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The Crystal and Molecular Structure of 3,3,5,6-Tetraphenyl-2,3-dihydro-1,4-oxathiin-2-one-4,4-dioxide

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The structure of a reaction product of azibenzil with sulphur dioxide has been confirmed by a three-dimensional X-ray analysis to be 3,3,5,6-tetraphenyl-2,3-dihydro-1,4-oxathiin-2-one-4,4-dioxide. The crystals are monoclinic and belong to space group $P2_1/n$ (No. 14). The unit cell contains four formula units and has the dimensions: $a=18{\cdot}692$ (3), $b=9{\cdot}840$ (2), $c=12{\cdot}962$ (2) Å, and $\beta=104{\cdot}44$ (2)°. The structure was established by the heavy-atom method and refined by the least-squares procedure to $R=0{\cdot}057$ for 2045 observed reflexions. The six-membered ring containing the sulphur atom is non-planar. The S(VI)–C(sp^2) and S(VI)–C(sp^3) bonds have distances of 1·762 (6) and 1·837 (6) Å respectively, and there is no evidence to indicate any conjugation between the sulphone group and the adjacent unsaturated bond.

Introduction

Nagai, Tanaka & Tokura (1968) have reported a novel reaction of azibenzil (I) with sulphur dioxide, involving a partial Wolff rearrangement to give diphenylketene and a keto-sulphene. These undergo cyclo-addition to form products (II) and (III). Nagai *et al.* have assigned their structures as (II*a*) and (III*a*) respectively (Fig. 1). Stothers, Danks & King (1971), however, proposed that these compounds would be more satisfactorily described by structures (II*b*) and (III*b*), based on their careful examination of spectroscopic data, especially those of ^{13}C n.m.r. The present X-ray study was undertaken to determine unambiguously whether the structure of the high-melting point product (II) is (II*a*) or (II*b*), and also to obtain structural information, in particular the conformation of the ring system containing a sulphone group.

Crystal data

$C_{28}H_{20}O_4S$, F.W.452·5.
Monoclinic, space group $P2_1/n$ (No. 14).

$a=18{\cdot}692$ (3) Å	$U=2309$ Å^3
$b=\ 9{\cdot}840$ (2)	$D_m=1{\cdot}29$ g.cm^{-3}
$c=12{\cdot}962$ (2)	$D_c=1{\cdot}30$ for $Z=4$
$\beta=104{\cdot}44$ (2)°	$\mu=14{\cdot}7$ cm^{-1} for Cu $K\alpha$.

Experimental

Crystals suitable for X-ray analysis were grown from methanol. The crystals are prisms with the *c* axis parallel to the long prism axis. Multiple-level Weissenberg photographs showed the systematic absences $0k0$ when k is odd, and $h0l$ when $(h+l)$ is odd. These extinctions uniquely indicate the space group $P2_1/n$. The crystal density, measured by flotation in an aqueous zinc chloride solution, determined the number of molecules per unit cell to be four. Unit-cell dimensions were obtained by a least-squares refinement of 2θ values of 18 reflexions measured on a diffractometer equipped with a single-crystal orienter using Mo $K\alpha$ radiation ($\lambda=0{\cdot}71069$ Å).

Intensity data were collected on a Rigaku automated four-circle single-crystal diffractometer with nickel-filtered Cu $K\alpha$ radiation. The crystal used had the dimensions $0{\cdot}2\times0{\cdot}1\times0{\cdot}15$ mm. The integrated intensity of each reflexion was determined by scanning over the peak at a rate of 4° per min, and subtracting the background obtained by averaging the two values measured for 7·5 sec at both ends of a scan. The 2θ scan width was determined to be $(2{\cdot}4+0{\cdot}30\tan\theta_c)°$, where θ_c denotes the calculated Bragg angle for Cu $K\alpha_1$, and the beginning of the scan was set to be $(2\theta_c-1{\cdot}2)°$.

Of the 3154 independent reflexions measured within the range $(\sin\theta)/\lambda\le0{\cdot}55$, 2045 had net intensities larger than 3σ of the measurement and were taken as 'observed data'. All the calculations throughout this work were carried out with these observed data. Lorentz and polarization corrections were made in the usual way, but no corrections were made for absorption.

