

every copper atom is coordinated with four oxygen atoms and one copper atom from its own dimer and by a single oxygen atom from a neighbouring dimer. The arrangement is indicated in Fig. 1, while Fig. 2 shows diagrams of the structure in projections from which the side-by-side packing of these chains of dimers may be visualized.

The components of the vibration tensor, reported in Table 1, are defined by  $\overline{U}_i^2 = \sum_j U_{ij} l_j$  where  $\overline{U}_i^2$  is the

mean-square displacement of the atom in the direction defined by the unit vector  $\mathbf{l}$  which has components  $l_1$ ,  $l_2$  and  $l_3$  referred to reciprocal cell axes.

The principal values and axes of the vibration tensor were calculated for each atom from the  $U_{ij}$  values in Table 1.

The only atoms showing marked anisotropy of their thermal motions are C(3), C(4), and C(5), which lie near the ends of the hydrocarbon chains. As usual in these cases the direction of maximum displacement is perpendicular to the chain.

The similarity of the structures of copper butyrate and copper acetate, together with the similarity of the magnetic properties of these compounds to those of the higher copper soaps, suggests that the higher copper soaps will prove to have structures based on the same copper ion environment, and that distortions of the acid groups will occur in such a way as to allow the long hydrocarbon chains to pack together in one

or other of the known packing arrangements for such chains.

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## The Crystal Structure of a Sulfone, 4,5-Dihydrothiepin 1,1-Dioxide

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4,5-Dihydrothiepin 1,1-dioxide,  $C_6H_8SO_2$ , crystallizes in the monoclinic space group  $P2_1/n$  with cell dimensions of  $a = 11.415$ ,  $b = 6.476$ ,  $c = 9.597$  Å,  $\beta = 108.02^\circ$ , and with  $Z = 4$ . Three-dimensional X-ray intensity data were collected with Mo radiation using a Picker diffractometer. The structure was solved with direct methods. Full-matrix least-squares refinement, using anisotropic temperature factors for C, O, and S and isotropic terms for H, gave an  $R$  of 0.049 (weighted  $R = 0.039$ ). The conformation of the 7-membered ring is not symmetrical. Although the C-S lengths are typical of many of the values reported for aromatic sulfones, the C=C distances are smaller than the usual 1.34 Å ethylenic value. A possible rationale for this shortening is given.

#### Introduction

A number of examples of the  $Csp^2-SO_2$  distance in phenyl sulfones and vinyl sulfones can be found in the crystallographic literature. There are, however, no

reported\* examples of this length in 'simple' vinyl sulfones, molecules in which the C-S bonds should be free

\* We make this statement with some hesitation, knowing well that a simple sulfone or two may have escaped our literature searches.

Table 1. *Fractional atomic coordinates and thermal parameters* ( $\times 100 \text{ \AA}^2$ )

E.s.d.'s are given in parentheses.

Thermal parameters are of the form:  $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}klb^*c^*)]$ .The final value for the extinction parameter  $g$  was  $5.4 (\pm 0.4) \times 10^{-6}$ .Non-hydrogen atoms (positional parameters  $\times 10^4$ )

