

The Structure of 4-Methyl-1,2-Dithia-4-cyclopentene-3-Thione

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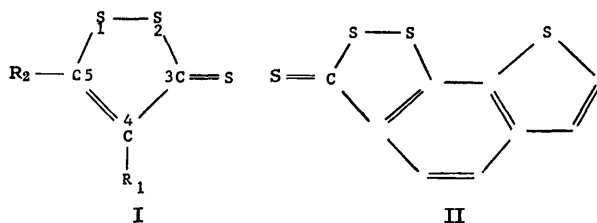
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(Received 12 May 1958)

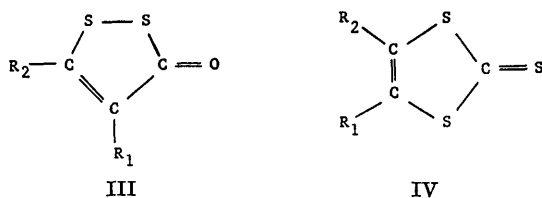
The compound 4-methyl-1,2-dithia-4-cyclopentene-3-thione is a member of a large class of compounds of a general type which have been obtained from reactions of olefins and sulfur. The crystal structure was solved for the well-resolved *c*-axis projection by the Harker-Kasper inequalities method, and was refined first by difference syntheses on the (*hk*0) data, and then by least-squares and differential syntheses on the 680 observed (*hkl*) reflections. The two three-dimensional refinements gave results differing by as much as 0.09 Å in the position of one of the carbon atoms, and the differential synthesis method gave the atomic parameters which are more consistent with a planar molecule and with chemical theory. The observed bond lengths indicate that the five-membered ring has some aromatic character, since within the ring the two C-S bonds are shorter than single bonds, while the two C-C bonds are intermediate in length between single and double bonds. This π -bonding does not, however, appear to include the S-S link which has a normal single bond length. The molecules lie in planes inclined at approximately 25° to the (001) plane.

Introduction

Since 1947 a large number of compounds of the general type, I, have been obtained from reactions of olefins with sulfur. Several variations in name have been used to describe these compounds; that recommended by Patterson & Capell (1940) for I is 4-R₁-5-R₂-1,2-dithia-4-cyclopentene-3-thione. The parent compound, C₃H₂S₃, was first obtained from the reaction of propylene and sulfur by Böttcher & Lüttringhaus (1947), who assigned to this class of compounds the trivial name of trithiones. Subsequent papers by these and many other workers (e.g., review by Bauer, 1951) suggest that there is no limit to the variation for R₁ and R₂, including fused ring systems such as II prepared by Lozac'h & Legrand (1951).



Related series of compounds based on III and IV are also known, e.g.:



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III with R₁=R₂=H from Baumer & Fromm (1897), IV with R₁=R₂=H from Challenger & Emmott (1951).

The crystal structure of 4-methyl-5-phenyl-1,2-dithia-3-thione, I with R₁=CH₃, R₂=C₆H₅, was studied by Zaslavskii & Kondroshov (1949) who showed that four molecules based on configuration I with reasonable assumed dimensions could be fitted to the unit cell and space group to give a qualitative agreement with some seventy observed X-ray intensities.

The 4-methyl-1,2-dithia-4-cyclopentene-3-thione (C₄H₄S₃) used in this work was isolated from the reaction products of heating isobutylene with sulfur at 170 °C. in a high pressure bomb by Spindt, Stevens & Baldwin (1951). Previously, Friedmann (1951) and Selker & Kemp (1947) had considered alternate structures for these derivatives and the initial purpose of the X-ray crystal structure analysis was to provide confirmatory evidence of the ring structure assigned by Spindt, Stevens & Baldwin (1951) to that particular compound. This was obtained at an early stage in the structure analysis by means of a well-resolved Fourier projection (Fig. 2) and was reported by Jeffrey, Kehl & Wahl (1951).

The common occurrence of the 1,2-dithiacyclopentene ring as the product of several different cyclizing reactions suggests that this system is resonance stabilized; the parent compound C₃H₂S₃, for example, was also prepared by Challenger, Mason, Holdsworth & Emmott (1953) from the reaction of acetylene and sulfur at 450 °C.* It was therefore of interest to determine by bond length measurements from a complete structure analysis the conjugative interactions of the three groups, S-S, C=C, C=S,

* The reaction may be due to the formation of propylene from acetone with which the acetylene was contaminated.

each of which has π -type electronic orbitals relative to the plane of the dithiacyclopentene ring.

