Fig. 5. Structure of $\text{Rb}_5\text{Zr}_4\text{F}_{21}$.

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS, A Fortran Crystallographic Least-Squares Program*, Report ORNL-TM-305. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- CROMER, D. T. (1965). *Acta Cryst.* **18**, 17.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.
- DREW, M. G. B. (1967). Program *PHASEM*. Lawrence Radiation Laboratory, Berkeley, California.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502.

- LEVY, H. A., THIESSEN, W. E. & BROWN, G. M. (1970). Report ORNL-4581, p. 135. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- SEARS, D. R. & BURNS, J. H. (1964). *J. Chem. Phys.* **41**, 3478.
- SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**, 925.
- THOMA, R. E. (1959). Report ORNL-2548, p. 59. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558.
- ZACHARIASEN, W. H. (1968). *Acta Cryst.* **A24**, 212.

Acta Cryst. (1971). **B27**, 1948

The Crystal and Molecular Structures of Some Molecules Showing $\text{S} \cdots \text{O}$ Interaction.

I. The Desaurin from Acetophenone.

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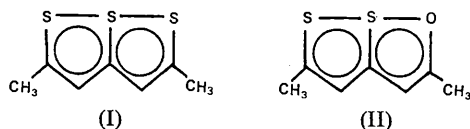
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(Received 9 July 1970)

The crystal structure of the 'desaurin from acetophenone', $\text{C}_{18}\text{H}_{12}\text{O}_2\text{S}_2$, has been determined as part of a program to investigate the $\text{S} \cdots \text{O}$ interactions in a range of molecules. The crystals belong to the monoclinic space group $P2_1/c$ with $a = 5.740$ (8), $b = 4.848$ (12), $c = 28.299$ (8) Å, $\beta = 96.9$ (1)°. The structure was solved from the Patterson function using 1020 photographically determined intensities and refined to $R = 0.124$. The molecule shows an $\text{S} \cdots \text{O}$ distance of 2.640 (6) Å.

Introduction

The two-dimensional crystal structure analysis of 2,5-dimethylthiophthene (I) by Bezzi, Mammi & Garbuglio (1958)



indicated a symmetrical molecule with $\text{S} \cdots \text{S}$ distances of 2.36 Å. This early crystal structure analysis has since

been subjected to three-dimensional refinement in these Laboratories (Leung & Nyburg, 1969) and $\text{S} \cdots \text{S}$ determined as 2.358 (1) Å. As pointed out by Bezzi *et al.* at the time, this is substantially longer than any 'formal' S-S bond known. A subsequent examination of S-S bond lengths by Hordvik (1966) suggests that the longest possible S-S bond, *i.e.* a single bond with no π character, would be 2.10 Å long. On the other hand, an examination of a number of sulphur-containing crystal structures shows that the minimum van der Waals radius of sulphur is about 1.65 Å [a value as high as 1.85 Å has been suggested by Pauling (1960)]. Accordingly, 2,5-dimethylthiophthene was the first

example of a molecule in which, for no obvious reasons, sulphur atoms were separated by a distance substantially longer than a chemical bond but substantially shorter than that known hitherto for non-bonded atoms. Later Mammi, Bardi, Traverso & Bezzi (1961) carried out a two-dimensional structure analysis of 2,5-dimethyldithiofurophthene (II) and found in this case that S-S was only slightly longer than single (2.12 Å) but S...O was 2.41 Å. A single S-O bond would be 1.65 to 1.70 Å whereas the sum of van der Waals radii for O and S would be about 3.25 Å or possibly a little shorter. Hence this molecule shows an S...O effect analogous to S...S in (I).

Since then a number of other structures exhibiting S...S or S...O interactions have been analysed and are set out in Table 1. In addition, it has been reported (van den Hende & Klingsberg, 1966) that in the selenium analogue of (II) S...S is 2.49 Å and S...Se 2.33 Å. Some of the now known nitrogen analogues also show the effect (Leung & Nyburg, 1971). A preliminary communication on the structure of a bis-alkylidene-1,2,4,5-tetrathiin (Alcock & Kirby, 1966) in which similar short S...O distances might be expected does

not appear to have been followed by complete analysis. There have been a number of theoretical studies of these and related systems and this discussion is deferred. A substantial number of the earlier of the above analyses were two-dimensional and therefore of limited accuracy. There does therefore seem to be a need for further more accurate studies on related systems if the nature of the interaction is to be better understood.

