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THE X-RAY STRUCTURE OF A BIS-ALKYLIDENE-1,2,4,5-TETRATHIIN

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Abstract—The product from the reaction of carbon disulphide and the cyclic phosphorane from diacetyl and trimethyl phosphite is identified, principally by a direct two-dimensional X-ray determination, as 3,6-bis-2-oxobut-3-ylidene-1,2,4,5-tetrathiin (I).

THE cyclic phosphorane from trimethyl phosphite and diacetyl reacts with carbon disulphide to give a yellow crystalline compound of empirical formula $C_5H_6S_2O$.[1] This paper is concerned with the determination of its structure. The structures of two other new compounds derived from this material are supported by this determination.

Two independent methods agreed on a dimeric mol. wt,[1] and the molecular formula is therefore $C_{10}H_{12}S_4O_2$. The PMR spectrum showed two peaks only, of equal intensities, at $\tau = 7{\cdot}66$ and $7{\cdot}75$. Evidently, the carbon skeletons of two molecules of the phosphorane have been incorporated intact, either as MeCOCMe═, or as —O—CMe═CMe—; and electrophilic attack by CS_2 has occurred at either carbon or oxygen. The IR spectrum showed strong bands at 1640 and 1497 cm^{-1}, and neither this, nor the unusual UV spectrum[1] gives a clear decision between the possible forms of the carbon skeleton.

Because of the lack of nucleophilic reactivity of the four sulphur atoms, it proved difficult also to determine how the two molecules of carbon disulphide are incorporated, and a crystallographic investigation was undertaken. The unit cell dimensions suggested that a satisfactory identification could be obtained from two-dimensional work only.

EXPERIMENTAL

$C_{10}H_{12}S_4O_2$ crystallizes as well-formed rhombs and prisms from CS_2. The unit cell parameters were measured approximately from single crystal photographs, and refined by a least squares fit to data obtained with a Nonius type Guinier camera.

Unit cell parameters in Å.

$$a = 12{\cdot}87 \pm 0{\cdot}01; \quad b = 7{\cdot}939 \pm 0{\cdot}006;$$
$$c = 12{\cdot}502 \pm 0{\cdot}004; \quad V = 1277{\cdot}6 \pm 1{\cdot}6$$

(Standard deviations obtained from the inverse matrix in the least squares fit. Internal calibration with monomethylammonium alum, a = 12·5025 Å; and sodium chloride, a = 5·6394 Å. λ Cu K_α = 1·5405 Å.)

Density (by flotation) between 1·5 and 1·6. $Z = 4$ gives $\rho_x = 1{\cdot}520$.

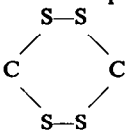
Systematic absences indicated the space group Pbcn in which the 8-fold multiplicity of the general positions requires the molecule to be centrosymmetric.

hol intensity data were estimated visually from multiple film Weissenberg photographs. No correction for absorption was made. 130 reflections were observable, of which 30 had zero intensity.

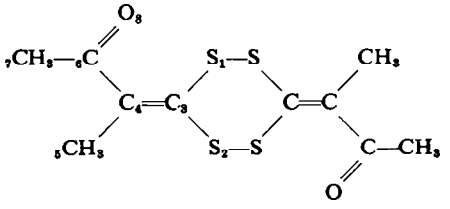
A direct method seemed most suitable for this compound, as a number of trial structures were

[1] A. J. Kirby, *Tetrahedron* **22**, 3001 (1966).

possible. Signs for 73 reflections were easily determined by the application of inequalities, with a few confirmed by Sayres' relationship. A Fourier synthesis using these reflections showed the S atoms very clearly as part of a



ring, and gave probable positions for the other atoms:—



(The atomic numbering is that used in the X-ray investigation only.)

The R factor for this structure was 32%, which was refined by 3 cycles of 2-D differential synthesis to 13·8%, and to 9·7% by 2 cycles of full matrix least squares refinement with individual isotropic temp factors (using the Busing-Levy program). The final atomic positions and B-values are given in Table 1, the final Fourier synthesis in Fig. 1, and the observed and calculated structure factors in Table 2. The structure proposed from the first "direct" Fourier synthesis is therefore fully confirmed.

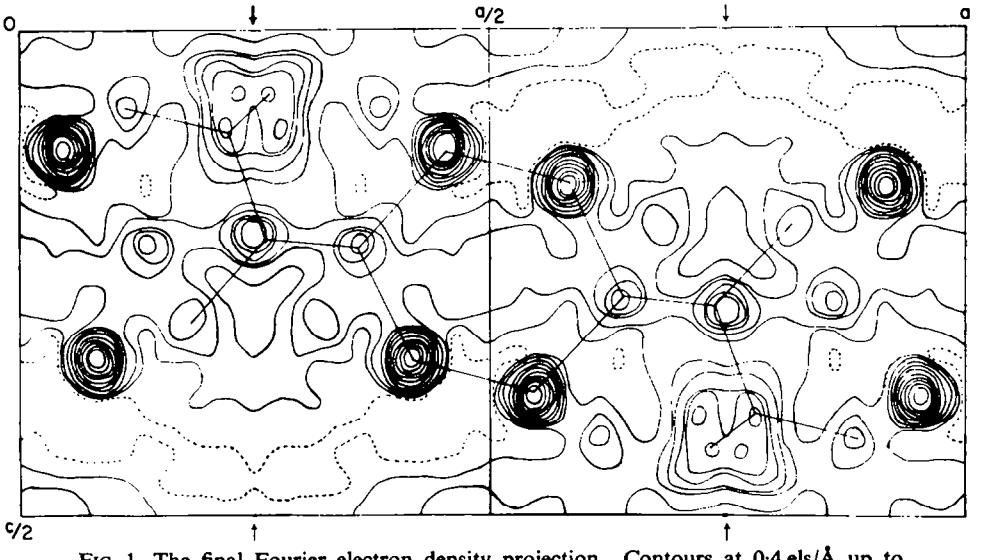


FIG. 1. The final Fourier electron density projection. Contours at 0·4 els/Å up to 2·4 els/Å, and thereafter at 0·8 els/Å. The zero contour is dotted, and negative contours are omitted. The arrows indicate the mirror planes.