Crystal data

Orange lath-shaped crystals (m.p. 41 °C.) suitable for X-ray study were obtained from an ethyl ether and pentane solution. The following data were measured: orthorhombic,

$$a = 12.35 \pm 0.02, \quad b = 12.44 \pm 0.02, \quad c = 4.11 \pm 0.01 \text{ \AA}, \\ U = 631.4 \text{ \AA}^3, \quad D_m = 1.560 \text{ g.cm.}^{-3}, \quad Z = 4, \\ D_x = 1.559 \text{ g.cm.}^{-3},$$

$F(000) = 304$; space group $P2_12_12_1$ from systematic extinctions.

Experimental

The unit-cell dimensions were obtained from Weissenberg photographs taken about [100] and [001] with the film in the Straumanis position using unfiltered Cu K radiation, ($\lambda_{\alpha_1} = 1.5405$, $\lambda_{\alpha_2} = 1.5443$, $\lambda_{\beta} = 1.3922 \text{ \AA}$).

The intensity data were obtained by visual estimation from multifilm Weissenberg photographs which were made for the zero, first and second layers about [001], zero through fourth layer about [010] and zero

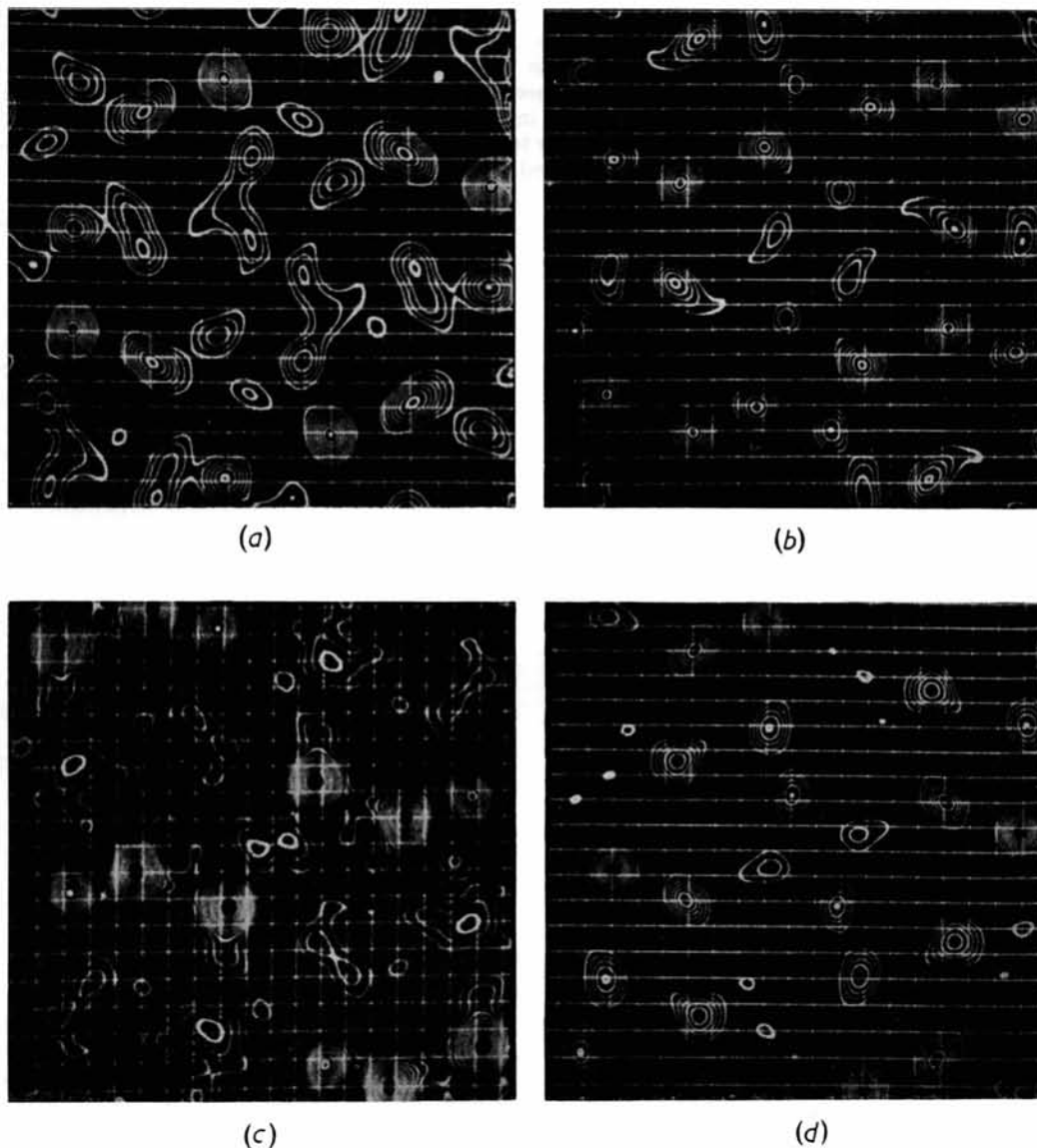


Fig. 1. Fourier projections on the x, y plane corresponding to the four sign combinations from Harker-Kasper inequalities (computed on X-RAC).

