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## The Crystal and Molecular Structure of Sulphur-Containing Heterocyclic Ring Compounds. III. 3-Methyl-4-oxo-1,3-thiazine-2-thione

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3-Methyl-4-oxo-1,3-thiazine-2-thione,  $C_5H_7NOS_2$ , is monoclinic, space group  $P2_1/c$ ,  $Z=4$ . The structure was solved by Patterson and minimum function methods with 623 visually estimated X-ray intensities, and refined to  $R=0.108$ . The six-membered ring has a boat conformation with the outer sulphur atom at the 2-position *trans* to the methyl group and to the methylene carbon atom at the 6-position. These latter two groups are *cis* to one another.

### Introduction

3-Methyl-4-oxo-1,3-thiazine-2-thione is the third in a series of sulphur-containing heterocyclic compounds to be subjected to X-ray structure analysis in this department. Of interest is the state of conjugation in the six-membered ring, and also its geometry and conformation in comparison with similar planar five-membered rings whose structures have been reported (Amirthalingam & Muralidharan, 1972*a, b*).

### Experimental

The yellow needles are monoclinic. The unit-cell parameters derived from Weissenberg photographs taken with Cu  $K\alpha$  radiation ( $\lambda=1.542 \text{ \AA}$ ) are  $a=8.02$  (1),  $b=7.11$  (1),  $c=15.47$  (2)  $\text{\AA}$ ,  $\beta=124$  (1) $^\circ$ . There are four molecules in the cell ( $d_o=1.45$ ,  $d_c=1.47 \text{ g.cm}^{-3}$ ). The systematic absences  $h0l$  for  $l$  odd and  $0k0$  for  $k$  odd characterize the space group as  $P2_1/c$ . The reflexions  $h0l$  to  $h6l$ , and  $hk0$  were recorded with Cu  $K\alpha$  radiation using the equi-inclination Weissenberg method, and their intensities were estimated visually. 623 unique

reflexions were measured and corrected for Lorentz, polarization, and spot-size effects, but not for absorption. Scaling was achieved by using Wilson plots.

A three-dimensional Patterson synthesis was computed and the peaks near the origin as well as the Harker peaks were examined. It was possible to identify the peaks due to intramolecular non-bonded S...S atoms, and also those from symmetry related S atoms. Minimum function methods revealed the image of the six-membered ring, and iterative Fourier methods located the remaining atoms. The structure was refined by full-matrix least-squares calculations. In the final stage of the refinement, a Cruickshank weighting scheme with  $w=(2.0+F_o+0.053F_o^2)^{-1}$  was used. The S atoms, the O atom and the methyl C atom were allowed to vibrate anisotropically. The final value of  $R$  for all observed reflexions was 0.108. Hydrogen atoms were ignored. Form factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1962). The structure projected down  $b$  is shown in Fig. 1. The final parameters are given in Table 1. Table 2 lists the values of  $F_o$  and  $F_c$ .

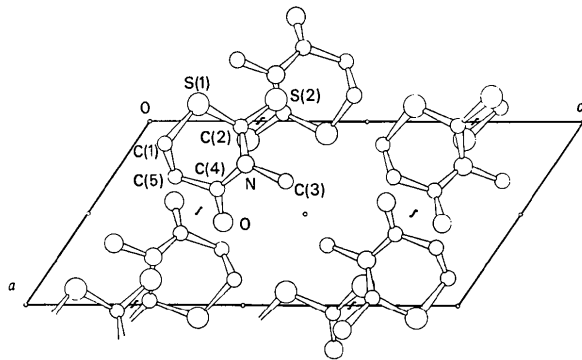


Fig. 1. The contents of the unit cell projected down *b*.

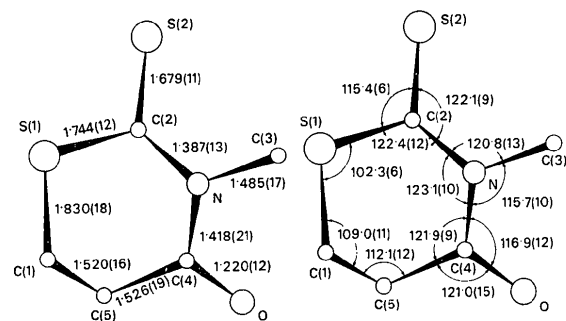


Fig. 2. Bond lengths and angles.

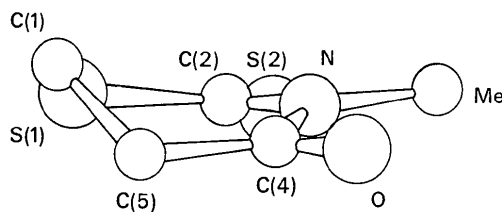


Fig. 3. End view of the molecule as seen in projection down *a*.