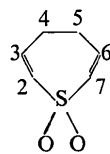
	<i>x</i>	<i>y</i>	<i>z</i>	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
S	-2946 (5)	2566 (1)	2734.0 (7)	3.73 (3)	3.98 (3)	4.94 (3)	0.59 (3)	1.23 (2)	0.18 (3)
O(1)	136 (2)	3575 (3)	1656 (2)	7.5 (1)	4.6 (1)	6.8 (1)	-0.2 (1)	2.7 (1)	1.5 (1)
O(2)	-1171 (2)	3675 (3)	3253 (2)	5.5 (1)	7.7 (1)	8.4 (1)	2.6 (1)	2.6 (1)	-0.5 (1)
C(2)	955 (2)	2015 (4)	4297 (3)	4.0 (1)	5.7 (2)	4.7 (1)	-0.4 (1)	0.7 (1)	-0.9 (1)
C(3)	1708 (2)	418 (5)	4501 (3)	3.7 (1)	6.8 (2)	5.2 (2)	0.0 (1)	0.3 (1)	0.1 (1)
C(4)	1793 (3)	-1354 (5)	3557 (3)	5.3 (2)	6.5 (2)	7.3 (2)	1.8 (2)	1.7 (1)	0.4 (2)
C(5)	1030 (3)	-1246 (5)	1951 (3)	7.8 (2)	5.3 (2)	6.3 (2)	1.2 (2)	3.1 (6)	-0.3 (2)
C(6)	-324 (3)	-1323 (4)	1747 (3)	6.8 (2)	4.4 (2)	5.2 (2)	-0.9 (1)	0.5 (1)	0.0 (1)
C(7)	-956 (2)	187 (4)	2056 (3)	3.7 (1)	5.5 (2)	5.3 (2)	-0.6 (1)	0.4 (1)	0.8 (1)

Table 1 (cont.)

Hydrogen atoms (positional parameters  $\times 10^3$ )

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
H(2)	90 (3)	300 (5)	516 (3)	8.5 (1.0)
H(3)	241 (3)	36 (5)	543 (3)	7.9 (9)
H(4a)	271 (3)	-144 (5)	360 (3)	8.9 (1.0)
H(4b)	158 (3)	-273 (5)	403 (3)	8.3 (1.0)
H(5a)	133 (2)	12 (4)	154 (3)	6.3 (8)
H(5b)	127 (2)	-247 (5)	142 (3)	7.5 (8)
H(6)	-76 (3)	-266 (5)	140 (3)	7.6 (9)
H(7)	-175 (2)	17 (4)	198 (3)	6.2 (8)

from interfering electronic (*e.g.* conjugative) and steric factors. We became interested in this problem as a consequence of some recent work on the structure of thiepin 1,1-dioxide (Ammon, Watts & Stewart, 1970). It was predicted that the  $Csp^2-SO_2$  distance would increase from thiepin 1,1-dioxide to a vinyl sulfone to a divinyl sulfone. Herein, we report the structure of a divinyl sulfone, *viz.* 4,5-dihydrothiepin 1,1-dioxide.



### Experimental

A crystalline sample of 4,5-dihydrothiepin 1,1-dioxide was kindly given to us by Dr William Mock (Mock, 1970) of Carnegie-Mellon University. The crystals formed colorless plates with heavily striated surfaces. Oscillation and Weissenberg survey photographs (Cu radiation) showed that the sample belonged to the monoclinic crystal system. Density measurements were made by the neutral-buoyancy technique in cyclohexane-*sym*-tetrabromoethane. Some difficulty was experienced in achieving a satisfactory neutral-buoyancy condition, since the crystals slowly dissolved in both organic and aqueous solvents. The unit-cell parameters were obtained by least-squares methods from 12 Bragg angles, determined manually on a Picker diffractometer with Mo  $K\alpha$  radiation at both  $+2\theta$  and  $-2\theta$ .

After refinement, the average value of  $|2\theta_o - 2\theta_c|$  was  $0.004^\circ$  for these data. Crystal data are:

 $C_6H_8SO_2$ ; M.W. 144.2

Systematic absences:  $0k0$  absent for  $k$  odd and  $h0l$  absent for  $h+l$  odd

Space group:  $P2_1/n$  $a = 11.415 \pm 0.003 \text{ \AA}$  $b = 6.476 \pm 0.001$  $c = 9.597 \pm 0.002$  $\beta = 108.02 \pm 0.01^\circ$  $V = 674.6 \text{ \AA}^3$  $D_{\text{exp}} = 1.45 \text{ g.cm}^{-3}$  $D_{\text{calc}} = 1.42 \text{ g.cm}^{-3}$  for  $Z = 4$ .