- | | |
|--------------|--------------|
| (a) $a+, b+$ | (c) $a+, b-$ |
| (b) $a-, b-$ | (d) $a-, b+$ |

through ninth layer about [100]. The 680 observed intensities were converted to structure amplitudes by the usual angle factors and the appropriate scale and overall temperature factors were obtained graphically from a Wilson plot of the observed structure amplitudes.

The structure determination

From the cell dimensions the *c*-axis projection was that most likely to give a resolved or partly resolved electron-density distribution. Since several of the reflections in this zone had unitary structure factors greater than 0.4, the Harker-Kasper inequalities method for phase determination was used. The results are summarized in Table 1. The sign of (600) was given

Table 1. Unitary structure factors and sign determination from inequalities

<i>hk0</i>	100 <i>U</i>	<i>hk0</i>	100 <i>U</i>
140*	+34	600	-55
250*	-32	670*	<i>b</i> 45
360†	<i>b</i> 48	720†	<i>a, b</i> 38
380	- <i>a</i> 49	740	-47
410†	<i>a</i> 22	850	+55
440*	<i>a</i> 39	910	-49
4,10,0†	<i>b</i> 38	10,4,0	- <i>a</i> 50

* Sign assumed.

† Borderline case, sign determined by Zachariasen's method (1952).

uniquely from the inequality for 2_12_1 ,

$$4U_{HK0}^2 \leq \{1 + (-1)^{H+K} [U_{2H,0,0} + U_{0,2K,0} + U_{2H,2K,0}]\}$$

and those of the other reflections were given either uniquely or in terms of two variables, *a*, *b*, from the relationship

$$(U_{H\pm}U_{H'})^2 \leq (1 \pm U_{H+H'})(1 \pm U_{H-H'})$$

The four syntheses corresponding to the sign combinations for *a* and *b* were computed on X-RAC and are shown in Fig. 1. Although it was not immediately obvious which was the correct solution, a choice was made by using as a criterion the (530) reflection which had a large unitary structure factor, 0.42, but could not be correlated through the inequalities. With the aid of a Bragg-Lipson chart it was found that only the combination *a* = -, *b* = +, Fig. 1(d), would lead to an assignment of atomic position to satisfy this re-

flection. The refinement of the projection on X-RAC gave a well-resolved electron-density map, Fig. 2, and

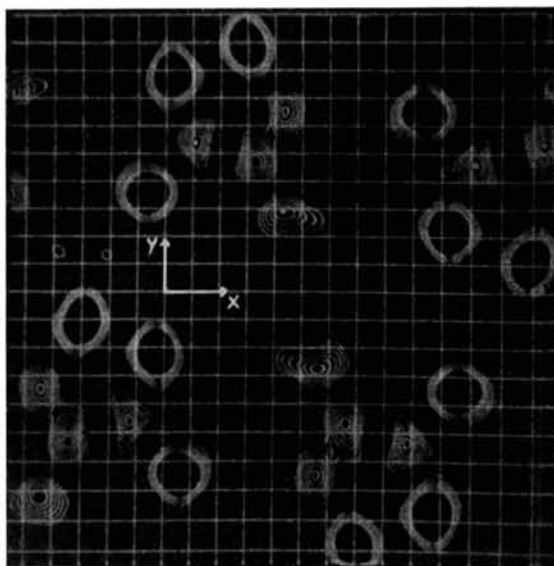


Fig. 2. Electron-density distribution for whole unit cell projected onto the *x, y* plane (computed on X-RAC).

a disagreement index of $R = 0.18$ for the 150 *hk0* structure factors.

The *x, y* coordinates and isotropic temperature factors were further refined by the difference syntheses of this projection with a reduction in *R* to 0.150. These parameters are given in Table 2. The atoms are numbered as in I, with R_1 as the methyl group (C_6); the thione sulfur is S_3 . The approximate *z* coordinates were obtained from the completely unresolved (010) projection by assuming a planar model for the molecule with bond lengths $S-S \approx 2.0$, $C-S \approx 1.8$, $C-C \approx 1.5$, $C=C \approx 1.4$ Å. However, the projection was too complex to resolve satisfactorily by difference synthesis, and the subsequent refinement showed that there were large errors in the initial *z* coordinates.