The final difference synthesis showed an anomaly around S_1, possibly due to anisotropic thermal vibration. However, as the purpose of the investigation was the identification of the structure, no further refinement was attempted. It should be noted that the inverse matrix shows several strong interactions, in particular between the scale factor and the temp. factors, as is to be expected for 2-dimensional refinement of a structure containing atoms overlapped in projection. This means that the results in Table 1 are of only limited accuracy, and no meaningful discussion of bond lengths is possible, beyond noting that the observed values are consistent with the molecule being nearly planar and parallel to the projection axis.

We thank Dr. O. Kennard for valuable discussion, and Mrs. J. Dye for estimating the intensities.

TABLE 1. ATOMIC POSITIONS AND TEMPERATURE FACTORS; THE STANDARD DEVIATIONS ARE AS CALCULATED IN THE LEAST SQUARES REFINEMENT

Atom	$\frac{x}{a}$	±	$\frac{z}{c}$	±	B	±
S_1	0·4551	0·0005	0·1249	0·0004	2·00	0·13
S_2	0·4189	0·0005	0·3414	0·0005	2·31	0·14
C_3	0·3606	0·0018	0·2232	0·0016	1·95	0·45
C_4	0·2648	0·0026	0·2139	0·0015	2·64	0·68
C_5	0·1815	0·0024	0·3003	0·0026	4·36	0·75
C_6	0·2211	0·0018	0·1089	0·0023	2·99	0·73
C_7	0·1101	0·0025	0·0807	0·0023	4·23	0·68
O_8	0·2838	0·0014	0·0490	0·0019	4·07	0·57

The standard deviation of the scale factor is ±2·16%. Overlaps occur in projection between atoms C_4 and C_4', C_6, C_6', O_8 and O_8'.

TABLE 2. OBSERVED AND CALCULATED STRUCTURE FACTORS, ON AN ABSOLUTE SCALE:

h.	l.	F_O	F_O	h.	l.	F_O	F_C	h.	l.	F_O	F_C
0	4	52·41	66·00*	5	6	20·95	19·19	10	8	18·95	−19·02
0	6	12·35	8·97	5	8	15·93	12·81	10	10	6·13	−5·03
0	8	16·75	12·81	5	10	25·50	−26·43	10	12	14·45	15·81
0	10	12·93	−11·66	5	12	9·05	−9·07	10	16	7·50	−6·63
0	12	15·99	−14·44	5	14	22·09	23·90	11	2	15·22	−15·96
0	14	7·93	6·15	5	18	7·76	−8·19	11	6	5·39	4·68
0	18	8·04	8·25	6	0	43·74	−48·67	11	8	8·88	−9·50
1	4	47·02	−45·56	6	4	29·46	24·70	11	10	6·35	5·46
1	6	12·92	−11·55	6	6	19·89	−18·64	12	0	8·15	−6·42
1	8	25·11	25·05	6	10	15·77	15·09	12	2	11·27	−10·12
1	10	19·82	−21·27	6	12	12·08	−9·51	12	4	6·42	6·90
1	14	10·49	8·97	6	16	7·77	7·36	12	6	16·69	16·05
2	4	48·32	62·20*	7	2	20·22	−22·98	12	8	13·83	−14·47
2	6	25·00	25·87	7	4	6·62	4·44	12	10	7·80	−7·27
2	8	29·76	29·13	7	6	34·08	35·20	12	12	14·83	15·56
2	10	13·33	−13·59	7	8	21·27	−18·21	12	16	9·27	−9·48
2	16	5·74	6·18	7	10	12·34	−11·98	13	2	16·97	16·08
3	2	18·03	22·47	7	12	5·70	2·95	13	6	5·40	−4·58
3	4	23·97	−23·96	7	14	7·30	6·35	13	10	7·18	6·35
3	6	24·78	21·61	8	0	22·59	−24·59	14	6	7·29	4·59
3	8	27·60	28·98	8	2	3·81	2·36	14	8	5·26	−5·77
3	10	21·42	−20·98	8	4	29·63	28·23	14	10	6·15	−5·25
3	12	9·80	−7·91	8	6	22·03	−19·49	14	12	7·44	6·66
3	14	17·98	19·18	8	8	11·68	−9·37	15	2	17·80	16·48
3	18	11·71	−13·44	8	12	7·66	9·01	15	4	7·42	−6·62
4	0	11·34	9·15	8	14	5·79	2·11	15	6	11·90	−12·99
4	2	19·10	17·37	9	2	34·64	−38·66	15	8	7·06	8·48
4	4	12·80	−7·40	9	4	27·98	27·55	16	4	7·77	4·96
4	6	11·70	−9·68	9	6	7·37	9·33	17	2	15·48	14·86
4	8	11·15	11·94	9	8	7·58	−8·08	17	6	8·26	−9·72
4	10	9·20	7·66	9	10	6·59	−6·86				
4	12	18·53	−19·51	9	12	8·77	9·00				
4	16	8·93	9·42	10	0	11·43	−11·77				
5	2	33·06	−32·24	10	4	9·51	9·08				
5	4	16·84	−15·28	10	6	8·39	5·64				

* Indicates reflections suffering from extinction