We report here and in the two following papers the crystal structures of three molecules of this type. The present paper is concerned with the crystal structure of the desaurin from acetophenone (III, R=C₆H₅, R'=H).

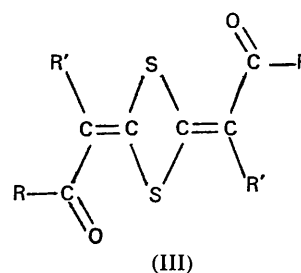


Table 1. *Crystal structure analyses showing S...S and S...O distances intermediate between single bond and van der Waals contact*

(a) S...S distances (Å). Single bond, <i>ca.</i> 2.10 Å; van der Waals sum, <i>ca.</i> 3.30 Å.		
2,5-dimethylthiophthene	2.358 (1)	Bezzi, Mammi & Garbuglio (1958), Leung & Nyburg (1969)
3-benzoyl-5- <i>p</i> -bromophenyl-2-methylthio-6a-thiothiophthene	2.18 (7) 2.52 (7)	Johnson, Newton & Paul (1969)
2,5-diphenylthiothiophthene	2.36 (3) 2.30 (3)	Hordvik (1969)
3,4-diphenylthiothiophthene	2.232 (4) 2.434 (4)	Johnson & Paul (1969a)
2,4-diphenylthiothiophthene	2.499 (3) 2.218 (3)	Hordvik, Sletten & Sletten (1969)
2,4-diphenyldithiofurophthene	2.088 (8)	Hordvik, Sletten, Sletten, Nyburg & Leung (1970)
2,3,4-triphenylthiothiophthene	2.266 (3) 2.371 (3)	Hordvik (1969)
isothiathiophthene derivative	2.91 (1)	Beer, Frew, Johnson & Paul (1970)
1-bromo-2,4-epidithio-1-nitrophenylbutadiene	2.075 (3)	Reid & Paul (1970)
(b) S...O distances (Å). Single bond, <i>ca.</i> 1.67 Å; van der Waals sum, <i>ca.</i> 3.25 Å		
2,5-dimethyldithiofurophthene (II)	2.41	Mammi, Bardi, Traverso & Bezzi (1961)
*2-benzoylimino-3-thiazolid-5-one	2.67	Steeple (1961)
*merocyanine	2.80	Germain, Piret & van Meerssche (1962)
<i>o</i> -nitrobenzenesulfinic acid	2.44	Hamilton & Laplaca (1964)
sodium-3,5-diacetylamino-1,2-dithiole	2.63	Hordvik & Sletten (1966)
3,5-diacetamido-1,2-dithiolium bromide	2.57, 2.52	Hordvik & Kjøge (1966)
desaurin from acetophenone	2.640 (6)	Present work
2-methylene-1,3-dithiacyclobutane derivative (IV)	2.63	Kapecki, Baldwin & Paul (1968)
2-desylidene-1,3-dithiolane	2.70	Schmidt & Tulinsky (1967)
3,5-epidithio-2-nitroso-1,5-diphenylpenta-2,4-dien-1-one	2.034	Johnson & Paul (1969b)
octathiatricycloicosahexane derivative	2.78	Bernal & Ricci (1969)
<i>o</i> -dinitrophenyldisulfide	2.588 (7), 2.636 (8)	Ricci & Bernal (1969)
3-phenyl-1-propene-1,3-dione-1-(dimethyl mercaptole)	2.727 (10)	Mellor & Nyburg (1971a)
3,5-bis(pivaloylmethylene)-1,2,4-trithiolane	2.509 (5), 2.517 (5)	Mellor & Nyburg (1971b)

* Distances not given by author(s)

Experimental

The desaurins (*L. aureus*, golden) were originally so named by Meyer (1890) and have come to be associated with compounds generally agreed (Yates & Moore, 1958) since Meyer's first assignment, to contain the dithiacyclobutane ring.