The structure refinement

A three-dimensional refinement of the atomic parameters and isotropic temperature factors was first carried out by the least-squares minimization procedure described by Friedlander, Love & Sayre (1955)

Table 2. Fractional atomic coordinates and isotropic temperature factors

	Difference refinement			Least-squares refinement				Differential refinement			
	<i>x/a</i>	<i>y/b</i>	<i>B</i> (Å ²)	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (Å ²)	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (Å ²)
S_1	0.150	0.441	4.19	0.1511	0.4414	0.500	4.63	0.1512	0.4416	0.4982	4.73
S_2	0.012	0.391	4.19	0.0108	0.3897	0.288	4.47	0.0111	0.3898	0.2832	4.57
S_3	-0.031	0.176	4.19	-0.0313	0.1785	0.007	5.10	-0.0313	0.1780	0.0087	5.20
C_3	0.050	0.265	5.25	0.0560	0.2620	0.177	4.13	0.0537	0.2618	0.1908	4.22
C_4	0.163	0.242	5.25	0.1618	0.2386	0.293	4.97	0.1601	0.2391	0.3027	5.08
C_5	0.216	0.326	5.25	0.2171	0.3240	0.462	4.96	0.2126	0.3228	0.4575	5.06
C_6	0.215	0.126	5.25	0.2152	0.1259	0.261	7.03	0.2131	0.1323	0.2551	7.13

and computed through five cycles on the observed (hkl) reflections by the International Business Machines Corporation using a 704 computer. The parameter shifts on the final cycle were less than 0.005 Å. The final atomic parameters and isotropic temperature factors are shown in Table 2. The overall R factor for the observed (hkl) reflections was 0.208. For the ($hk0$) reflections alone it was 0.197, which compares rather unfavorably with the 0.15 obtained by difference synthesis refinement of the ($hk0$) data alone. This could be ascribed to the use of isotropic temperature factors in the least-squares refinement of the three-dimensional data. The corresponding bond lengths are shown in Table 3. An unexpected feature

the C-C bonds which, although chemically more satisfactory, could not be regarded with any more confidence.

Starting with the coordinates and temperature factors from the least-squares refinement, a three-dimensional Fourier differential synthesis refinement was carried out on an IBM 650 computer using a program written by Shiono (1957). The shifts in sulfur atom positions were very small, being less than 0.006 Å in the x and y parameters and less than 0.012 Å in z . Significant differences appeared, however, in the light atom positions and were as large as 0.09 Å for C₆, for example. There was a small improvement in the overall R factor to 0.17, excluding non-observed amplitudes.

Table 3. Bond lengths calculated from refined atomic parameters

Bond	Least-squares Refinement	Differential Refinement
S ₁ -S ₂	2.04 Å	2.04 Å
S ₂ -C ₃	1.75	1.72
C ₃ -S ₃	1.66	1.66
C ₃ -C ₄	1.42	1.42
C ₄ -C ₅	1.44	1.38
C ₄ -C ₆	1.55	1.49
C ₅ -S ₁	1.68	1.67

of these results is that within the ring the formal double bond C₄-C₅ is 0.02 Å longer than the formal single bond C₃-C₄. The large deviations from planarity of the molecule, Table 4, led us further to suspect the accuracy of the refinement.

A composite set of parameters obtained by using the difference refinement of the ($hk0$) data for x and y and the IBM 704 calculations for the z coordinates gave a significantly different set of bond lengths for

The atomic coordinates are given in Table 2, and the corresponding bond lengths and planarity in Tables 3 and 4. Both with respect to consistency with the chemical theory and the planarity of the molecule, these results are preferable to those obtained from the least-squares refinement. Without being prepared, at present, to analyze the reasons for the discrepancy between the results of the two methods beyond noting the omission of weighting factors in the least-squares calculations, we regard the differential refinement data as the final results for the isotropic analysis.

The observed and calculated shifts of the atomic parameters obtained from the slopes and curvatures of the differential synthesis are shown in Table 5. A 1.5 back-shift was used to obtain the final coordinates corrected for termination of series.

The peak heights and the ratio of observed and calculated peak heights are shown in Table 6. The slopes and curvatures are shown in Table 7. These values give a very clear indication of anisotropic

Table 4. Deviations from the plane determined by atoms S₁, S₃ and C₄ for atomic coordinates from both the least-squares and the differential refinement

Atom	Least-squares refinement		Differential refinement	
	d (Å)*		d (Å)*	
S ₂	0.021		0.030	
C ₃	0.066		-0.023	
C ₅	-0.061		0.022	
C ₆	-0.144		-0.011	
Equation of plane				
2.211x + 2.227y - 6.050z - 3.855 = 0 2.430x + 2.038y - 6.038z - 3.350 = 0				

* Positive values correspond to atom above plane.