Determination of the structure

It was not possible to deduce the coordinates for the sulphur atom unambiguously from a three-dimensional Patterson synthesis. One of the possible positions was chosen because it provided the most satisfactory interpretation of the vector map assuming a tetrahedral environment for the sulphur atom. The Fourier synthesis based on these coordinates of the sulphur atom revealed all the non-hydrogen atoms, although there were many spurious peaks in the map. It is noteworthy that the heavy-atom method could be applied to solving this structure, in spite of the fact that the ratio $f_S^2/\sum f_L^2$ has a low value of 0·20, where f_S and f_L are the scattering factors of the sulphur atom and other light atoms respectively. The calculation of structure factors based on the coordinates from this Fourier map resulted in an R index of 0·33, and the second Fourier synthesis appeared to be an improvement. Thus the structure was established. The block-diagonal least-squares refinement of these 33 atoms with isotropic temperature factors gave an R index of 0·12 after four cycles. Introduction of anisotropic thermal parameters reduced R to 0·08. A difference map calculated at this stage resolved the hydrogen atoms. Isotropic thermal parameters of the hydrogen atoms were given the same values as those obtained at the final stage of the isotropic refinement for the atoms to which the hydrogen atoms are bonded. After several cycles of refinement including hydrogen atoms R was reduced to 0·057. The least-squares refinement was carried out with the program *HBLS* (Ashida, 1967). Atomic scattering factors calculated by Hanson, Herman, Lea & Skillman (1964) were used. The function minimized was $w(|F_o|-|F_c|)^2$, where w was determined as follows:

$$\begin{array}{ll} w=1 & |F_{\min}| \le |F_o| \le |F_{\max}| \\ w=(|F_{\max}|/|F_o|)^2 & |F_o| > |F_{\max}| \\ |F_{\min}|=6{\cdot}3\,, \quad |F_{\max}|=63\,. & \end{array}$$

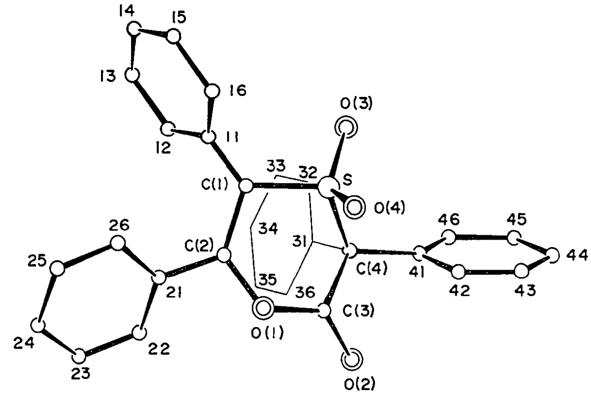


Fig. 2. The molecular structure projected onto the best plane through S, C(1), C(2), and O(1) and the numbering system in the molecule. Only the numbers are shown for carbon atoms in the phenyl groups;hydrogen atoms are omitted.

The observed and calculated structure factors are listed in Table 1. Final atomic coordinates and thermal parameters are given in Table 2.

Discussion

Fig. 2 shows the molecular structure projected onto the least-squares plane of S, C(1), C(2) and O(1), and