The cell parameter and all X-ray intensity measurements were made using a  $0.1 \times 0.2 \times 0.2$  mm crystal specimen and a Picker FACS-I diffractometer with monochromatized Mo radiation (highly oriented graphite crystal, Mo  $K\alpha$   $\lambda = 0.71069 \text{ \AA}$ ). The crystal was mounted and aligned to place  $b^*$  parallel to the diffractometer  $\phi$  axis. Intensity data were collected using the  $2\theta-\theta$  scan method with a  $2\theta$  speed of  $1^\circ \text{ min}^{-1}$  and  $2\theta$  scan range calculated from  $2.2^\circ + 2.7^\circ \tan \theta$ , and two 20-sec background measurements. Three standard reflections, measured at 80 reflection intervals, were used to monitor and later correct for intensity variations. There were 1556 unique reflections in a total of 2259 data measured to a  $2\theta$  maximum of  $55^\circ$ ; 309 of the 1556 reflections were found to be less than three standard deviations above background, and were coded as 'unobserved.'

The data were scaled from the standard reflection measurements, averaged, converted to  $|F|$ 's, and placed on an absolute scale using the appropriate program links of the *X-ray System for Crystallographic Computing* (1970). A sharpened Patterson synthesis, computed using  $E^2-1$  for the Fourier series coefficients, was dominated by three peaks, two of which were located on the Harker plane ( $v = \frac{1}{2}$ ), while the third was positioned on the Harker line ( $u = w = \frac{1}{2}$ ) at  $v = 0$ . These maxima were consistent with locations of the S atoms on the glide planes at  $y = \frac{1}{4}$  and  $\frac{3}{4}$ . Our initial attempts



Table 2 (cont.)

-11,2,L	-11,4,L	5 39	46	12,2,L	-12,0,L	8 30*	-8	-12,3,L	5 0*	-10	1 32	-31	2 33	-39	8 0*	11	14,0,L	2 22	12	
10 29	-10	1 75	-71	0 74	79	2 105	103	2 32	-53	6 44	43	13,3,L	4 0*	11	-13,3,L	0 119	-116	3 32	43	
-11,3,L	2 0*	5 24	-5	1 16*	1	4 131	-138	-12,2,L	4 91	58	0 0*	4	5 0*	11	2 18*	11	14,1,L	5 22	-2	
1 42	-45	3 30	37	2 30	-30	6 73	71	1 42	-35	4 91	58	0 0*	4	6 27	-28	1 65	-64	5 22	-33	
2 21	24	5 46	-37	3 14*	-12	8 78	-74	2 96	-92	5 74	0	1 48	53	-13,0,L	8 22	-7	3 93	62	0	
3 08	89	7 78	13	10 30	29	2 96	-92	3 3*	15	6 0*	-8	13,1,L	1 31	-30	-13,2,L	6 0*	5	-14,0,L	-14,2,L	
4 0*	6	8 0*	10	0 39	-37	5 46	-45	4 13*	133	7 13*	12	0 17	0	3 52	56	6 20	-18	1 11*	-29	
5 95	-95	0 74	75	1 45	64	1 27	-30	6 95	-92	1 36	0	5 3*	12	1 20	16	6 70	65	2 67	-63	
6 21	20	1 37	-34	2 *51	40	2 70	0*	7 13*	12	2 37	37	9 28	24	4 22	5	-13,4,L	6 31	30	4 77	74
7 76	75	2 125	-105	3 35	23	8 59	62	8 22	-8	3 3*	3	0	0	5 74	6	3 31	45	-14,1,L	6 76	-76
8 15*	13	1 26	21	4 21	11	9 27	10	1 18*	0	2 42	42	13,2,L	-13,1,L	5 3*	-3	4 0*	-16	1 0*	-5	
9 79	-79	2 10*	0	0 14*	-17	6 30*	-1	2 42	42	3 3*	3	0	0	6 3*	-15	4 0*	-16	1 0*	-5	
4 17*	1	1 0*	1	1 0*	-11	7 18	-3	4 42	-45	0 0*	-3	1 53	59	7 15*	17	4 0*	-16	1 0*	-5	