The X-ray crystal analysis of the 'desaurin from acetophenone' (*i.e.* III, $R=C_6H_5$, $R'=H$) was undertaken to verify the proposed molecular structure, to establish the stereochemistry and in the hope of adding further accurate data to our knowledge of the S...O interactions. A preliminary note on this structure analysis has been published (Lynch, Mellor, Nyburg & Yates, 1967).

Crystals were kindly supplied by Professor P. Yates and were recrystallized from nitrobenzene as bright yellow plates. On the axial system given below, {001} predominate. X-ray intensity data were recorded on multiple-pack equi-inclination Weissenberg photographs using Ni-filtered Cu $K\alpha$ radiation. Two crystals were used to collect two sets of visually estimated data: $h0l$ through $h3l$ and $0kl$ through $4kl$. The $0kl$ set was taken as arbitrary standard for scaling between sets, by least squares.

The crystals belong to the monoclinic system, space group $P2_1/c$ with the following cell dimensions obtained by aluminum powder line calibration and least-squares refinement: $a=5.470$ (8), $b=4.848$ (12), $c=28.299$ (8) Å; $\beta=96.9$ (1)°. The measured density (benzene/ CCl_4) was 1.45 g.cm^{-3} ; the density calculated for $M=324$ and $Z=2$ is 1.44 g.cm^{-3} .

The largest crystal used for three-dimensional data collection measured $0.20 \times 0.20 \times 0.02$ mm. Since μ is 33.15 cm^{-1} , no absorption corrections were applied.

Initial structural information was determined using those 334 observable reflexions lying in $0 < 2\theta \leq 80^\circ$. The Patterson function could be interpreted with sulphur lying in the pseudo-special position (0.190, 0, 0.023). This position was used to phase the reflexions for $k+l=2n$. Because of the resultant false planes of symmetry at $y=0$, $\frac{1}{2}$ some difficulty was experienced in locating the lighter atoms. In the end we moved sulphur arbitrarily to $y=0.01$ and kept it there until all the lighter atoms had been phased in.

Full-matrix anisotropic refinement was carried out on all the data, 1020 observed reflexions out of a possible 1493, using a local modification of *ORFLS* (Busing, Martin & Levy, 1962). Hughes's (1941) weighting scheme was used with F_{\min} set at 3.0. For each unobserved reflexion the maximum possible structure amplitude $|F_{\max}|$ was calculated and replaced by its statistically most probable value $F_{\max}/\sqrt{3}$ as given by Hamilton (1955).

The y -projected view of the asymmetric half of the molecule and the atomic numbering scheme is given in Fig. 1. The final atomic parameters and anisotropic thermal parameters are listed in Table 2. All hydrogen atoms could be easily identified from a difference synthesis and their positions (Table 3) and the scattering factor of McWeeny (1951), were used for the F_c listed in Table 4. Other scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Also in Table 3 the hydrogen positions used are com-

Table 2. Fractional atomic coordinates of non-hydrogen atoms, anisotropic thermal parameters (Å²) and their standard deviations

The temperature factor T is of form $\exp[-\frac{1}{4}(h^2a^*2B_{11} + k^2b^*2B_{22} + l^2c^*2B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

	10^4x	10^4y	10^5z	10^2B_{11}	10^2B_{22}	10^2B_{33}	10^2B_{12}	10^2B_{13}	10^2B_{23}
S	-1969 (2)	22 (3)	2352 (5)	282 (6)	383 (7)	420 (7)	-39 (5)	55 (4)	-53 (5)
O	-1506 (7)	3345 (11)	9797 (16)	338 (17)	573 (28)	581 (22)	-145 (17)	111 (14)	-149 (20)
C(1)	945 (9)	1614 (13)	2628 (19)	241 (18)	386 (31)	405 (23)	2 (18)	24 (15)	12 (21)
C(2)	1970 (9)	3399 (13)	5813 (21)	305 (20)	352 (31)	468 (25)	7 (19)	18 (17)	-11 (22)
C(3)	545 (10)	4272 (14)	9602 (20)	304 (20)	365 (31)	416 (24)	6 (19)	21 (16)	-18 (21)
C(4)	1607 (9)	6315 (12)	13243 (20)	315 (20)	255 (27)	433 (23)	33 (18)	19 (16)	22 (20)
C(5)	357 (11)	6716 (14)	17243 (22)	468 (27)	340 (33)	477 (27)	23 (23)	74 (21)	-30 (24)
C(6)	1219 (14)	8600 (16)	20662 (24)	602 (34)	389 (36)	474 (28)	4 (23)	43 (24)	-23 (26)
C(7)	3314 (13)	10131 (15)	20196 (26)	513 (31)	355 (35)	558 (32)	54 (24)	-85 (25)	28 (25)
C(8)	4587 (13)	9748 (15)	16246 (28)	437 (27)	366 (35)	649 (36)	14 (23)	-23 (25)	-13 (27)
C(9)	3714 (11)	7813 (14)	12761 (24)	408 (24)	303 (31)	531 (28)	-41 (21)	41 (20)	-2 (24)