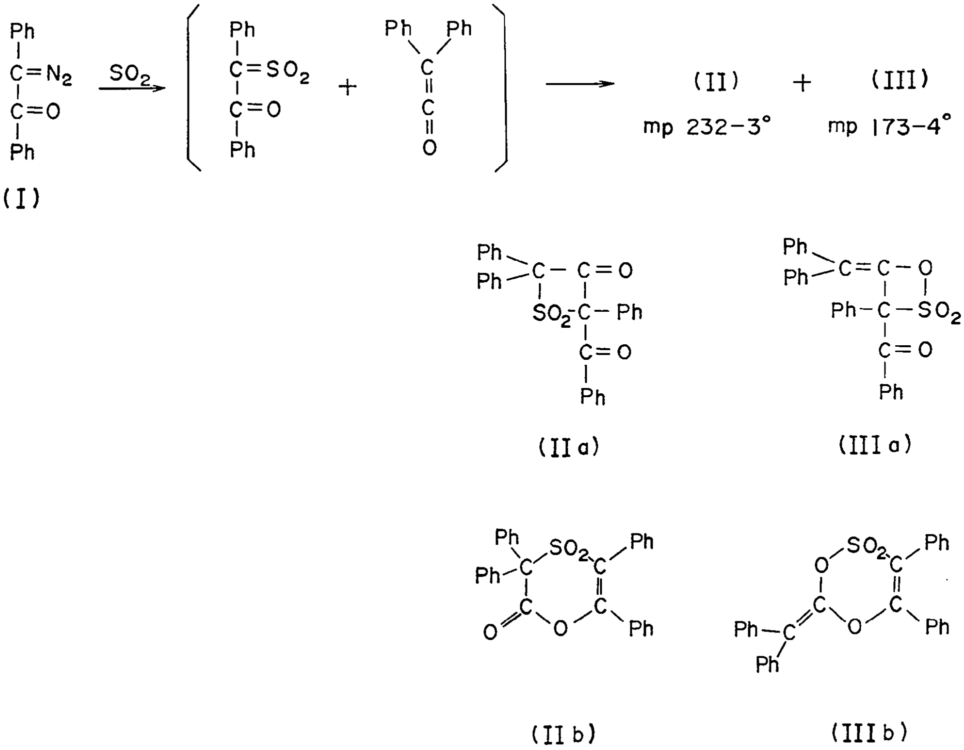
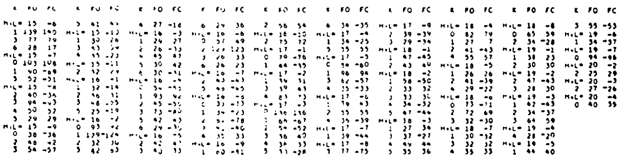


Fig. 1. The reaction of azibenzil with sulphur dioxide, and structures of the products proposed by Nagai, Tanaka & Tokura (1968) (II*a* and III*a*), and by Stothers, Danks & King (1971) (II*b* and III*b*).

Table 1. *Observed and calculated structure factors* (×4)

Table 1 (*cont.*)



also the numbering system in the molecule. It can be seen that the structure of the high-melting point product (II) is 3,3,5,6-tetraphenyl-2,3-dihydro-1,4-oxathiin-2-one-4,4-dioxide (II*b*); that is, the (4+2) cycloaddition scheme suggested by Stothers *et al.* (1971) is correct instead of the (2+2) mechanism.

The six-membered ring containing the sulphur atom is not planar, and it is not easy to describe the conformation of the ring in any simple terms. Table 3 lists the torsion angles in the ring, calculated according to the definition of Klyne & Prelog (1960). Fig. 3 shows the atoms constituting the ring projected onto the mean plane of the five atoms (excluding the sulphur atom), and their elevation from the plane. It is hard to believe that these five atoms lie on a plane. On the other hand, the four atoms S, C(1), C(2) and O(1) almost lie on a plane, the maximum deviation being 0·02 Å for C(2); C(3) and C(4) are located 0·46 and 1·19 Å above the plane respectively.

The bond distances and bond angles in the molecule are summarized in Table 4. C(sp^2)–S and C(sp^3)–S distances are 1·767 and 1·838 Å respectively. A long-standing controversy exists regarding the participation of sulphur 3*d* orbitals in the conjugation between sulphur and other atoms (Moffitt, 1950; Koch & Moffitt, 1951; Cruickshank, 1961; Jordan, Smith, Lohr & Lipscomb, 1963; Cooper, Kenny, Edmonds, Nagel, Wudl & Coppens, 1971). Ammon, Watts & Stewart (1970) discussed C(sp^2)–S bond distances and pointed out that normal carbon–sulphur bonds range in length from 1·75 to 1·80 Å. They therefore submit that trigonal carbon–sulphur bond distances of 1·73 Å or shorter probably resulted from a significant π-bond

Table 2. *Atomic parameters* ($\times 10^4$) *and their estimated standard deviations*

Positional parameters are expressed as fractions of cell edges. Hydrogen coordinates are $\times 10^3$. Anisotropic temperature factors are expressed as:

$$\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\right]$$

and all values listed should be multiplied by 10^{-4}. Isotropic temperature factors are of the form: $\exp(-B\sin^2\theta/\lambda^2)$ with B values in Å². E.s.d.'s are listed in parentheses with respect to the least significant digit of any parameter. Hydrogen atoms are given the same numbers as those atoms to which they are bonded.