Instead of committing more time to this one problem area, we turned our attention to direct methods, as implemented in subprogram *PHASE* (*X-ray System for Crystallographic Computing*, 1970). Problems arising from the 'special' position of the S atoms were also encountered here. Of the 482 reflections ( $|E| > 1$ ) used in this approach, only 60 belonged to the  $h+l$  odd

parity groups, and only a single  $h+l$  odd reflection was among the 50 reflections of largest  $E$  value used as a base for the phase pyramid. The phases of 47 of these 50 data were solved for in terms of 3 origin-fixing phases, and the 50 phases were then expanded to a total of 416 (212+, 204-). Of the 60  $h+l$  odd reflections, 26 were contained in this set. The nine C, O and S atoms were located in an  $E$  map computed with these 416 terms, although remnants of the false symmetry were still present. A structure-factor calculation using an overall isotropic temperature factor of  $3.3 \text{ \AA}^2$  gave an initial residual of 0.23 for all observed data.

Least-squares refinement of the data used the full matrix of the normal equations and minimized the quantity  $\sum w(|F_o| - |F_c|)^2$ . Individual isotropic temperature factors for C, O, and S and unit weights ( $w=1$ ) were used in the first few cycles. The final cycles of least-squares refinement were calculated using an isotropic extinction correction (Larson, 1967), anisotropic temperature factors for C, O, and S, isotropic terms for H (these atoms were originally located from a difference map), and weights defined by  $w = \{0.1/\text{MAX}[\sigma(F), 0.00333F, 0.1]\}^2$ . This weighting scheme gave  $w = [0.1/\sigma(F)]^2$  for  $F$ 's  $< 8$ ,  $w = 1.0$  for  $F$ 's in the range 8–30, and  $w = (0.1/0.00333F)^2$  for  $F$ 's  $> 30$ . The unobserved data were included in the refinement only if  $I_c > 3\sigma(I_o)$  (97 of the 309 unobserved data). From the last cycle of least-squares refinement the average and maximum parameter shifts were 0.01 and 0.10, respectively, and the  $R$  and weighted  $R$  values were 0.049 and 0.039, respectively, where weighted  $R = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ . Atomic form factors for C and O were taken from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955); for S from *International Tables for X-ray Crystallography* (1962); for H from Stewart, Davidson & Simpson (1965). The atomic parameters are given in Table 1 and the structure factors are listed in Table 2.

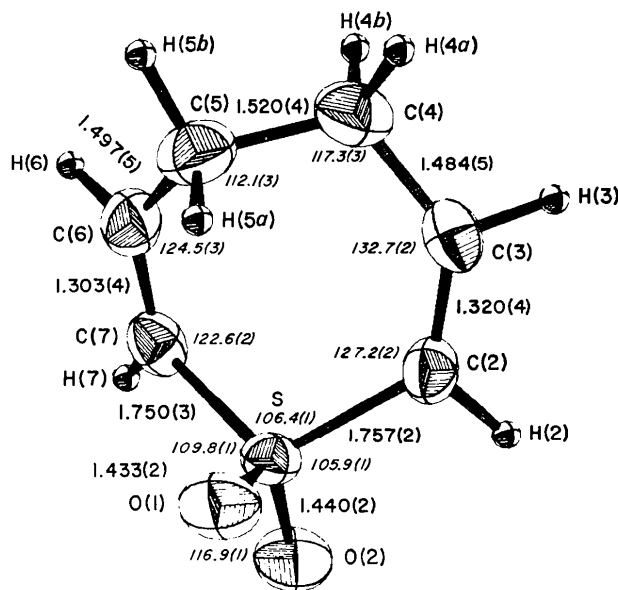


Fig. 1. Bond lengths (Å) and angles (°) for C, O, and S included with an ORTEP (Johnson, 1965) drawing. E.s.d.'s are given in parentheses. 40% ellipsoids were used for C, O, and S with the H's represented as spheres 0.1 Å in diameter. Angles not shown are O(1)-S-C(2) = 109.9° (1) and O(2)-S-C(7) = 107.6°(1).