Table 1. Final positional ( $\times 10^4$ ) and thermal parameters of the atoms with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
S(1)	-860 (4)	2387 (4)	803 (2)	—
S(2)	-1252 (4)	2178 (4)	2548 (2)	—
C(1)	1272 (19)	2826 (18)	703 (9)	3·4 (3)
C(2)	314 (17)	2282 (15)	2156 (8)	2·3 (2)
C(3)	3358 (25)	2440 (24)	4003 (10)	—
C(4)	3720 (17)	1702 (17)	2565 (9)	2·7 (2)
C(5)	2972 (17)	1467 (17)	1419 (9)	2·8 (2)
N	2399 (12)	2209 (11)	2860 (6)	2·0 (2)
O	5509 (13)	1546 (16)	3268 (7)	—

Table 1 (cont.)

The anisotropic temperature factor is of the form:  $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) \times 10^{-4}]$

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
S(1)	107 (6)	122 (7)	25 (2)	-34 (10)	35 (5)	-7 (5)
S(2)	119 (7)	91 (2)	52 (2)	21 (9)	111 (6)	3 (6)
C(3)	282 (45)	336 (47)	32 (7)	-36 (20)	6 (10)	-1 (7)
O	114 (20)	312 (27)	64 (6)	129 (38)	85 (20)	30 (22)