Table 3. Hydrogen positions

(a) as observed from a difference synthesis and used in F_c ; (b) as calculated making normal bond angle assumptions and assuming a C-H length of 1.075 Å

	Attached to carbon atom	(a)			(b)		
		x	y	z	x	y	z
H(1)	C(2)	0.372	0.421	0.055	0.3793	0.4184	0.0561
H(2)	C(5)	-0.085	0.529	0.175	-0.1277	0.5546	0.1762
H(3)	C(6)	-0.058	0.914	0.221	0.0259	0.8890	0.2372
H(4)	C(7)	0.404	1.150	0.227	0.3963	1.1616	0.2289
H(5)	C(8)	0.614	1.081	0.159	0.6220	1.0925	0.1589
H(6)	C(9)	0.487	0.783	0.098	0.4683	0.7496	0.0972

pared with those calculated on the basis of a C—H length of 1.075 Å.

Conventional R values were 0.124 (unobserved reflexions taken as $F_{\max}/\sqrt{3}$) and 0.110 (unobserved reflexions omitted). After the structure analysis had been completed Leung (1967) attempted a solution by direct methods using Σ_1 , Σ_1' and Σ_3 of Hauptman & Karle (1953) to assign signs to seven E values. Using Σ_2 , a large number of further signs were generated but only those 133 involving at least two Σ_2 relations were included. The resultant E map gave the virtually correct sulphur positions but, of course, had the same false symmetry as the F map derived from the Patterson

function. After suitable change of signs (due to change in origin) all but one of these 133 reflexions had signs the same as those given in Table 4. No further generation of phases by direct methods was attempted.

Discussion

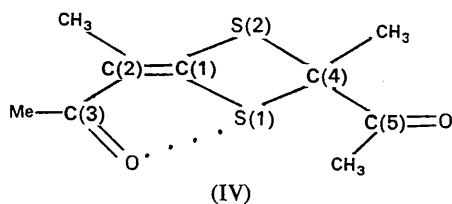
The chemically assigned structure (III) is shown to be correct and the fact that the molecule is centrosymmetric immediately requires it to be the *trans* isomer about the C(1)–C(2) double bond and requires the dithiacyclobutane ring to be planar. In addition the molecule is shown to be *s-cis* about C(2)–C(3).

Table 4. Calculated and observed structure factors

Unobserved reflexions are marked *.

K=0				L 10% 10% 10%				H L 10% 10% 10%				K=1				L 10% 10% 10%				H L 10% 10% 10%				K=2				L 10% 10% 10%				H L 10% 10% 10%																							
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Bond lengths and angles involving non-hydrogen atoms are given in Fig. 1 (no librational corrections were made) together with the thermal ellipsoids. The two independent C-S distances 1.766 (6) and 1.764 (6) Å are remarkably similar. With S...S' and C(1)...C(1') distances of 2.655 (6) and 2.315 (9) Å respectively the ring must be subject to considerable strain and the larger effective size of the sulfur atoms may itself be sufficient to account for a larger S-C(1)-S' angle of 98.0 (4)° than C(1)-S-C(1'), 82.0 (4)°. By contrast, the dithia-cyclobutane ring system (IV) studied by Kapecki, Baldwin & Paul (1968) shows surprisingly large differences in the two corresponding bond lengths which are C(1)-S(1), 1.79, and C(1)-C(2), 1.72 Å.