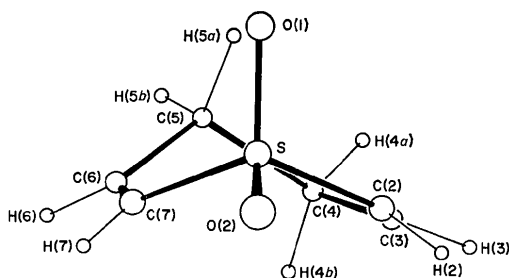


Fig. 2. Conformation of 4,5-dihydrothiepin 1,1-dioxide. The drawing was made looking parallel to a line connecting S and the center of the C(4)-C(5) bond.

## Discussion

Bond lengths and angles for the carbon, oxygen, and sulfur atoms are shown in Fig. 1 and lengths and angles for the hydrogen atoms are given in Table 3. Fig. 2 illustrates the molecular conformation. The sulfone group has almost exact  $mm2$  ( $C_{2v}$ ) symmetry, distortions from tetrahedral bonding being due to the bond-angle restrictions imposed by the 7-membered ring and to the repulsion between the oxygen atoms. The C-S-C & O-S-O angles and the average of the four O-S-C angles are 106.4, 116.9, and 108.3°, respectively

(103.3, 117.7, and 108.7° in thiepin 1,1-dioxide; Ammon *et al.*, 1970). The angle between the C–S–C and O–S–O planes is 89.3°. The distances of C(2) and C(7) from the O–S–O planes are about equal, as are the distances of O(1) and O(2) from the C–S–C plane.

Table 3. Bond lengths and angles to hydrogen with *e.s.d.*'s (in parentheses)

C(2)–H(2)	1.07 (3) Å	H(2)–C(2)–S	108 (1)°
C(3)–H(3)	1.00 (2)	H(2)–C(2)–C(3)	123 (1)
C(4)–H(4a)	1.03 (3)	H(3)–C(3)–C(2)	118 (2)
C(4)–H(4b)	1.06 (3)	H(3)–C(3)–C(4)	109 (2)
C(5)–H(5a)	1.07 (3)	H(4a)–C(4)–C(3)	106 (2)
C(5)–H(5b)	1.03 (3)	H(4a)–C(4)–C(5)	108 (2)
C(6)–H(6)	1.00 (3)	H(4a)–C(4)–H(4b)	108 (2)
C(7)–H(7)	0.88 (3)	H(4b)–C(4)–C(3)	109 (2)
		H(4b)–C(4)–C(5)	109 (1)
		H(5a)–C(5)–C(4)	105 (1)
		H(5a)–C(5)–C(6)	115 (1)
		H(5a)–C(5)–H(5b)	107 (2)
		H(5b)–C(5)–C(4)	108 (1)
		H(5b)–C(5)–C(6)	109 (2)
		H(6)–C(6)–C(5)	117 (2)
		H(6)–C(6)–C(7)	118 (2)
		H(7)–C(7)–S	111 (2)
		H(7)–C(7)–C(6)	127 (2)

A model of the structure was built from a Framework Molecular Models kit (Prentice–Hall Inc., Englewood Cliffs, N.J.) using the observed C–C and C–S

bond lengths, tetrahedral atoms (109.5°) for S, C(4), and C(5), and trigonal atoms (120°) for C(2), C(3), C(6), and C(7). There is no easy way of restricting rotation about multiple bonds in these models, and it was quickly discovered that the most 'comfortable' geometry for the model was a twisted one with  $C_2$  symmetry about a line connecting S and the center of the C(4)–C(5) bond. The C=C torsion angles in this arrangement (about 70°) were clearly unsatisfactory, since observed torsion angles about C(2)–C(3) and C(6)–C(7) (see Table 4) were both 1.2°. All attempts to maintain the double-bond planarity and still achieve a symmetrical molecule resulted in 'uncomfortable' model geometries.