Negative values correspond to atom below plane.

Table 5. Observed and calculated shifts of atomic parameters (in Å) obtained from the slopes and curvatures of the differential synthesis

	ϵ_x		ϵ_y		ϵ_z	
	obs.	calc.	obs.	calc.	obs.	calc.
S ₁	-0.0062	-0.0062	0.0025	0.0000	-0.0012	0.0033
S ₂	0.0012	-0.0012	0.0000	0.0000	-0.0148	-0.0021
S ₃	0.0012	0.0012	0.0012	0.0050	0.0021	-0.0062
C ₃	0.0037	0.0235	0.0199	0.0224	0.0777	0.0390
C ₄	-0.0136	0.0000	0.0174	0.0137	0.0074	-0.0193
C ₅	-0.0519	-0.0148	-0.0286	-0.0187	-0.0144	-0.0029
C ₆	-0.0469	-0.0284	0.0274	-0.0261	0.0016	0.0181

Table 6. Peak heights, ratio of observed and calculated peak heights and ratio of observed and calculated curvatures

Atom	$Q_{\text{obs.}}$ e.Å ⁻³	$Q_{\text{calc.}}$ e.Å ⁻³	$\frac{Q_{\text{obs.}}}{Q_{\text{calc.}}}$	$\frac{A_{hh}}{A_{hh'}}$	$\frac{A_{kk}}{A_{kk'}}$	$\frac{A_{ll}}{A_{ll'}}$
S ₁	23.2	24.1	0.960	1.04	0.886	0.807
S ₂	23.6	24.4	0.967	1.07	0.897	0.773
S ₃	21.7	22.6	0.962	1.04	0.892	0.832
C ₃	6.8	7.0	0.974	1.06	0.865	0.777
C ₄	6.4	6.7	0.960	1.02	0.877	0.847
C ₅	6.6	6.9	0.952	1.02	0.918	0.726
C ₆	5.0	5.1	0.976	0.998	0.936	0.734
Mean:			0.964	1.03	0.896	0.785

thermal motion of the molecule as a whole, least in the x direction and greatest in the z direction. The more elaborate computation with anisotropic temperature factors has not yet been attempted. While this would improve the R factor it is doubtful whether the resulting small parameter changes would be significant relative to the experimental errors. It should also improve the accuracy of the atomic parameters as calculated by the method of Cruickshank (1949, 1950), which gave r.m.s. standard deviations of $\sigma(\text{S}) = 0.009$, $\sigma(\text{C}) = 0.03$, $\sigma(\text{CH}_3) = 0.05$ Å. These values, although in the correct relative sequence, appeared to be larger than would be expected from the self-consistency checks on the results.

Discussion of the structure

The literature on the stereochemistry of sulfur compounds has been summarized recently by Abrahams (1956). The bond lengths and angles found from the present work are shown in Fig. 3. The S-S length is

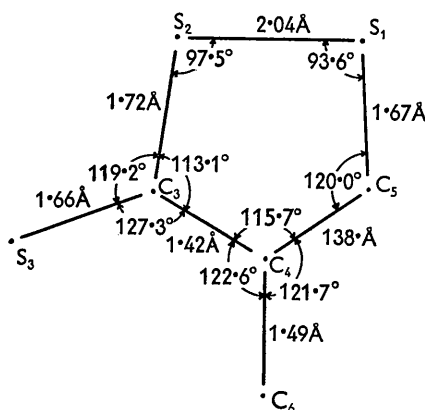


Fig. 3. Structure of the $\text{C}_4\text{H}_4\text{S}_3$ molecule, showing the bond angles and bond lengths.

the same as that in S_8 and close to the average value of 2.08 Å for the 43 S-S bond lengths listed by Abrahams (1956). These results show therefore that bonding between the sulfur atoms is little affected by forming part of the ring system in which there is appreciable conjugative π -bonding. In contrast, the ring C-S

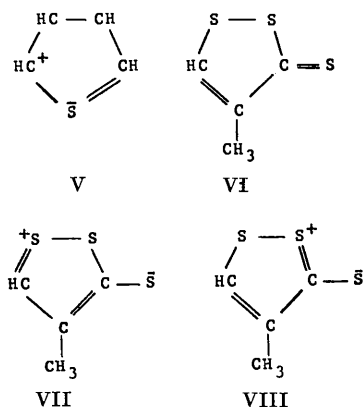
Table 7. Observed and calculated slopes and curvatures of electron-density peaks