Table 2. Observed and calculated structure factors

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>o</sub>	<i>F</i> <sub>c</sub>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>o</sub>	<i>F</i> <sub>c</sub>
0	0	0	18.69	18.69	12	15	29	11.90	11.90
0	0	10	9.75	7.64	14	9	7.76	8.19	
0	0	20	11.60	11.60	16	15	11.60	11.60	
0	1	0	1.81	1.92	18	9	39.71	37.96	
0	2	0	1.98	1.98	20	15	17.79	17.79	
0	3	0	4.98	5.03	22	15	19.95	17.30	
0	4	0	2.94	2.94	24	15	17.79	17.79	
0	5	0	10.10	9.74	26	15	9.60	47.89	
0	6	0	7.09	10.47	28	15	24.05	18.76	
0	7	0	11.58	11.58	30	15	11.58	11.58	
0	8	0	3.56	3.69	32	15	37.07	20.09	
0	9	0	6.22	6.22	34	15	66.86	37.67	
0	10	0	10.52	10.49	36	15	14.52	17.39	
0	11	0	15.11	15.11	38	15	15.11	17.39	
0	12	0	18.11	18.11	40	15	43.12	19.19	
0	13	0	22.11	22.11	42	15	55.99	37.07	
0	14	0	25.11	25.11	44	15	66.86	37.67	
0	15	0	29.11	29.11	46	15	12.77	17.34	
0	16	0	33.11	33.11	48	15	13.67	17.34	
0	17	0	37.11	37.11	50	15	13.67	17.34	
0	18	0	41.11	41.11	52	15	13.67	17.34	
0	19	0	45.11	45.11	54	15	13.67	17.34	
0	20	0	49.11	49.11	56	15	13.67	17.34	
0	21	0	53.11	53.11	58	15	13.67	17.34	
0	22	0	57.11	57.11	60	15	13.67	17.34	
0	23	0	61.11	61.11	62	15	13.67	17.34	
0	24	0	65.11	65.11	64	15	13.67	17.34	
0	25	0	69.11	69.11	66	15	13.67	17.34	
0	26	0	73.11	73.11	68	15	13.67	17.34	
0	27	0	77.11	77.11	70	15	13.67	17.34	
0	28	0	81.11	81.11	72	15	13.67	17.34	
0	29	0	85.11	85.11	74	15	13.67	17.34	
0	30	0	89.11	89.11	76	15	13.67	17.34	
0	31	0	93.11	93.11	78	15	13.67	17.34	
0	32	0	97.11	97.11	80	15	13.67	17.34	
0	33	0	101.11	101.11	82	15	13.67	17.34	
0	34	0	105.11	105.11	84	15	13.67	17.34	
0	35	0	109.11	109.11	86	15	13.67	17.34	
0	36	0	113.11	113.11	88	15	13.67	17.34	
0	37	0	117.11	117.11	90	15	13.67	17.34	
0	38	0	121.11	121.11	92	15	13.67	17.34	
0	39	0	125.11	125.11	94	15	13.67	17.34	
0	40	0	129.11	129.11	96	15	13.67	17.34	
0	41	0	133.11	133.11	98	15	13.67	17.34	
0	42	0	137.11	137.11	100	15	13.67	17.34	
0	43	0	141.11	141.11	102	15	13.67	17.34	
0	44	0	145.11	145.11	104	15	13.67	17.34	
0	45	0	149.11	149.11	106	15	13.67	17.34	
0	46	0	153.11	153.11	108	15	13.67	17.34	
0	47	0	157.11	157.11	110	15	13.67	17.34	
0	48	0	161.11	161.11	112	15	13.67	17.34	
0	49	0	165.11	165.11	114	15	13.67	17.34	
0	50	0	169.11	169.11	116	15	13.67	17.34	
0	51	0	173.11	173.11	118	15	13.67	17.34	
0	52	0	177.11	177.11	120	15	13.67	17.34	
0	53	0	181.11	181.11	122	15	13.67	17.34	
0	54	0	185.11	185.11	124	15	13.67	17.34	
0	55	0	189.11	189.11	126	15	13.67	17.34	
0	56	0	193.11	193.11	128	15	13.67	17.34	
0	57	0	197.11	197.11	130	15	13.67	17.34	
0	58	0	201.11	201.11	132	15	13.67	17.34	
0	59	0	205.11	205.11	134	15	13.67	17.34	
0	60	0	209.11	209.11	136	15	13.67	17.34	
0	61	0	213.11	213.11	138	15	13.67	17.34	
0	62	0	217.11	217.11	140	15	13.67	17.34	
0	63	0	221.11	221.11	142	15	13.67	17.34	
0	64	0	225.11	225.11	144	15	13.67	17.34	
0	65	0	229.11	229.11	146	15	13.67	17.34	
0	66	0	233.11	233.11	148	15	13.67	17.34	
0	67	0	237.11	237.11	150	15	13.67	17.34	
0	68	0	241.11	241.11	152	15	13.67	17.34	
0	69	0	245.11	245.11	154	15	13.67	17.34	
0	70	0	249.11	249.11	156	15	13.67	17.34	
0	71	0	253.11	253.11	158	15	13.67	17.34	
0	72	0	257.11	257.11	160	15	13.67	17.34	
0	73	0	261.11	261.11	162	15	13.67	17.34	
0	74	0	265.11	265.11	164	15	13.67	17.34	
0	75	0	269.11	269.11	166	15	13.67	17.34	
0	76	0	273.11	273.11	168	15	13.67	17.34	
0	77	0	277.11	277.11	170	15	13.67	17.34	
0	78	0	281.11	281.11	172	15	13.67	17.34	
0	79	0	285.11	285.11	174	15	13.67	17.34	
0	80	0	289.11	289.11	176	15	13.67	17.34	
0	81	0	293.11	293.11	178	15	13.67	17.34	
0	82	0	297.11	297.11	180	15	13.67	17.34	
0	83	0	301.11	301.11	182	15	13.67	17.34	
0	84	0	305.11	305.11	184	15	13.67	17.34	
0	85	0	309.11	309.11	186	15	13.67	17.34	
0	86	0	313.11	313.11	188	15	13.67	17.34	
0	87	0	317.11	317.11	190	15	13.67	17.34	
0	88	0	321.11	321.11	192	15	13.67	17.34	
0	89	0	325.11	325.11	194	15	13.67	17.34	
0	90	0	329.11	329.11	196	15	13.67	17.34	
0	91	0	333.11	333.11	198	15	13.67	17.34	
0	92	0	337.11	337.11	200	15	13.67	17.34	
0	93	0	341.11	341.11	202	15	13.67	17.34	
0	94	0	345.11	345.11	204	15	13.67	17.34	
0	95	0	349.11	349.11	206	15	13.67	17.34	
0	96	0	353.11	353.11	208	15	13.67	17.34	
0	97	0	357.11	357.11	210	15	13.67	17.34	
0	98	0	361.11	361.11	212	15	13.67	17.34	
0	99	0	365.11	365.11	214	15	13.67	17.34	
0	100	0	369.11	369.11	216	15	13.67	17.34	
0	101	0	373.11	373.11	218	15	13.67	17.34	
0	102	0	377.11	377.11	220	15	13.67	17.34	
0	103	0	381.11	381.11	222	15	13.67	17.34	
0	104	0	385.11	385.11	224	15	13.67	17.34	
0	105	0	389.11	389.11	226	15	13.67	17.34	
0	106	0	393.11	393.11	228	15	13.67	17.34	
0	107	0	397.11	397.11	230	15	13.67	17.34	
0	108	0	401.11	401.11	232	15	13.67	17.34	
0	109	0	405.11	405.11	234	15	13.67	17.34	
0	110	0	409.11	409.11	236	15	13.67	17.34	
0	111	0	413.11	413.11	238	15	13.67	17.34	
0	112	0	417.11	417.11	240	15	13.67	17.34	
0	113	0	421.11	421.11	242	15	13.67	17.34	
0	114	0	425.11	425.11	244	15	13.67	17.34	
0	115	0	429.11	429.11	246	15	13.67	17.34	
0	116	0	433.11	433.11	248	15	13.67	17.34	
0	117	0	437.11	437.11	250	15	13.67	17.34	
0	118	0	441.11	441.11	252	15	13.67	17.34	
0	119	0	445.11	445.11	254	15	13.67	17.34	
0	120	0	449.11	449.11	256	15	13.67	17.34	
0	121	0	453.11	453.11	258	15	13.67	17.34	
0	122	0	457.11	457.11	260	15	13.67	17.34	
0	123	0	461.11	461.11	262	15	13.67	17.34	
0	124	0	465.11	465.11	264	15	13.67	17.34	
0	125	0	469.11	469.11	266	15	13.67	17.34	
0</									

