BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
DIETERLE, J. M. & ROBESON, C. D. (1954). *Science*, **120**, 219.
EICHHORN, E. L. & MACGILLAVRY, C. H. (1959). *Acta Cryst.* **12**, 872.
GILARDI, R. D., KARLE, I. L., KARLE, J. & SPERLING, W. (1971). *Nature, Lond.* **232**, 187.
HAMANAKA, T., MITSUI, T., ASHIDA, T. & KAKUDO, M. (1972). *Acta Cryst.* B**28**, 214.
HONIG, B. & KARPLUS, M. (1971). *Nature, Lond.* **229**, 558.
HUBBARD, R. & KROPF, A. (1958). *Proc. Natl. Acad. Sci. U.S.* **44**, 130.
HUBBARD, R. & WALD, G. (1968). *Structural Chemistry and Molecular Biology*, p. 545. Edited by A. RICH & N. DAVIDSON. San Francisco: Freeman.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849.
KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521.
NASH, H. A. (1969). *J. Theor. Biol.* **22**, 314.
OROSHNIK, W., BROWN, P. K., HUBBARD, R. & WALD, G. (1956). *Proc. Natl. Acad. Sci. U.S.* **42**, 578.
PATEL, D. J. (1969). *Nature, Lond.* **221**, 825.
PULLMAN, B., LANGLET, J. & BERTHOD, H. (1969). *J. Theor. Biol.* **23**, 492.
SCHENK, H. (1971). *Acta Cryst.* B**27**, 667.
WALD, G. (1968). *Nature, Lond.* **219**, 800.
WIESENFELD, J. R. & ABRAHAMSON, E. W. (1968). *Photochem. Photobiol.* **8**, 487.

Acta Cryst. (1972). B**28**, 2612

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

BY V. AMIRTHALINGAM AND V. S. JAKKAL

Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay-85, India

(*Received* 25 *April* 1972)

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 $R=0{\cdot}108$. 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 ($\lambda=1{\cdot}542$ Å) are $a=8{\cdot}02$ (1), $b=7{\cdot}11$ (1), $c=15{\cdot}47$ (2) Å, $\beta=124$ (1)°. There are four molecules in the cell ($d_o=1{\cdot}45$, $d_c=1{\cdot}47$ 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 $w=(2{\cdot}0+F_o+0{\cdot}053F_o^2)^{-1}$ 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.

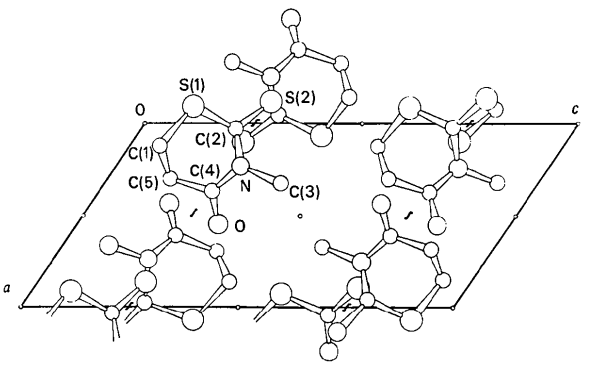

Fig. 1. The contents of the unit cell projected down **b**.

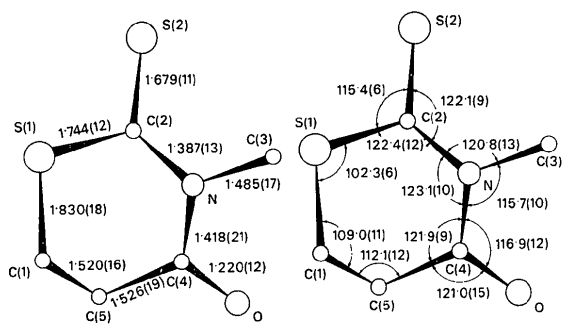

Fig. 2. Bond lengths and angles.

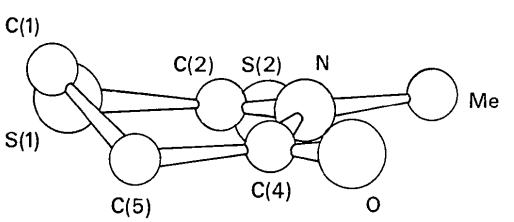

Fig. 3. End view of the molecule as seen in projection down **a**.