Atom	$-\partial q/\partial x$		$-\partial q/\partial y$		$-\partial q/\partial z$		$-\partial^2 q/\partial x \partial y$		$-\partial^2 q/\partial y \partial z$		$-\partial^2 q/\partial z \partial x$		$-\partial^2 q/\partial x^2$		$-\partial^2 q/\partial y^2$		$-\partial^2 q/\partial z^2$	
	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
S ₁	1.141	1.214	-0.315	0.073	0.150	-0.598	9.538	5.412	2.795	0.048	-1.383	2.644	202.7	195.0	187.3	211.4	152.9	189.5
S ₂	-0.201	0.284	-0.027	0.047	2.223	0.431	3.096	2.953	0.642	0.313	3.633	3.942	214.3	201.0	192.1	214.2	149.2	193.1
S ₃	-0.334	-0.354	-0.168	-0.961	0.302	1.065	12.75	0.038	-2.384	-0.456	3.498	-0.978	187.9	180.3	169.9	190.3	140.8	169.2
C ₃	-0.153	-1.142	-0.628	-1.056	-2.907	-1.838	0.566	-1.007	-4.527	-3.468	-1.178	-1.689	55.01	52.03	47.92	55.38	38.75	49.87
C ₄	0.601	0.023	-0.807	-0.723	-0.239	0.893	2.477	1.249	-0.466	2.519	3.346	2.592	48.20	47.26	47.90	54.59	40.45	47.72
C ₅	2.717	0.719	1.213	0.929	0.708	0.206	-3.307	-3.543	1.009	2.653	3.405	0.869	53.50	52.43	47.80	52.07	35.18	48.46
C ₆	1.716	1.008	-0.976	0.751	-0.044	-0.567	-2.387	-2.054	0.256	4.254	0.089	-2.196	35.46	35.55	31.94	34.10	24.79	33.73

Units e.Å⁻⁴

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bonds of 1.72 and 1.67 Å are significantly shorter than the 1.83 Å associated with the carbon-sulfur single bond. They may also be shorter than the 1.74 Å bonds in thiophene for which it is proposed that the sulfur 3*d* orbitals are used for valence bond structures such as V (Longuet-Higgins, 1949),



On the basis of the bond order *vs* bond length curves proposed by Cox & Jeffrey (1951) and Abrahams (1956), 1.72 and 1.67 Å correspond to about 50% and 75% double bond character, respectively. The thione bond is also 1.67 Å and is longer than the extrapolated value of 1.61 Å for the double bond, indicating intermediate bond character. The ring carbon to carbon bonds are intermediate in length between single and double bonds, in agreement with the aromatic character of the compound and usual effects of conjugation to decrease the length of the formal single bonds and increase that of the double bonds.

These results can be interpreted in terms of the resonance structures VI, VII and VIII in the ratio 5:4:1. This accounts qualitatively for the observations that S₁-C₅ is shorter than S₂-C₃, and C₄-C₅ is shorter than C₃-C₄, but it may not adequately describe the thione group.

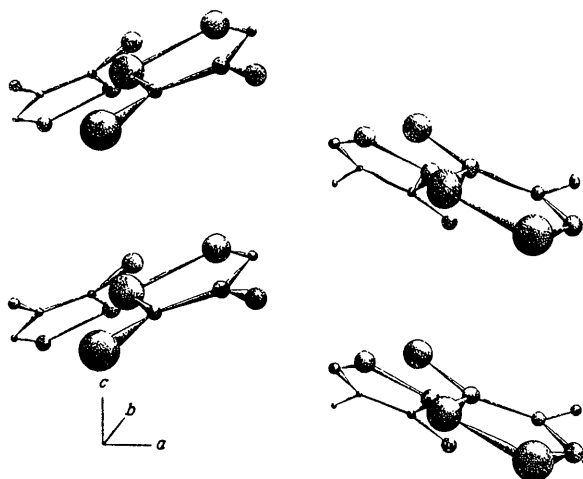
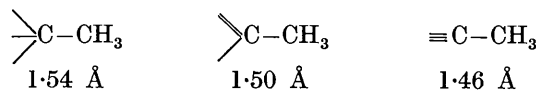


Fig. 4. Structure of C₄H₄S₃ viewed along *b*.