	x/a	y/b	z/c	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	394·5 (8)	2267·7 (16)	1968·0 (11)	25·6 (4)	111 (2)	54·4 (9)	−12·5 (16)	22·3 (10)	−2 (2)
O(1)	186 (2)	1975 (4)	4087 (3)	39 (1)	135 (6)	47 (2)	27 (5)	10 (3)	25 (6)
O(2)	993 (2)	321 (5)	4410 (3)	42 (2)	160 (6)	51 (3)	34 (5)	3 (3)	6 (7)
O(3)	194 (2)	2196 (4)	834 (3)	42 (1)	158 (6)	55 (3)	−19 (5)	37 (3)	18 (7)
O(4)	1102 (2)	2830 (5)	2486 (3)	29 (1)	153 (6)	96 (3)	−33 (5)	28 (4)	−37 (8)
C(1)	−297 (3)	3107 (6)	2431 (4)	27 (2)	95 (7)	54 (4)	−14 (6)	13 (4)	4 (8)
C(2)	−296 (3)	2880 (6)	3451 (4)	32 (2)	90 (7)	58 (4)	2 (6)	11 (4)	8 (9)
C(3)	550 (3)	931 (6)	3750 (4)	31 (2)	107 (8)	56 (4)	−1 (6)	13 (4)	−18 (9)
C(4)	344 (3)	581 (6)	2553 (4)	29 (2)	113 (8)	43 (4)	−3 (6)	16 (4)	9 (8)
C(11)	−841 (3)	3957 (6)	1669 (4)	33 (2)	114 (8)	47 (4)	−10 (6)	24 (4)	−3 (9)
C(12)	−1581 (3)	3623 (7)	1439 (5)	31 (2)	169 (10)	73 (5)	−17 (8)	14 (5)	39 (12)
C(13)	−2093 (4)	4402 (9)	723 (5)	40 (3)	231 (13)	84 (5)	13 (10)	8 (6)	34 (14)
C(14)	−1869 (4)	5519 (8)	254 (5)	63 (3)	189 (12)	78 (5)	71 (10)	31 (7)	84 (13)
C(15)	−1130 (4)	5830 (7)	467 (6)	71 (4)	134 (10)	100 (6)	17 (10)	69 (8)	77 (13)
C(16)	−615 (4)	5061 (7)	1174 (5)	45 (3)	121 (9)	94 (5)	−6 (8)	46 (6)	56 (12)
C(21)	−739 (3)	3571 (6)	4093 (4)	32 (2)	111 (8)	50 (4)	3 (6)	15 (4)	−16 (9)
C(22)	−957 (4)	2839 (7)	4869 (5)	46 (3)	164 (10)	62 (4)	8 (9)	37 (5)	5 (11)
C(23)	−1313 (4)	3491 (9)	5551 (5)	50 (3)	266 (14)	79 (5)	31 (11)	61 (7)	15 (15)
C(24)	−1463 (4)	4852 (9)	5441 (6)	42 (3)	238 (13)	86 (6)	13 (10)	27 (6)	−89 (14)
C(25)	−1252 (4)	5583 (7)	4669 (6)	49 (3)	145 (10)	106 (6)	−8 (9)	33 (7)	−107 (13)
C(26)	−889 (4)	4953 (7)	3982 (5)	45 (3)	129 (9)	73 (5)	−5 (8)	26 (6)	−50 (11)
C(31)	−449 (3)	40 (6)	2244 (4)	24 (2)	109 (7)	56 (4)	0 (6)	26 (4)	0 (9)
C(32)	−883 (3)	100 (7)	1199 (5)	30 (2)	162 (10)	62 (4)	−23 (7)	2 (5)	43 (11)
C(33)	−1586 (3)	−435 (8)	955 (5)	33 (2)	188 (11)	89 (5)	−21 (8)	− 1 (6)	52 (13)
C(34)	−1871 (3)	−1050 (8)	1704 (6)	29 (2)	222 (13)	112 (6)	−48 (9)	18 (6)	25 (15)
C(35)	−1444 (4)	−1140 (9)	2720 (6)	36 (2)	277 (15)	101 (6)	−67 (10)	48 (6)	27 (16)
C(36)	−738 (3)	−612 (8)	2992 (5)	33 (2)	219 (12)	65 (5)	−25 (8)	27 (5)	24 (12)
C(41)	916 (3)	−353 (6)	2254 (4)	27 (2)	112 (7)	50 (4)	13 (6)	15 (4)	3 (9)
C(42)	1666 (3)	−103 (7)	2614 (5)	30 (2)	146 (9)	85 (5)	9 (7)	11 (5)	−21 (11)
C(43)	2184 (3)	−912 (8)	2323 (5)	28 (2)	198 (12)	97 (6)	40 (8)	30 (6)	−11 (13)
C(44)	1960 (3)	−2010 (8)	1670 (5)	42 (2)	190 (11)	68 (5)	61 (9)	34 (6)	−15 (12)
C(45)	1216 (4)	−2282 (8)	1304 (5)	47 (3)	166 (10)	69 (5)	40 (9)	21 (6)	−53 (12)
C(46)	700 (3)	−1461 (7)	1606 (5)	33 (2)	144 (9)	68 (4)	5 (7)	25 (5)	−25 (11)