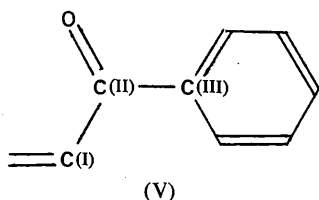
The most striking feature of the desaurin structure is the close planarity of the (*s-cis*) $\alpha\beta$ -unsaturated carbonyl and sulphur atom systems. The least-squares plane calculated for the central ten atoms of the molecule and the atomic deviations from it are given in Table 5. We defer a detailed discussion of the S...O interaction except to note here the S...O distance 2.64 Å and compare it with others given in Table 1. The benzene ring least-squares plane $2.752x - 3.443y + 12.125z = -0.1237$ is not coplanar with the rest of the molecule, being inclined at 11.4° to it.

Table 5. *Least-squares plane of the central position of the molecule*

$1.796x - 3.121y + 15.131z = 0$ where x, y, z are fractional coordinates.

Atom	Δ
(S'), S	0.0060 Å
(O'), O	0.0012
[C(1')], C(1)	0.0168
[C(2')], C(2)	0.0021
[C(3')], C(3)	0.0036

As far as the benzoyl end of the molecule is concerned there are relatively few structure analyses available with which a pertinent comparison can be made. If we compare systems where the ketoxy-carbon atom is bonded (on the side away from phenyl group) to an sp^2 carbon atom (V)



we can make comparisons with bis-*m*-bromobenzoyl-methane (Williams, Dumke & Rundle, 1962), dibenzoylmethane (Williams, 1966), 2-desylidene-1,3-dithiolane (Schmidt & Tulinsky, 1967) and this desaurin. In the first two molecules the situation is complicated by the keto-oxygen atom being hydrogen bonded; nevertheless the bond length variations are surprisingly large: C(I)-C(II) from 1.393 to 1.49 Å, C(II)-C(III) from 1.44 to 1.495 Å, C(II)-O from 1.216 to 1.306 Å. This latter range shows how short C=O is in desaurin compared with that in other comparable structures. Bond angles in the first two compounds may be affected by hydrogen bonding; in the latter two compounds all three angles about C(II) are close to 120°.

A general view of the crystal structure is given in Fig. 2 and a list of interatomic contacts less than 3.90 Å given in Table 6. The closest contacts between molecules with their midpoints on the $z=0$ plane and those with midpoints on $z=\frac{1}{2}$ are all larger than 3.90 Å; hence Table 6 is concerned only with molecules centred on the $z=0$ plane. The closest S...S distance of 3.42 Å is relevant to our discussion of the van der Waals radius of sulphur given above.

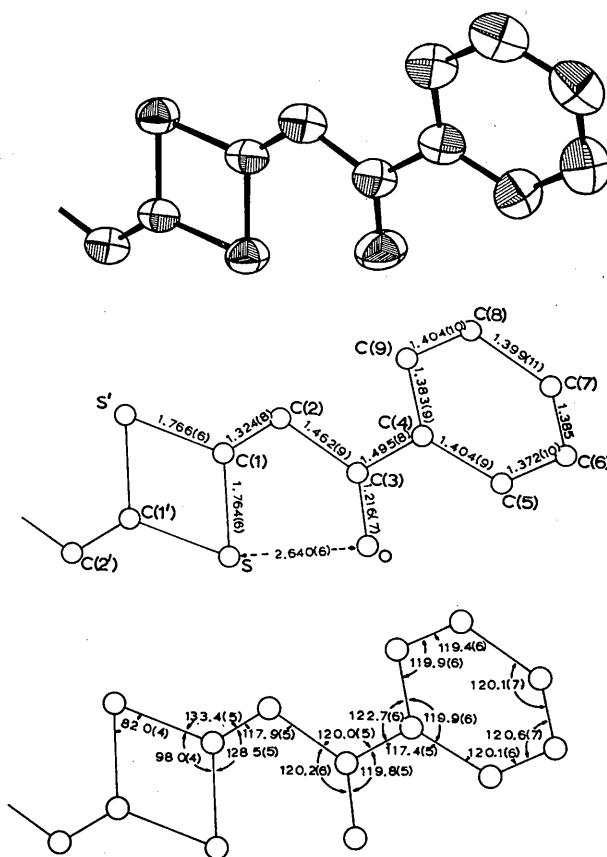


Fig. 1. Perspective view of the half-molecule seen from about 80 Å showing 50% probability thermal ellipsoids (Johnson, 1965), atomic numbering scheme, bond lengths and bond angles.