### Description of the structure

An examination of the bond lengths (Fig. 2) clearly shows the double-bond character of S(1)–C(2), S(2)–C(2), and C(2)–N, and the extent of partial conjugation in the ring. The angle C(1)–S(1)–C(2) is 102.3 (6)° and is comparable with CSC angles of 104.9 and 100.7° found in 1-acetyl-1-thiona-5-thiacyclooctane perchlorate (Johnson, Maier & Paul, 1970) and in some 1,4-dithianes (Chao & McCullough, 1960). Other bond lengths and angles are normal.

The geometry of the molecule can be described in terms of three planes: plane *A* containing S(1), C(2), C(4), and C(5); plane *B* containing C(2), C(3), and N; and plane *C* containing S(1), C(1), and C(5) (Table 3). Plane *B* and *C* are *cis* while the outer S atom S(2) is *trans* to the atoms in planes *B* and *C*. This can be seen in Fig. 3 which shows an end view of the molecule projected down *a*. The angle between *A* and *B* is 7.6° and between *A* and *C* is 57.0°. Thus it is clear that the molecule exists in a boat conformation. In order to confirm this, we calculated intermolecular distances with atom C(1) in the alternative chair conformation. The intermolecular distance C(1)···C(1') across a centre of symmetry then adopts the very low value of 2.11 Å, whereas its actual value is 4.47 Å. We also performed a least-squares refinement which resulted in C(1), which was initially in the chair conformation, being refined to the boat position (Amirthalingam & Jakkal, 1970).

Table 3. Equations of mean planes and deviations of the atoms

Plane	Equation
<i>A</i>	0.2095 <i>x</i> + 0.9776 <i>y</i> + 0.0182 <i>z</i> = 1.3428
<i>B</i>	0.1945 <i>x</i> + 0.9742 <i>y</i> – 0.1137 <i>z</i> = 0.9644
<i>C</i>	0.0615 <i>x</i> – 0.6601 <i>y</i> – 0.7486 <i>z</i> + 1.9731 = 0

#### Deviations of atoms from planes

Plane <i>A</i>		Plane <i>B</i>		Interplanar angles	
S(1)	–0.044 Å	N	+0.138 Å	<i>AB</i>	7.6°
C(2)	–0.048	C(3)	+0.276	<i>AC</i>	57°
C(4)	+0.055	S(2)	–0.447		
C(5)	–0.050	O	+0.134		
C(1)	+0.723				
Plane <i>B</i>					
C(2)	–0.014 Å				
C(3)	–0.012				
C(4)	–0.013				
N	+0.039				

The intramolecular S(1)···S(2) distance is 2.90 Å, which is shorter than would be expected from close packing considerations but is comparable with the values, 2.91–2.97 Å, found in similar structures (Sletten, 1969). The intermolecular S···S distances are 4.01 and 4.27 Å. The S···N intermolecular contacts of 3.66 and 3.61 Å are normal.

Regarding the S···O interaction in this compound (Table 4), the values found, S(1)···O = 3.39, S(2)···O = 3.38 Å, show that it is practically non-existent. Thus the molecules are held in the structure by normal van der Waals forces only.

Table 4. Intermolecular distances less than 3.5 Å with *e.s.d.*'s in parentheses

First designated atom of each pair belongs to reference molecule and has the coordinates listed in Table 1.

S(1)···O <sup>(i)</sup>	3.392 (8)
S(2)···O <sup>(ii)</sup>	3.388 (14)
O···C <sup>(1iii)</sup>	3.398 (16)

#### Key to symmetry operations

i	<i>x</i> – 1, $\frac{1}{2}$ – <i>y</i> , – $\frac{1}{2}$ + <i>z</i>
ii	<i>x</i> – 1, <i>y</i> , <i>z</i>
iii	1 – <i>x</i> , – $\frac{1}{2}$ + <i>y</i> , $\frac{1}{2}$ – <i>z</i>

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