Table 2 (*cont.*)

H(12)	−177 (3)	280 (7)	177 (5)	3·7 (15)
H(13)	−261 (3)	412 (7)	56 (5)	4·4 (17)
H(14)	−222 (4)	615 (7)	−23 (5)	4·8 (17)
H(15)	−97 (4)	662 (8)	17 (6)	6·6 (21)
H(16)	−8 (3)	526 (7)	136 (5)	4·5 (17)
H(22)	−88 (3)	179 (7)	495 (5)	5·1 (17)
H(23)	−150 (4)	294 (7)	605 (5)	5·1 (18)
H(24)	−171 (4)	532 (8)	595 (6)	6·3 (20)
H(25)	−135 (4)	656 (7)	461 (5)	6·1 (19)
H(26)	−70 (4)	549 (7)	344 (5)	5·7 (18)
H(32)	−67 (3)	51 (7)	64 (5)	3·8 (16)
H(33)	−193 (4)	−35 (7)	23 (5)	4·8 (18)
H(34)	−236 (3)	−145 (7)	147 (5)	4·6 (17)
H(35)	−167 (4)	−157 (8)	326 (6)	6·2 (20)
H(36)	−40 (3)	−68 (7)	372 (5)	5·2 (18)
H(42)	182 (3)	75 (7)	308 (5)	4·7 (17)
H(43)	274 (3)	−71 (7)	258 (5)	4·4 (17)
H(44)	234 (3)	−261 (7)	143 (5)	4·1 (16)
H(45)	103 (3)	−309 (7)	84 (5)	4·2 (16)
H(46)	17 (3)	−165 (6)	133 (4)	2·6 (14)

order between the two atoms. According to their criterion, the C(1)–S bond distance of 1·767 Å is a quite normal C(sp^2)–S(VI) distance, and there can be no evidence for π-electron delocalization between the sulphur and carbon atoms. This conclusion is also consistent with the analysis made by Koch & Moffitt (1951), who suggested that an appreciable conjugation may occur when a sulphone group is parallel to a π orbital of an adjacent carbon atom. The dihedral angle between the plane through S, O(3) and O(4) and

Table 3. *Torsion angles in the six-membered ring containing the sulphur atom, defined according to Klyne & Prelog* (1960)

S——C(1)–C(2)–O(1)	+ 3·7°
C(1)–C(2)–O(1)–C(3)	+21·9
C(2)–O(1)–C(3)–C(4)	+ 7·6
O(1)–C(3)–C(4)–S	−50·0
C(3)–C(4)–S——C(1)	+62·3
C(4)–S——C(1)–C(2)	−43·8

All the signs could be reversed simultaneously because the crystal has a centre of symmetry.