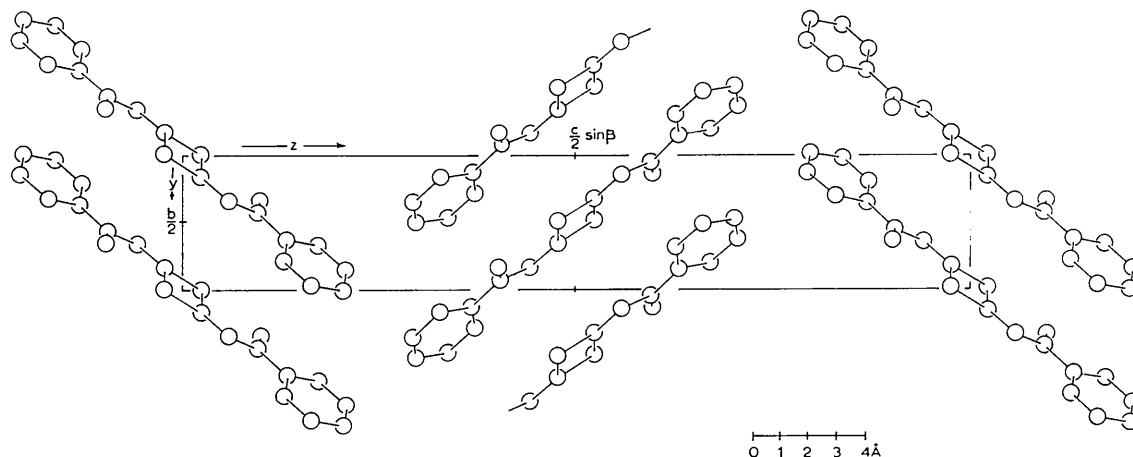


Fig. 2. Molecular packing viewed along [100].

Table 6. Interatomic contacts between molecules less than 3.90 Å

Atom B is generated from the coordinates listed in Table 2 where i is x, y, z and ii $\bar{x}, \bar{y}, \bar{z}$.

Atom A	Atom B	Unit translation on atom B	Distance
S	S ₂	(-1, 0, 0)	3.42 Å
S	O ₁	(0, -1, 0)	3.85
S	C(3 ⁱ)	(0, -1, 0)	3.63
S	C(4 ⁱ)	(0, -1, 0)	3.89
O	C(2 ⁱ)	(-1, 0, 0)	3.61
O	C(4 ⁱ)	(0, -1, 0)	3.88
O	C(8 ⁱ)	(-1, -1, 0)	3.45
O	C(9 ⁱ)	(-1, 0, 0)	3.57
C(1)	C(1 ⁱⁱ)	(0, 1, 0)	3.70
C(1)	C(2 ⁱⁱ)	(0, 1, 0)	3.63
C(1)	C(9 ⁱ)	(0, -1, 0)	3.59
C(2)	C(8 ⁱ)	(0, -1, 0)	3.59
C(2)	C(9 ⁱ)	(0, -1, 0)	3.42
C(3)	C(8 ⁱ)	(0, -1, 0)	3.50
C(3)	C(9 ⁱ)	(0, -1, 0)	3.64
C(4)	C(7 ⁱ)	(0, -1, 0)	3.65
C(4)	C(8 ⁱ)	(0, -1, 0)	3.63
C(5)	C(7 ⁱ)	(0, -1, 0)	3.63
C(5)	C(8 ⁱ)	(-1, 0, 0)	3.46
C(5)	C(9 ⁱ)	(-1, 0, 0)	3.74

