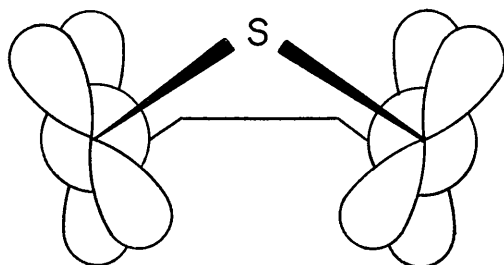


Fig. 2. A view of the thiapin 1,1-dioxide boat showing the twist of the C(1)-C(2) and C(5)-C(6) double bond $2p$ orbitals. The twist has been exaggerated, and the two oxygen atoms have been omitted for clarity.

with the carbon π -orbitals in thiapyran 1,1-dioxide should be energetically more feasible than in aromatic sulfones.

Another probable reason for the short carbon-sulfur bond in (*c*) is that the sulfone group is linked to only one carbon substituent capable of π -bond formation (the sulfur-oxygen bonds have substantial double-bond character; Moffitt, 1950), and therefore the strongest possible bond is formed. In a compound with two trigonal carbon atoms linked to a sulfur atom, π -bond interactions necessarily must occur between the sulfur atom and both carbon atom substituents, and the extent of π -bond formation with each substituent should be less than in a molecule in which the sulfur atom had to accommodate only one trigonal substituent. From the preceding arguments, we would predict a shorter Csp^2 -S bond in 2*H*-thiapyran 1,1-dioxide than in say, methyl vinyl sulfone, and a shorter Csp^2 -S distance in this latter compound than in divinyl sulfone. Although bond length data are not available for these last two compounds, the structure of 2,5-di-*t*-butylthiophene 1,1-dioxide (*i*) may serve to illustrate this hypothesis. Since the highest filled molecular orbital in butadiene may have essentially the same symmetry (a_2) as two isolated ethylenic groups, the C-S distance in (*i*) probably would not differ appreciably from the C-S length in divinyl sulfone. The C-S distance found in (*i*), 1.79 Å, is in accord with the hypothesis. Furthermore, we note that the C-S distance in (*i*), a 4π -electron planar molecule, is substantially longer than the C-S distance in thiapin 1,1-dioxide, a 6π -electron boat-shaped molecule.

Table 5. Some bond lengths (Å) for polyenes

	Terminal C=C ^a	Central C=C ^b	Single C-C ^c	Reference
Thiapin 1,1-dioxide	1.342	1.333	1.433	This work
Cycloheptatriene	1.356 ^d	1.356 ^d	1.446	Traetteberg (1966)
Cycloheptatriene moiety of thujic acid	1.329	1.338	1.446	Davis & Tulinsky (1966)
Heptafulvalene	1.348	1.338	1.437	Coppens (1969)
<i>t</i> -1,3,5-Hexatriene	1.337	1.368	1.457	Traetteberg (1968)
<i>c</i> -1,3,5-Hexatriene	1.336	1.362	1.467	Table 3 in Traetteberg (1968)
Cyclo-octatetraene		1.340	1.476	Table 3 in Traetteberg (1968)

^a Average of the C(1)-C(2) and C(5)-C(6) bond lengths.

^b C(3)-C(4) bond length.

^c Average of the C(2)-C(3) and C(4)-C(5) bond lengths.

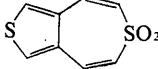

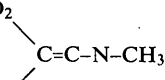
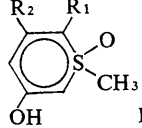
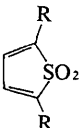
^d Gas electron diffraction experiment. The terminal and central double bond lengths were assumed to be equal in this determination.

The bond distances reported for compound (b), Table 6, suggest that the molecule is best represented as a substituted thiophene, and not as the 10π -electron delocalized structure, in which the lone pair on sulfur and the sulfone d orbitals contribute to the formation of a cyclic 10π -electron system. This is quite reasonable since the sulfone group would have to provide a very low energy path to cyclic delocalization for the 10π -system to be more stable than the 6π thiophene moiety. The similarity of the Csp^2 -S(IV) lengths in (b)-(f), however, may indicate that the carbon-sulfone linkages in (b) have some double-bond character. In any case, we would predict the relative magnitudes of the C-S(IV) distances in (b) and (a).