The actual molecular conformation is far from symmetrical and can be visualized as resulting from the intersection of two planes ( $\angle 57^\circ$ ) of atoms, S–C(2)=C(3)–C(4)–C(5) and S–C(7)=C(6)–C(5), at a line connecting S and C(5). Fig. 2 emphasizes this analogy, and additional data in support of it are given in Tables 4 and 5. For example, C(5) deviates by only 0.29 Å from the plane of S–C(2)=C(3)–C(4) (no. 3, Table 5), whereas C(4) is found at a distance of 1.35 Å from the S–C(7)=C(6)–C(5) plane (no. 4). The average distance of the atoms defining the least-squares plane of S–C(2)=C(3)–C(4)–C(5) from the plane (no. 6) is 0.060 Å, and the distances of C(6) and C(7) from the plane are 1.04 and

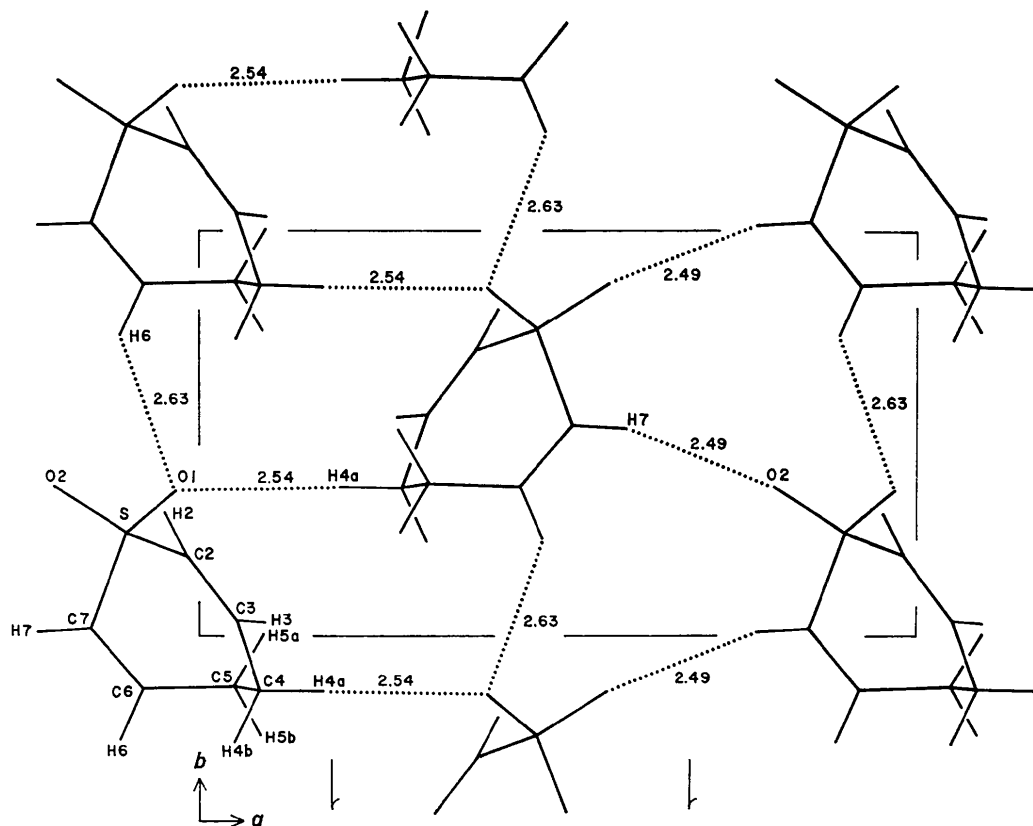


Fig. 3 An intermolecular packing drawing looking normal to the *ab* plane. The shortest H...O approaches (Å) are indicated with dotted lines.