References

- ALCOCK, N. W. & KIRBY, A. J. (1966). *Tetrahedron*, p. 3007.
- BEER, R. J. S. & FREW, D., JOHNSON, P. L. & PAUL, I. C. (1970). *Chem. Commun.* p. 154.
- BERNAL, I. & RICCI, J. S. (1969). *Chem. Eng. News*, **47**, 40.
- BEZZI, S., MAMMI, M. & GARBUGLIO, C. (1958). *Nature, Lond.* **182**, 247.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS, A Fortran Crystallographic Least-Squares Program*. ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
- GERMAIN, G., PIRET, P. & VAN MEERSSCHE, M. (1962). *Acta Cryst.* **15**, 373.
- HAMILTON, W. C. (1955). *Acta Cryst.* **8**, 185.
- HAMILTON, W. C. & LA PLACA, S. L. (1964). *J. Amer. Chem. Soc.* **86**, 2289.
- HAUPTMAN, H. & KARLE, J. (1953). *Solution of the Phase Problem*. A.C.A. Monograph.
- HENDE, J. H. VAN DEN & KLINGSBERG, E. (1969). *J. Amer. Chem. Soc.* **88**, 5045.
- HORDVIK, A. (1966). *Acta Chem. Scand.* **20**, 1885.
- HORDVIK, A. (1969). Private communication.
- HORDVIK, A. & KJØGE, H. M. (1966). *Acta Chem. Scand.* **20**, 1923.
- HORDVIK, A. & SLETTEN, E. (1969). *Acta Chem. Scand.* **20**, 2043.
- HORDVIK, A., SLETTEN, E. & SLETTEN, J. (1969). *Acta Chem. Scand.* **23**, 1852.
- HORDVIK, A., SLETTEN, E., SLETTEN, J., NYBURG, S. C. & LEUNG, F. (1970). Unpublished results.
- HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
- International Tables for X-ray Crystallography* (1962). Vol. III, p. 202. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.
- JOHNSON, P. L. & PAUL, I. C. (1959a). *Chem. Commun.* p. 1014.
- JOHNSON, P. L. & PAUL, I. C. (1969b). *J. Amer. Chem. Soc.* **91**, 781.
- JOHNSON, S. M., NEWTON, M. G. & PAUL, I. C. (1967). *Chem. Commun.* p. 1170.
- JOHNSON, S. M., NEWTON, M. G. & PAUL, I. C. (1969). *J. Chem. Soc. (B)*, p. 986.
- KAPECKI, J. A., BALDWIN, J. E. & PAUL, I. C. (1968). *J. Amer. Chem. Soc.* **90**, 5800.
- LEUNG, F. (1967). M. Sc. Thesis. Univ. of Toronto.
- LEUNG, F. & NYBURG, S. C. (1969). *Chem. Commun.* p. 137.
- LEUNG, F. & NYBURG, S. C. (1971). *Canad. J. Chem.* **49**, 167.
- LYNCH, T. R., MELLOR, I. P., NYBURG, S. C. & YATES, P. (1967). *Tetrahedron Letters*, 373.
- MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.
- MAMMI, M., BARDI, R., TRAVERSO, G. & BEZZI, S. (1961). *Nature, Lond.* **192**, 1282.
- MELLOR, I. P. & NYBURG, S. C. (1971a). *Acta Cryst.* **B27**, 1954.

- MELLOR, I. P. & NYBURG, S. C. (1971b). *Acta Cryst.* B27, 1959.
- MEYER, V. (1890). *Ber. deutsch. Chem. Ges.* 23, 1571.
- PAULING, L. (1960). *Nature of the Chemical Bond*. 3rd ed. p. 260. Ithaca: Cornell Univ. Press.
- REID, K. I. G. & PAUL, I. C. (1970). *Chem. Commun.* p. 329.
- RICCI, J. S. & BERNAL, I. (1969). *Acta Cryst.* A25, 5149.
- SCHMIDT, W. H. & TULINSKY, A. (1967). *Tetrahedron Letters*, 5311.
- STEEPLE, H. (1961). *Acta Cryst.* 14, 847.
- WILLIAMS, D. E., DUMKE, W. C. & RUNDLE, R. E. (1962). *Acta Cryst.* 15, 627.
- WILLIAMS, D. E. (1966). *Acta Cryst.* 21, 340.
- YATES, P. & MOORE, D. R. (1958). *J. Amer. Chem. Soc.* 80, 5577.