Table 4. *Interatomic distances* (Å) *and angles* (°) *with estimated standard deviations*

(*a*) Within and around the six-membered ring containing sulphur

S——C(1)	1·761 (6)	S——C(1)–C(2)	115·9 (4)
C(1)–C(2)	1·341 (8)	C(1)–C(2)–O(1)	122·4 (5)
C(2)–O(1)	1·383 (7)	C(2)–O(1)–C(3)	126·7 (5)
O(1)–C(3)	1·364 (7)	O(1)–C(3)–C(4)	118·1 (5)
C(3)–C(4)	1·541 (8)	C(3)–C(4)–S	100·8 (4)
C(4)–S	1·838 (6)	C(4)–S——C(1)	99·5 (3)
S——O(3)	1·426 (5)	O(3)–S——O(4)	118·5 (3)
S——O(4)	1·436 (5)	O(3)–S——C(1)	110·3 (3)
C(1)–C(11)	1·485 (8)	O(3)–S——C(4)	110·7 (3)
C(2)–C(21)	1·477 (8)	O(4)–S——C(1)	109·2 (3)
C(3)–O(2)	1·193 (7)	O(4)–S——C(4)	106·9 (3)
C(4)–C(31)	1·531 (8)	S——C(1)–C(11)	118·4 (4)
C(4)–C(41)	1·532 (8)	C(2)–C(1)–C(11)	125·6 (5)
		C(1)–C(2)–C(21)	128·0 (5)
		O(1)–C(2)–C(21)	109·5 (5)
		O(1)–C(3)–O(2)	117·5 (5)
		C(4)–C(3)–O(2)	124·3 (5)
		C(3)–C(4)–C(31)	108·9 (5)
		C(3)–C(4)–C(41)	111·9 (5)
		S——C(4)–C(31)	110·6 (4)
		S——C(4)–C(41)	109·0 (4)

(*b*) Within and around the phenyl groups

(1)

C(11)–C(12)	1·380 (9)		C(11)–C(12)–C(13)	120·0 (7)
C(12)–C(13)	1·387 (11)		C(12)–C(13)–C(14)	120·2 (8)
C(13)–C(14)	1·371 (12)		C(13)–C(14)–C(15)	119·5 (8)
C(14)–C(15)	1·373 (12)		C(14)–C(15)–C(16)	120·8 (7)
C(15)–C(16)	1·378 (11)		C(15)–C(16)–C(11)	119·9 (6)
C(16)–C(11)	1·380 (9)		C(16)–C(11)–C(12)	119·5 (6)
			C(1)—C(11)–C(12)	119·5 (6)
			C(1)—C(11)–C(16)	121·0 (5)
C–H	0·95 (8)–1·02 (6)	mean 0·98		
C–C–H	117 (4) –124 (4)	mean 120		

(2)

C(21)–C(22)	1·379 (9)		C(21)–C(22)–C(23)	119·9 (7)
C(22)–C(23)	1·388 (11)		C(22)–C(23)–C(24)	120·3 (8)
C(23)–C(24)	1·368 (12)		C(23)–C(24)–C(25)	120·1 (8)
C(24)–C(25)	1·368 (11)		C(24)–C(25)–C(26)	120·6 (7)
C(25)–C(26)	1·392 (10)		C(25)–C(26)–C(21)	119·2 (6)
C(26)–C(21)	1·389 (9)		C(26)–C(21)–C(22)	119·9 (6)
			C(2)—C(21)–C(22)	118·7 (6)
			C(2)—C(21)–C(26)	121·3 (5)
C–H	0·97 (7)–1·04 (7)	mean 1·00		
C–C–H	118 (4) –122 (4)	mean 120		

(3)

C(31)–C(32)	1·395 (9)		C(31)–C(32)–C(33)	119·8 (6)
C(32)–C(33)	1·378 (10)		C(32)–C(33)–C(34)	121·8 (7)
C(33)–C(34)	1·361 (11)		C(33)–C(34)–C(35)	118·7 (8)
C(34)–C(35)	1·361 (12)		C(34)–C(35)–C(36)	121·0 (8)
C(35)–C(36)	1·380 (12)		C(35)–C(36)–C(31)	120·8 (7)
C(36)–C(31)	1·379 (10)		C(36)–C(31)–C(32)	117·9 (6)
			C(4)—C(31)–C(32)	121·9 (5)
			C(4)—C(31)–C(36)	120·1 (6)
C–H	0·97 (7)–1·00 (7)	mean 0·99		
C–C–H	116 (4)–124 (4)	mean 120		

(4)