1.18 Å. It is clear that this conformation is responsible for the enlarged endocyclic angles at C(2), C(3), and C(4) (127.2, 132.7, 117.3°) relative to those at C(7), C(6), and C(5) (122.6, 124.5, 112.1°).

The C–C single bond distances of 1.520 ( $sp^3$ – $sp^3$ ) and 1.490 Å (average,  $sp^2$ – $sp^3$ ), and the average S–O length of 1.436 Å, have normal values for these kinds of connections. In harmony with the prediction (Ammon *et al.*, 1970) that the C( $sp^2$ )–SO<sub>2</sub> distance would increase in the series thiepin 1,1-dioxide (1.719 Å) < 2*H*-thiapyran 1,1-dioxide (1.739 Å; Boelma, Visser & Vos, 1967) < a divinyl sulfone, we found an average C–S length of 1.753 Å in 4,5-dihydrothiepin 1,1-dioxide. The value is typical of the C–S distance in many aromatic sulfones (ref. 7 in Ammon, Watts, Stewart & Mock, 1968). An unexpected structural feature is revealed in the C=C lengths, average 1.311 Å, which are shorter than the usual value of 1.34 Å (Table 5 in

Ammon *et al.*, 1970; March, 1968). With data from only a single compound, it is not possible to judge if the decrease in the C=C linkage is a function of the particular molecular conformation or a general phenomenon of vinyl sulfones. A possible rationale for the shortening might be obtained from a consideration of the SO<sub>2</sub> group electronegativity compared to the usual C=C substituents of C and H. The effect would lead to an increase in the *p* character of the C–S bond's  $\sigma$  orbital, and the concomitant increase of the *s* component in the  $\sigma$  orbital of the C=C moiety would cause a shortening of the C=C bond. Bent (1961) has described a similar effect to explain variations in bond lengths and angles with substituent electronegativities, and examples of the effect can be found in the double-bond lengths in tetracyanoethylene (1.317 Å, Bekoe & Trueblood, 1960) and 1,1,1-trifluoroazomethane (1.219 Å, compared to 1.254 Å in azomethane; Chang, Porter

Table 4. Angles (°) between least-squares planes

Planes						Planes					
Planes	2	3	4	5	6	7	8	9	10	11	12
1:						36.7	36.5	82.4	53.8	54.4	40.9
2:	89.3					68.0	59.5	64.7	61.8	60.7	63.6
3:		36.6				0.8	12.2	61.7	51.9	53.0	5.5
4:			53.7			53.2	63.9	73.5	0.8	0.7	56.8
5:				45.5		11.4	10.5	56.1	62.4	63.6	6.7
6:					35.9	1.2	12.3	51.6	52.7	52.7	6.1
							11.5	61.8	52.7	53.8	4.9
								66.6	63.4	64.6	10.5
									72.8	73.5	58.4
										1.2	56.2
											57.4

Table 5. Least-squares planes and deviations (Å)