Acta Cryst. (1971). B27, 1954

The Crystal and Molecular Structures of Some Molecules Showing S...O Interaction.

II. 3-Phenyl-1-propene-1,3-dione-1-(dimethyl mercaptole)

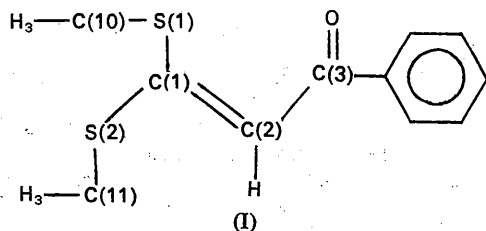
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(Received 9 July 1970)

Crystals of 3-phenyl-1-propene-1,3-dione-1-(dimethyl mercaptole), $C_{11}H_{12}OS_2$, belong to the monoclinic system, $a=5.972$ (7), $b=10.382$ (25), $c=19.536$ (11), $\beta=109.42$ (2) $^\circ$, space group $P2_1/c$, $Z=4$ molecules per cell. The structure was solved by direct methods using Cu $K\alpha$ diffractometric intensity data. The molecule shows an S...O distance of 2.727 (10) Å.

3-Phenyl-1-propene-1,3-dione-1-(dimethyl mercaptole) PDM, (I), was the second compound whose crystal



structure was examined in order to add more to our understanding of the S...O interaction. Enough is known of this type of interaction to expect that the central part of a molecule such as (I) will almost certainly be flat with sulphur quite close to oxygen. Crystal structure analysis confirms this.

Experimental

Crystals of PDM prepared by Kelber's (1910) method were kindly supplied by Professor P. Yates. They were obtained as somewhat poorly formed yellow needles, elongated along the monoclinic y axis, on crystallization from an ethyl acetate, pentane mixture.

Initial photographic examination of the crystals showed them to be monoclinic, space group $P2_1/c$. Subsequently they were studied with a Picker automated four-circle diffractometer using Ni-filtered Cu $K\alpha$ radiation. A least-squares refinement based on 2 θ of 42 reflexions gave the following cell dimensions: $a=5.972$ (7), $b=10.382$ (25), $c=19.536$ (11) Å, $\beta=$

109.42 (0.02) $^\circ$ whence $V=1142.3$ Å 3 . The crystal density, by flotation in n-hexane/carbon tetrachloride was 1.265 g.cm $^{-3}$ which, using a molecular weight of 224.3, calculates to 1.304 g.cm $^{-3}$ for four molecules of PDM per cell.

Intensity data were collected in θ -2 θ scanning mode with Al foil attenuators for counting rates in excess of 10 4 sec $^{-1}$. The scanning range $\Delta(2\theta)$ used was 1.80 + 0.86 tan θ_m degrees where θ_m was the computed position of the diffraction maximum for a mean weighted wavelength (Alexander & Smith, 1964). The maximum usable 2 θ was 130 $^\circ$. Only the independent reflexions were measured.

The crystal used for data collection measured 0.1 × 0.1 × 0.3 mm (along y) and, with $\mu=36.01$ cm $^{-1}$, no absorption corrections were made. Standard deviations in F_o were calculated by the statistical treatment given by Cetlin & Abrahams (1963); Abrahams (1964) and Abrahams & Bernstein (1965). Reflexions were regarded as unobserved if the background-corrected intensity was zero or negative and with a maximum possible intensity of 20 counts. If $0 \leq |F_o| < \sigma(|F_o|)$, the reflexion was retained with structure amplitude $|F_o|$ but still regarded as unobserved. Of the 1882 independent intensity measurements made, 322 were classified as unobserved.

The structure was solved by the symbolic addition procedure, Karle & Karle (1966). Conversion of F_o to normalized structure factors, E , was carried out by the method described by Norment (1961). There were 91 independent reflexions with $|E| \geq 2.0$ and 242 with $|E| \geq 1.5$ and reasonably uniform distribution between the eighty parity groups. Using only one symbol it was possible to generate phases for 198 reflexions from Σ_2