In thiepin 1,1-dioxide, which has an approximately tetrahedral arrangement of ligands about the sulfur atom, the sulfur $3d$ orbitals capable of forming π -bonds to appropriate ligand orbitals are d_{z^2} and d_{xz-yz} (angle distortion may permit some π -type interaction with d_{xy} ; Jaffé, 1954; Cruickshank, 1961). A detailed

analysis of π -bond formation in sulfones was made by Moffitt (1950), and Koch & Moffitt (1951) who, assuming C_{2v} symmetry for the sulfur atom, constructed two π -bonding group orbitals (GO) with the oxygen $2p$ and sulfur $3d$ orbitals. The interaction of these GO's with the $2p$ orbitals of two trigonal carbon ligands was then considered for two geometries (Koch & Moffitt, 1951). In case I, the axes of the $2p$ carbon orbitals were oriented perpendicular to the C-S-C plane (parallel to the O-S-O plane), which for the present example would correspond to an essentially planar thiepin 1,1-dioxide. If one dissects the molecule into SO_2 and *cis*-hexatriene moieties, and assumes that the highest occupied molecular orbital (HOMO) of the planar hexatriene is the one most available for π -interactions, it can be readily seen that the symmetry (b_2) of this MO is incompatible with either of the two sulfur-A weak donor type of interaction, however, would be possible with the sulfur $3d_{yz}$ orbital (this orbital is probably involved in σ -bond hybridization).

Table 6. Some carbon-sulfur bond lengths.

No.	Bond	Length*	Compound	Reference
(a)	Csp^2 -S(IV)	1.719 Å	thiepin 1,1-dioxide	This work
(b)	Csp^2 -S(IV)	1.739		Sakore, Schlessinger & Sobell (1969)
(c)	Csp^2 -S(IV)	1.730		Boelema, Visser & Bos (1967)
	Csp^3 -S(IV)	1.764		
(d)	Csp^2 -S(IV)	1.726	$(CH_3SO_2)_2C=C=N-CH_3$	Wheatley (1954)
	CH_3 -S(IV)	1.770		
(e)	Csp^2 -S(IV)	1.729		Bullough & Wheatley (1957)
	CH_3 -S(IV)	1.761		
	C_6H_5 -S(IV)	1.772		
(f)	Csp^2 -S(IV)	1.740	$(CH_3SO_2)_2C=C=N-C_2H_5$	Daly (1961)
	CH_3 -S(IV)	1.772		
(g)	Csp^2 -S(IV)	1.701		Tamura, Sato & Kishida (1968)
(h)	Csp^2 -S(III)	1.73	$(CH_3)_2-S^+-C^-(CN)_2$	Christensen & Whitmore (1969)
	CH_3 -S(III)	1.82		
(i)	Csp^2 -S(IV)	1.79		Vorontsova (1966)
(j)	Aromatic	1.75—	Variety of compounds with trigonal and tetrahedral C bonded to SO_2	†
	Csp^2 -S(IV) and Csp^3 -S(IV)	1.80		

* Chemically equivalent bond lengths have been averaged.

† Reference 7 in Ammon, Watts, Stewart & Mock (1968); Burzloff (1968); Sands & Day (1967); Jeffrey (1951); $(CH_3)_2S(NH)_2$, Webb & Gloss (1967); Truter (1962); Abrahams (1956); Bart (1968); Csp^2 -S(IV) = 1.74 Å in dibenzothiophene 1,1-dioxide. Kronfeld & Sass (1968). Desiderato & Sass (1967) reported a Csp^3 -S(IV) distance of 1.73 Å in 2,3-dimethylthiirane 1,1-dioxide. This distance is probably anomalously short because of its presence in a three-membered ring.

The second orbital geometry considered by Koch & Moffitt, case II, was one in which the carbon $2p$ orbitals had been rotated by 90° about the C-S bond from the case I orientation. In this configuration, the axes of the carbon $2p$ orbitals are coincident with the C-S-C plane, which in thiepin 1,1-dioxide would correspond to a molecule with as large a bow angle as possible (ideally 90°). An examination of molecular models suggests that a substantial rehybridization of the σ -bond network at C(1) and C(6) would have to occur to permit bow angles much greater than about 45° . Whereas the symmetry of the *cis*-hexatriene HOMO is still incompatible with either of the two sulfur-oxygen GO's for case II conjugation, it is compatible with the symmetry (a_1) of the $3d_{z^2}$ sulfur orbital. Cruickshank (1961) and Jaffé & Orchin (1965) have pointed out that this $3d$ orbital may also π -bond to the oxygen $2p$ orbitals, and hence donor-acceptor conjugation is possible for case II geometry. For steric reasons, the benzene ring-SO₂ orientation in diphenyl sulfones is that of case II, and there is evidence for conjugation between the two aromatic rings (Price & Oae, 1962). In dibenzothiophene 1,1-dioxide, an example of case I geometry, there is evidence to show that conjugation between benzene rings may occur *via* the single (biphenyl) carbon-carbon bond, but that conjugation does not take place through the sulfone moiety (Price & Oae, 1962; this may be simply an example in which the nodal properties of the a_2 sulfur-oxygen GO (the case I GO) restrict conjugation between the carbon substituents).

Jordan, Smith, Lohr & Lipscomb (1963) found that the orientation of dimethylamino substituents in di-(dimethylamino) sulfone was one in which the lone pairs of electrons on the nitrogen atoms were in the case II geometry. In an accompanying molecular orbital investigation of the case I and II geometries, using F in place of CH₃, they concluded that case II conjugation was more important than case I conjugation because the latter geometry involves the greater competition for the sulfur d orbitals by the unshared electron pairs on the oxygen atoms.