The carbon to methyl bond length is 1.49 Å, which is shorter than the standard 1.54 Å. Although the accuracy of the analysis does not permit too much weight to be put on this observation, it does, however, agree with the rationalization of C-CH₃ bond lengths on the basis of primary, secondary and tertiary substituted carbon atoms proposed by Stoicheff,* *i.e.*,



The bond angles in the ring show the well-known tendency for the divalent sulfur valency angle to lie between 90° and 100°. The angles at the sulfurs are less than the 108° for a regular pentagon while those

Table 8. *Intramolecular interatomic distances in C₄H₄S₃ (non-bonding distances)*

C ₃ -C ₅	2.37 Å	C ₅ -S ₂	2.72 Å
C ₅ -C ₆	2.56	C ₅ -S ₃	3.97
C ₃ -S ₁	2.84	C ₆ -S ₁	4.05
C ₄ -S ₁	2.65	C ₆ -S ₂	4.06
C ₄ -S ₂	2.63	C ₆ -S ₃	3.23
C ₄ -S ₃	2.76	S ₁ -S ₃	4.46
C ₅ -C ₆	2.51	S ₂ -S ₃	2.92

Table 9. *Intermolecular interatomic distances shorter than 5 Å in C₄H₄S₃*

C ₃ -C ₄	4.76 Å	I'	C ₅ -S ₃	3.85 Å	III'
C ₃ -C ₄	3.89	I''	C ₅ -S ₃	4.96	IV
C ₃ -C ₅	3.68	I'''	C ₆ -C ₆	3.99	II'
C ₃ -C ₅	4.58	III''''	C ₆ -S ₂	4.31	III
C ₃ -C ₆	4.61	I''	C ₆ -S ₂	4.15	III'
C ₃ -C ₆	4.77	III''''	C ₆ -S ₂	4.10	IV'
C ₃ -C ₆	4.96	III''''	C ₆ -S ₃	4.36	I'
C ₃ -S ₁	3.81	I''	C ₆ -S ₃	4.09	III
C ₃ -S ₁	4.78	IV'	C ₆ -S ₃	4.97	III'
C ₃ -S ₂	4.80	I'	S ₁ -S ₁	3.51	II
C ₃ -S ₂	4.08	I''	S ₁ -S ₂	3.72	I'
C ₃ -S ₂	4.70	IV'	S ₁ -S ₂	4.81	II
C ₃ -S ₃	3.67	I'	S ₁ -S ₃	4.50	I'
C ₄ -C ₅	4.90	I'	S ₁ -S ₃	4.68	III
C ₄ -C ₅	3.68	I''	S ₁ -S ₃	4.66	III'
C ₄ -C ₆	4.18	I'	S ₁ -S ₃	3.29	IV
C ₄ -C ₆	4.56	I''	S ₂ -S ₃	4.01	I'
C ₄ -S ₁	4.16	I''	S ₂ -S ₃	4.85	IV''
C ₄ -S ₁	4.77	V	S ₂ -S ₃	3.69	IV
C ₄ -S ₂	4.82	I'			
C ₄ -S ₂	4.94	I''	I	<i>x, y, z</i>	
C ₄ -S ₂	4.92	V''	I'	<i>x, y, 1+z</i>	
C ₄ -S ₂	4.85	IV'	I''	<i>x, y, -1+z</i>	
C ₄ -S ₃	3.82	I'	II	$\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$	
C ₄ -S ₃	4.15	III	II'	$\frac{1}{2}-x, \bar{y}, -\frac{1}{2}+z$	
C ₄ -S ₃	4.86	III'	III	$\frac{1}{2}+x, \frac{1}{2}-y, \bar{z}$	
C ₅ -C ₅	4.95	V'	III'	$\frac{1}{2}+x, \frac{1}{2}-y, 1-z$	
C ₅ -C ₆	4.04	I'	III''	$-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$	
C ₅ -S ₁	4.59	I'	III'''	$-\frac{1}{2}+x, \frac{1}{2}-y, \bar{z}$	
C ₅ -S ₁	4.28	I''	IV	$\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$	
C ₅ -S ₁	3.87	V	IV'	$\bar{x}, -\frac{1}{2}+y, \frac{1}{2}-z$	
C ₅ -S ₁	4.05	V'	IV''	$\bar{x}, \frac{1}{2}+y, -\frac{1}{2}-z$	
C ₅ -S ₂	4.29	I'	V	$\frac{1}{2}-x, 1-y, -\frac{1}{2}+z$	
C ₅ -S ₂	4.66	III	V'	$\frac{1}{2}-x, 1-y, \frac{1}{2}+z$	
C ₅ -S ₃	4.18	$\frac{1}{2}$ I'	V''	$\frac{1}{2}+x, \frac{1}{2}-y, 1-z$	
C ₅ -S ₃	3.70	III			

* Private communication.

at the carbons are greater. The thione bond is unsymmetrically oriented with respect to the adjacent carbon bonds. This could arise either from repulsion by the methyl group in the same molecule or by a sulfur atom in an adjacent molecule at a distance of 3.29 Å (S_1-S_3 , IV, in Table 9).