C(41)–C(42)	1·383 (9)		C(41)–C(42)–C(43)	121·8 (7)
C(42)–C(43)	1·378 (10)		C(42)–C(43)–C(44)	119·7 (7)
C(43)–C(44)	1·372 (11)		C(43)–C(44)–C(45)	119·5 (7)
C(44)–C(45)	1·378 (10)		C(44)–C(45)–C(46)	120·1 (7)
C(45)–C(46)	1·388 (10)		C(45)–C(46)–C(41)	121·0 (6)
C(46)–C(41)	1·374 (9)		C(46)–C(41)–C(42)	117·8 (6)
			C(4)—C(41)–C(42)	121·4 (5)
			C(4)—C(41)–C(46)	120·8 (5)
C–H	0·98 (6)–1·03 (7)	mean 1·01		
C–C–H	117 (4)–122 (4)	mean 120		

the one through S, C(1), C(2) and O(1) is observed to be 63·9°; this value does not favour the conjugation. Ammon *et al.* (1970) further discussed the structure and conformation which are suitable for π-electron delocalization, and predicted a shorter C(sp^2)–S(VI) bond in methyl vinyl sulphone than in divinyl sulphone. It is interesting to note that both the C(1)–S and C(4)–S bonds are quite normal, though the present compound is a substituted methyl vinyl sulphone.

One of the reasons why the 3*d* orbitals of the sulphur atom do not contribute to the conjugation of the C(1)–C(2) double bond in the present compound is perhaps that both C(1) and C(2) atoms carry a phenyl group as a substituent. This part of the molecule, a substituted *cis*-stilbene moiety, is not planar, the two phenyl groups making angles of 64·9 and 41·6° respectively with the least-squares plane through C(1), C(2), C(11), and C(21). The dihedral angle of the two phenyl groups is 68·1°. This situation is clearly shown in Fig. 2. There can be a certain degree of π-electron delocalization along the *cis*-stilbene moiety, although the degree is low because of non-planarity. Therefore, π-electron delocalization may not be appreciable in the C(1)–S bond.

The structure of *trans*-stilbene has been analysed (Robertson & Woodward, 1937) and reported to be coplanar, while *cis*-stilbene has never been investigated by X-ray analysis. Suzuki (1960) has studied the electronic spectra of *cis*- and *trans*-stilbene, and observed the hypsochromic shift of the conjugation band in *cis*-stilbene compared to *trans*-stilbene. He also estimated the interplanar angle to be 28° in the most probable configuration on the basis of his simple LCAO M.O. calculation. The ultraviolet absorption spectrum of the present compound, measured in a tetrahydrofuran solution, has a longer wavelength maximum, centred at 292 nm compared with the value of 280 nm reported by Suzuki. Although the difference in the observed interplanar angle in the *cis*-stilbene moiety from the one estimated by Suzuki cannot be accounted for at the present stage, a possible origin would be the error involved in the LCAO approximation and/or the substituent effect on the spectrum.

Two S–O distances of 1·426 (5) and 1·436 (5) Å are similar values to those found in other sulphones.

The bond lengths and angles in the phenyl groups are quite normal, but some C–C bonds which are far removed from the centre of the molecule show a tendency to shortening, owing to thermal motion.

A drawing showing the mode of packing is given in Fig. 4. The shortest intermolecular distances are observed between carbon and oxygen atoms, and these are listed in Table 5 together with those for probable hydrogen bonding. These hydrogen bonds might not play an important role in the crystal structure. Similar hydrogen bonding schemes in sulphones are also observed in thiopyran-1,1-dioxide (Boelema, Visser & Vos, 1967) and thiepin-1,1-dioxide (Ammon *et al.*, 1970).

Table 5. *Intermolecular contacts and hydrogen bonding*

(*a*) Shortest intermolecular distances less than 3·5 Å between heavier atoms

O(3)···C(45^{i})	3·314 Å
O(3)···C(46^{i})	3·267
O(3)···C(15^{ii})	3·339
O(2)···C(22^{iii})	3·252
O(1)···C(25^{iv})	3·278
O(4)···C(24^{iv})	3·460
O(4)···C(43^{v})	3·386

(*b*) Probable hydrogen bonding

	O···C	O···H	∠O···H–C
O(2)···H(22^{iii})–C(22^{iii})	3·252 Å	2·27 Å	157°
O(3)···H(15^{ii})-C(15^{ii})	3·339	2·47	153

Key for superscripts:

None	x	y	z
i	$-x$	$-y$	$-z$
ii	$-x$	$1-y$	$-z$
iii	$-x$	$-y$	$1-z$
iv	$-x$	$1-y$	$1-z$
v	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$

All the computations throughout this work were carried out on a NEAC 2200-500 computer at Osaka University and a FACOM 230-60 computer at Kyoto University.