The σ -bond network probably has a dominant role in determining the molecular conformation of the boat-shaped, seven-membered cyclic trienes since considerable angle strain would be present in a planar ring. In thiepin 1,1-dioxide, the sulfone and hexatriene moieties are situated about half-way between the unfavorable, case I, and favorable, case II, geometries for $d\pi-p\pi$ overlap. The C(1)-C(2) and C(5)-C(6) double bonds are twisted (Fig. 2, average 8.4°) in such a manner that the C(2) and C(5) $2p$ orbital lobes below the boat move outward from the center of the boat (the upper lobes move in opposite directions; it was assumed that the $2p$ orbitals would be normal to their respective C-C-S and C-C-C planes). This direction of twist leads to a flattening in the carbon portion of the ring.

From our analysis (*vide supra*) of the conformation and bond lengths of thiepin 1,1-dioxide, we conclude that there is strong evidence for π -electron delocaliza-

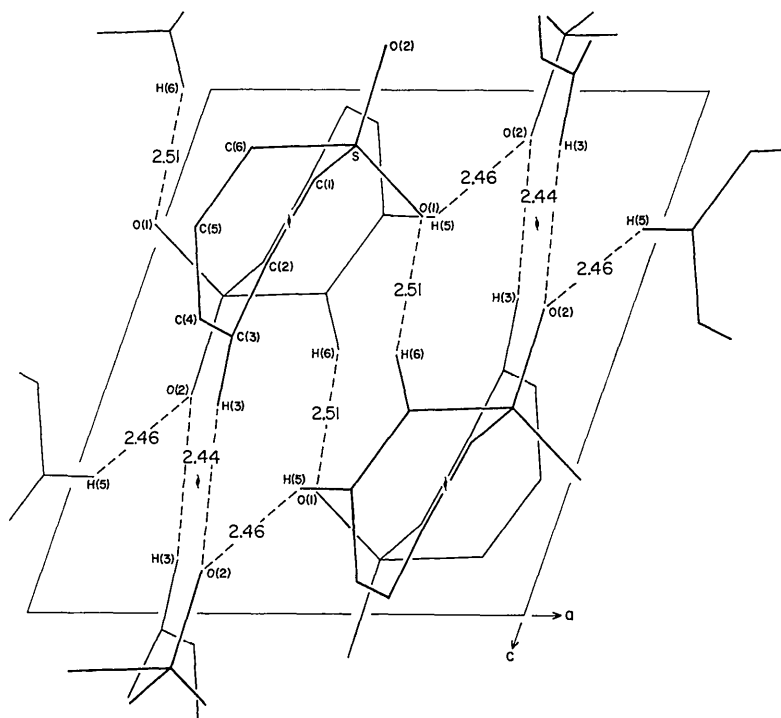


Fig. 3. The unit cell viewed normal to the ac plane. Some intermolecular contacts (\AA) are shown.

tion between the sulfur and the substituent carbon atoms; that this delocalization extends over the rest of the seven-membered ring is less certain.*

A drawing showing the mode of packing and probable intermolecular hydrogen bonding scheme is given in Fig. 3. The molecule is tipped in such a way that the mean plane of the boat is approximately parallel to the *b* axis (the angle between the *b* axis and the normal to the C(1)–C(2)–C(5)–C(6) plane is 71.2°) and oriented with a 22° angle between the bow–stern vector and the *c* axis. Thus, the boat may be imagined to be floating in the ocean of the *bc* plane and cruising in a direction parallel to *c*. The close proximity of the molecule (at x, y, z) to the twofold screw axis at $\frac{1}{2}, y, \frac{1}{4}$ places the screw image (at $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$) almost directly above the x, y, z molecule and accounts for the relatively long *b* axis. This arrangement gives a fairly high atom density around the screw axes at $\frac{1}{2}, y, \frac{1}{4}$ and $\frac{3}{4}, y, \frac{3}{4}$ compared with the empty quadrants of $\frac{3}{4}, y, \frac{1}{4}$ and $\frac{1}{4}, y, \frac{3}{4}$.

Although the structure would not be expected to form strong hydrogen bonds, there appears to be a well defined network of C–H...O bonds linking molecules of roughly the same height in *b*. Atom O(2) at x, y, z bonds simultaneously to H(3) at $x, y, 1+z$ and H(5) at $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; H(5) at x, y, z is linked to O(2) at $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$. Thus, the O(2)...H(3) interactions link molecules in the *c* axis direction while the O(2)...H(5) interactions link adjacent chains, to form sheets of molecules parallel to the *ac* plane. Adjacent rows (parallel to *c*) may be further tied together by weak O(1)...H(6) bonds. There are no obvious interactions in the direction of the *b* axis which would connect the adjacent *ac* sheets.

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* Bertelli, Andrews & Crews (1969) have done an impressive investigation of delocalization in cycloheptatriene derivatives. They found little evidence for delocalization in excess of that expected for similar polyenes.

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