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

	x	*y*	*z*	*B*
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 2. *Observed and calculated structure factors*

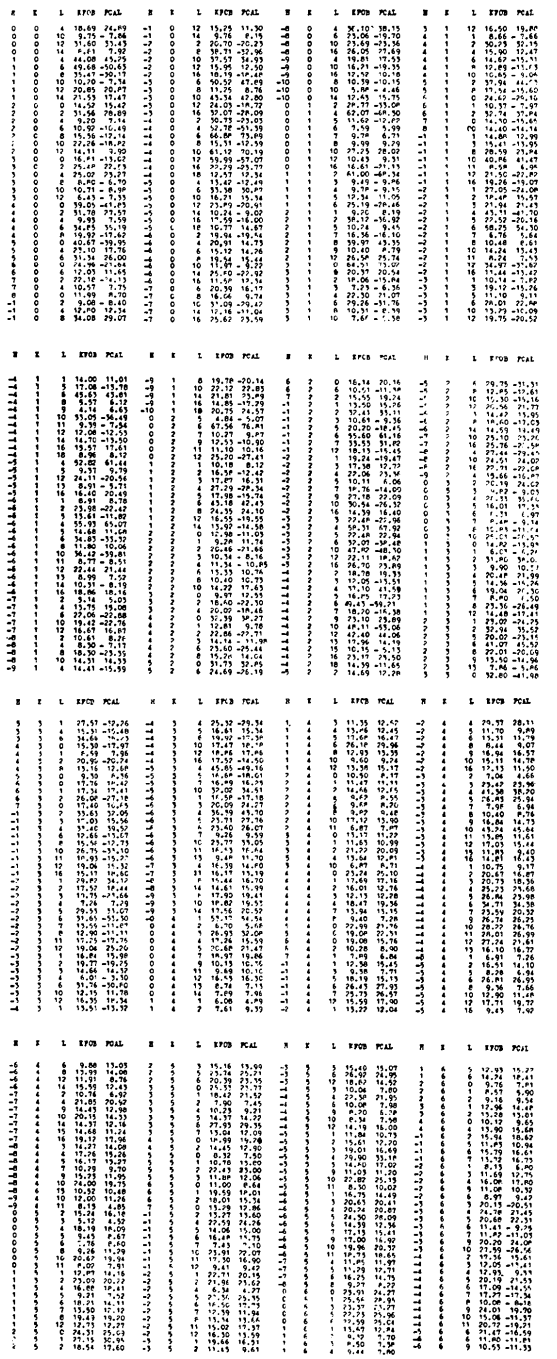

Table 1 (*cont.*)

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

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{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)

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 l-acetonyl-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

A	$0{\cdot}2095x+0{\cdot}9776y+0{\cdot}0182z=1{\cdot}3428$
B	$0{\cdot}1945x+0{\cdot}9742y-0{\cdot}1137z=0{\cdot}9644$
C	$0{\cdot}0615x-0{\cdot}6601y-0{\cdot}7486z+1{\cdot}9731=0$

Deviations of atoms from planes

Plane *A*			
S(1)	−0·044 Å	N	+0·138 Å
C(2)	−0·048	C(3)	+0·276
C(4)	+0·055	S(2)	−0·447
C(5)	−0·050	O	+0·134
C(1)	+0·723		

Plane *B*		Interplanar angles
C(2)	−0·014 Å	$AB=7{\cdot}6°$
C(3)	−0·012	
C(4)	−0·013	$AC=57°$
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(i)	3·392 (8)
S(2)···O(ii)	3·388 (14)
O···C(1iii)	3·398 (16)

Key to symmetry operations

i	$x-1,\ \frac{1}{2}-y,\ -\frac{1}{2}+z$
ii	$x-1,\ y\ ,\ z$
iii	$1-x,\ -\frac{1}{2}+y,\ \frac{1}{2}-z$

We thank Dr J. Shankar and Dr P. G. Kulchandani for their support and encouragement, Dr M. S. Chadha for supplying the compound, and Professor J. Trotter, Dr R. Chidambaram and Professor R. Srinivasan for computer programs.

References

AMIRTHALINGAM, V. & MURALIDHARAN, K. V. (1972*a*). *Acta Cryst.* B**28**, 2417.

AMIRTHALINGAM, V. & MURALIDHARAN, K. V. (1972*b*). *Acta Cryst.* B**28**, 2421.

AMIRTHALINGAM, V. & JAKKAL, V. S. (1970). *Chem. Commun.* p. 1117.

CHAO, G. Y. & MCCULLOUGH, J. D. (1960). *Acta Cryst.* **13**, 727.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

JOHNSON, S. M., MAIER, C. A. & PAUL, I. C. (1970). *J. Chem. Soc.* (*B*), p. 1603.

SLETTEN, J. (1969). *Chem. Commun.* p. 688.