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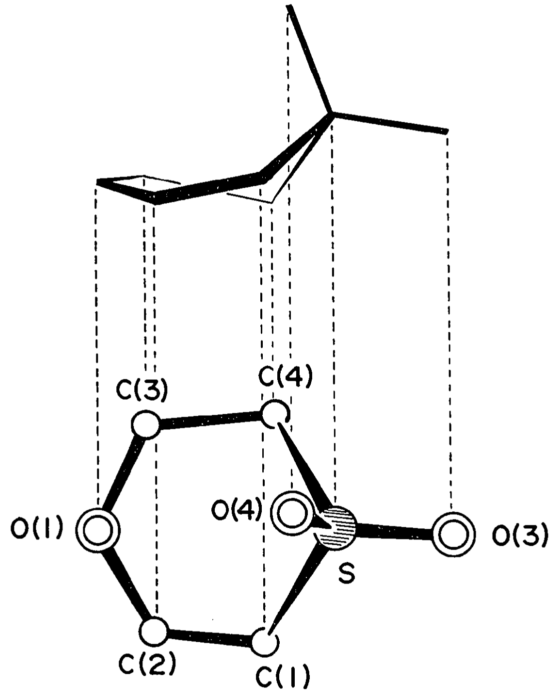

Fig. 3. The six-membered ring projected onto the mean plane of atoms C(1), C(2), O(1), C(3) and C(4), and their elevations from the plane.

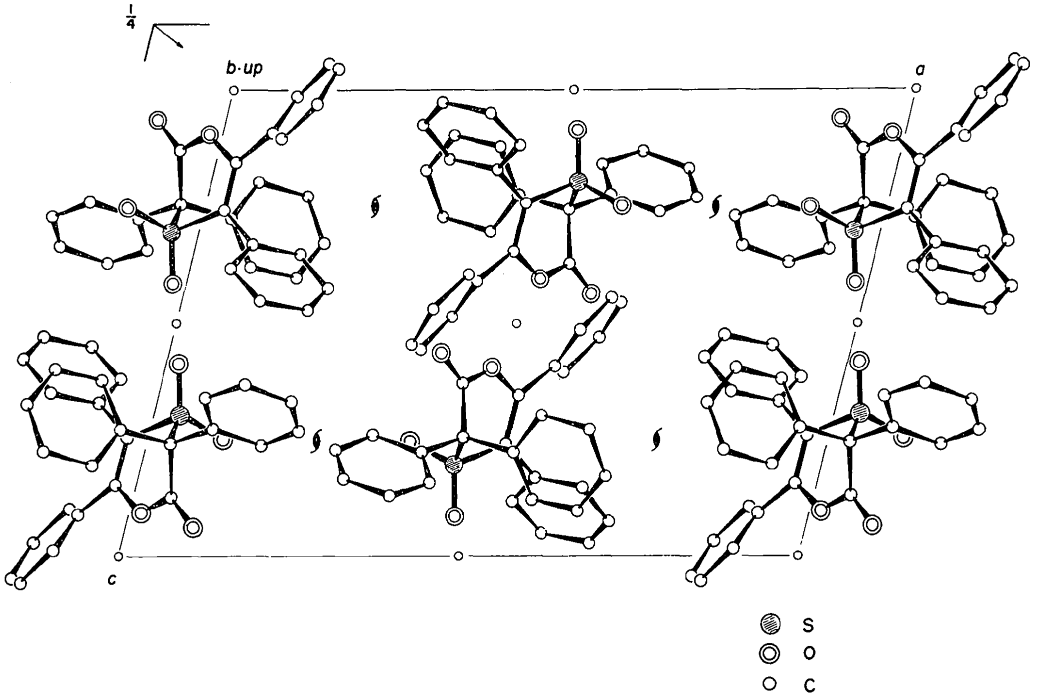

Fig. 4. The crystal structure as it appears when viewed along the *b* axis. The origin is situated half-way along the *a* axis.

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