The spatial arrangement of the molecules is shown in Fig. 4. It consists of rows extending in the b -axis direction with the plane of the molecules in adjacent rows tilted with respect to the a -axis in such a way as to form a herringbone-like pattern when projected onto the $x-z$ plane. This is a common form of packing for small planar organic molecules with weak intermolecular forces.

The non-bonding intramolecular distances are shown in Table 8 and the intermolecular distances shorter than 5 Å are given in Table 9. These distances were computed using an IBM 650 program prepared by Templeton (1957).

The authors wish to thank Prof. Ray Pepinsky for the use of X-RAC, Mr R. Shiono for the IBM 650 differential synthesis and structure factor calculations, and Dr Blaine B. Wescott, Executive Vice President, Gulf Research & Development Company for permission to publish this paper.

References

- ABRAHAM, S. C. (1956). *Quart. Rev. Chem. Soc. Lond.* **X**, 407.
- BAUER, F. (1951). *Chem.-Ztg.* **75**, 623.
- BAUMER, E. & FROMM, E. (1897). *Ber. dtsh. chem. Ges.* **30**, 110.
- BÖTTCHER, B. & LÜTTRINGHAUS, A. (1947). *Ann.* **557**, 89.
- CHALLENGER, F. & EMMOTT, R. (1951). *J. Inst. Pet.* **37**, 396.
- CHALLENGER, F., MASON, E. A., HOLDSWORTH, E. C. & EMMOTT, R. (1953). *J. Chem. Soc.* p. 292.
- COX, E. G. & JEFFREY, G. A. (1951). *Proc. Roy. Soc. Lond. A*, **207**, 110.
- CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
- CRUICKSHANK, D. W. J. (1950). *Acta Cryst.* **3**, 72.
- FRIEDLANDER, P. H., LOVE, W. & SAYRE, D. (1955). *Acta Cryst.* **8**, 732.
- FRIEDMANN, W. (1951). *J. Inst. Pet.* **37**, 40.
- JEFFREY, G. A., KEHL, W. L. & WAHL, D. (1951). Paper presented at meeting of Am. Cryst. Ass'n., Oct. 24–27, 1951.
- LONGUET-HIGGINS (1949). *Trans. Faraday Soc.* **45**, 173.
- LOZAC'H, N. & LEGRAND, L. (1951). *C. R. Acad. Sci. Paris*, **232**, 2330.
- PATTERSON, A. & CAPELL, L. T. (1940). 'The Ring Index', Rheinhold Publishing Corp., New York, N.Y., p. 43.
- SELKER, M. L. & KEMP, A. R. (1947). *Ind. Eng. Chem.* **39**, 895.
- SHIONO, R. (1957). Use of the IBM 650 for Crystal Structure Analysis Computations, Conference Report, *Acta Cryst.* **10**, 384.
- SPINDT, R. S., STEVENS, D. R. & BALDWIN, W. E. (1951). *J. Amer. Chem. Soc.* **73**, 3693.
- TEMPLETON, D. H. (1957). Use of the IBM 650 for Crystal Structure Analysis Computations, Conference Report, *Acta Cryst.* **10**, 384.
- ZACHARIASEN, W. H. (1952). *Acta Cryst.* **5**, 68.
- ZASLOVSKII, A. I. & KONDROSEV, Y. D. (1949). *J. Gen. Chem. U.S.S.R.* **19**, 1144.

Short Communications

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Acta Cryst. (1958). **11**, 819

A polynomial approximation to atomic scattering factor curves. By H. C. FREEMAN* and J. E. W. L. SMITH, *School of Chemistry, University of Sydney, Sydney, N.S.W., Australia*

(Received 6 January 1958 and in revised form 9 July 1958)

1. Introduction

In high speed computers with large memories, the storage of atomic scattering factors presents little difficulty. If 100–160 values of the scattering factor for each atomic species, at 0.006 intervals in $\sin \theta/\lambda$, can be stored, simple table-searching without interpolation yields the desired functions with 1% accuracy (Sparks, Prosen, Kruse & Trueblood, 1956). Greater accuracy is obtained by inter-

polation in tables of f versus $\sin^2 \theta$ (Ahmed & Cruickshank, 1953; Lavine & Rollett, 1956; Rollett, 1957): in this case, 48 to 100 values are stored for each atomic species, adequate accuracy being achieved by linear interpolation even in the 48-values tables if the intervals of tabulation are chosen so as to make successive increments in f approximately equal.

In other computers, a limited memory makes the storage of entire f -tables an impossibility. To this class belongs SILLIAC (the Sydney University version of the University of Illinois Automatic Computer), which at

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