Planes						
Planes	1	2	3	4	5	6
1:	6.3061x + 2.6441y + 4.9923z = 1.8575					
2:	9.3572x - 0.4278y - 7.6281z = -2.4708					
3:	8.6847x + 3.4205y - 5.6997z = -0.9350					
4:	-1.1500x - 2.2224y + 8.8216z = 1.8773					
5:	8.8785x + 3.8983y - 3.9587z = -0.3436					
6:	8.7350x + 3.7130y - 4.9433z = -0.5997					
Planes†						
	1	2	3	4	5	6
S	0.0*	0.0*	-0.002*	-0.002*	0.0*	-0.056*
O(1)	0.0*	1.182	1.332	-1.227	1.202	1.227
O(2)	0.0*	-1.263	-0.679	0.310	-0.551	-0.667
C(2)	1.423	0.0*	0.004*	1.356	0.267	0.058*
C(3)	1.577	0.616	-0.005*	1.804	0.241	0.021*
C(4)	0.691	1.493	0.002*	1.355	0.0*	-0.095*
C(5)	-0.563	1.999	0.291	0.002*	0.0*	0.072*
C(6)	-1.540	0.892	-0.795	-0.005*	1.151	-1.038
C(7)	-1.385	0.0*	-1.003	0.005*	-1.246	-1.183

\* Atoms used to define the planes.

† Columns give the atoms' deviations from designated planes.

& Bauer, 1970). We are planning to investigate some additional vinyl sulfones as well as some disulfonyl-ethylenes to provide more experimental test data for this hypothesis.

Fig. 3 shows a packing drawing viewed perpendicular to the *ab* plane. Since there are no close intermolecular distances to the viewing direction, only the molecules in one layer are shown. The shortest approaches are between hydrogen and the sulfone oxygen atoms and these distances are indicated with dotted lines in Fig. 3. The magnitudes of the distances indicate that H...O interactions are probably just those permitted by the van der Waals radii of H and O.

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## The Crystal Structure of Compounds with (N-P)<sub>n</sub> Rings. IX.\* Octabromocyclotetraphosphazene, N<sub>4</sub>P<sub>4</sub>Br<sub>8</sub>

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The crystal and molecular structure of octabromocyclotetraphosphazene, N<sub>4</sub>P<sub>4</sub>Br<sub>8</sub>, has been determined from three-dimensional intensity data collected at 110°K with Zr-filtered Mo radiation on a Nonius automatic three-circle single-crystal diffractometer. The space group is *P*4<sub>1</sub>/*n* and the edges of the tetragonal unit cell, determined at 110°K, are *a* = 11.187 (3) and *c* = 6.189 (2) Å. The crystal structure is isomorphous with that of N<sub>4</sub>P<sub>4</sub>Cl<sub>8</sub> (*K* form). There are three intermolecular Br...Br distances (3.66, 3.74, and 3.79 Å) that are shorter than the corresponding van der Waals distance (3.90 Å). The molecules N<sub>4</sub>P<sub>4</sub>Br<sub>8</sub> possess crystallographic fourfold inversion symmetry. Mean values (and individual standard deviations) of chemically equivalent bond lengths are P-N, 1.575(6), and P-Br, 2.171(2) Å. The more important valence angles are P-N-P, 131.0(4), N-P-N, 120.1(4), and Br-P-Br, 103.9(1)°. The conformation of the eight-membered ring is intermediate between a boat and a saddle. The dihedral angles of the ring bonds are 17 and 59° and the distances from the ring atoms to the mean molecular plane are ΔP = 0.36 and ΔN = 0.49 Å (ΔP/ΔN = 0.74). The molecular structure of N<sub>4</sub>P<sub>4</sub>Br<sub>8</sub> is compared with that of related compounds.

#### Introduction

The preparation of octabromocyclotetraphosphazene from phosphorus(V) bromide and ammonium bromide has been reported by Bode (1943) and by Bean & Shaw

(1960). Improved preparative methods, with the use of phosphorus(III) bromide and bromine instead of the pentabromide, have been described by John & Moeller (1961, 1963) and by Coxon, Sowerby & Tranter (1965).

The infrared spectrum of N<sub>4</sub>P<sub>4</sub>Br<sub>8</sub> has been measured by several workers and shows the characteristic P-N stretching vibration at 1272 cm<sup>-1</sup>. The <sup>31</sup>P nuclear

\* Part VIII: Mani & Wagner (1971).