3,6-Dimethyl-5-thioformylpyrrolo[2,1-*b*]thiazole

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$C_9H_9NS_2$, triclinic, space group $P\bar{1}$, $a=8\cdot360$ (3), $b=9\cdot113$ (3), $c=7\cdot772$ (3) Å, $\alpha=102\cdot36$ (5), $\beta=106\cdot90$ (5), $\gamma=119\cdot09$ (5)°, $Z=2$, $R=0\cdot028$, 824 reflexions. Although the expected position for the thioformyl group of all thioformylpyrrolo[2,1-*b*]thiazoles is a *syn* configuration due to the polarized sulphur and nitrogen atoms, in this molecule it is *anti*, with C–C$=1\cdot394$ (4) and C–S$=1\cdot656$ (2) Å. The bond lengths of the thioformyl group and the pyrrolo ring suggest a significant contribution from the ionic as well as the covalent from.

Introduction

The compound was synthesized and crystals grown by Webster (1972). The crystals are dark red needles elongated along [001]. Preliminary cell parameters were obtained from zero-layer Weissenberg photographs. A Delaunay (1933) reduction was used to obtain the reduced triclinic primitive cell. The final cell parameters were obtained from the best orientation matrix on a Siemens four-circle diffractometer.

The crystal data are:

Formula $C_9H_9NS_2$
$a=$ 8·360 (3); $b=$ 9·113 (3); $c=$ 7·772 (3) Å
$\alpha=102\cdot36$ (5); $\beta=106\cdot90$ (5); $\gamma=119\cdot09$ (5)°.
$V=447\cdot96$ Å^3; $D_c=1\cdot447$ (2) g cm^{-3}.
Space group $P\bar{1}$; $Z=2$; μ(Mo $K\alpha$)$=5\cdot15$ cm^{-1}.

A crystal $0\cdot2\times0\cdot3\times0\cdot3$ mm was chosen to obtain the intensities of 824 independent reflexions on the diffractometer with Mo $K\alpha$ radiation and a zirconium β-filter. The five-point measuring cycle was employed and most of the intensities were measured with an accuracy of between 2 and 6%. However, 40 of the intensities were measured within a counting statistics of 6 to 13%. As a check on electronic and crystal stability, three standard reflexions were measured before every 20 reflexions and no statistically significant changes were observed. Appropriate time scale and attenuator factors were applied to put the integrated intensities on the same scale, the attenuator factors being determined by a separate experiment. The intensities were corrected for Lorentz and polarization factors but not for absorption.

The coordinates of the two sulphur atoms were obtained from a Patterson synthesis calculated with 237 reflexions ($0<2\theta<30°$). A Fourier map phased on the two sulphur atoms yielded the positions of all the non-hydrogen atoms. Five cycles of full-matrix least-

squares refinement with isotropic temperature factors and all observed data gave an R of 0·077 where

$$R=\frac{\sum ||F_o|-|F_c||}{\sum |F_o|}.$$

Two further cycles with anisotropic temperature factors reduced R to 0·047. At this stage a difference synthesis clearly revealed the positions of the nine hydrogen atoms. The parameters of the hydrogen atoms were not refined and the isotropic temperature factor for each was assumed to be that of its attached carbon. Three more cycles reduced R to 0·029. Absolute weights (Killean & Lawrence, 1969) were assigned with the values $c^2=0\cdot0002$ and $k^2=0\cdot0008$. Two more cycles of refinement gave a final R of 0·028 and

$$\frac{\sum \omega \Delta^2}{m-n}=1\cdot04.^*$$

Table 1. *Atomic coordinates and standard deviations*

	x/a	y/b	z/c
S(1)	0·2173 (2)	0·0378 (2)	0·2082 (2)
S(2)	0·7629 (2)	−0·2949 (2)	0·2884 (2)
N	0·4753 (4)	−0·0428 (4)	0·2516 (4)
C(1)	0·2823 (5)	−0·1109 (5)	0·2309 (5)
C(2)	0·1919 (5)	−0·2857 (5)	0·2259 (6)
C(3)	0·3326 (5)	−0·3271 (5)	0·2432 (5)
C(4)	0·5132 (5)	−0·1774 (5)	0·2599 (5)
C(5)	0·2948 (6)	−0·5057 (5)	0·2432 (7)
C(6)	0·6992 (5)	−0·1493 (5)	0·2833 (5)
C(7)	0·5759 (6)	0·1315 (5)	0·2495 (5)
C(8)	0·4562 (7)	0·1909 (6)	0·2249 (6)
C(9)	0·7890 (7)	0·2342 (6)	0·2719 (7)
H(1)	0·310	−0·583	0·128
H(2)	0·180	−0·585	0·260
H(3)	0·400	−0·480	0·360
H(4)	0·038	−0·375	0·210
H(5)	0·805	−0·015	0·295
H(6)	0·470	0·305	0·210
H(7)	0·800	0·158	0·168
H(8)	0·813	0·340	0·270
H(9)	0·890	0·260	0·413

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Table 2. *Anisotropic temperature factors* ($\times 10^5$)

$$T = \exp\left[-(h^2 B_{11} + k^2 B_{22} + l^2 B_{33} + 2hk B_{12} + 2hl B_{13} + 2kl B_{23})\right]$$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S(1)	3171 (30)	2533 (25)	2302 (28)	2446 (25)	1197 (24)	1142 (21)
S(2)	2407 (26)	2308 (25)	3185 (34)	1934 (24)	1215 (24)	1042 (23)
N	1907 (68)	1453 (58)	1545 (64)	1229 (58)	685 (53)	700 (48)
C(1)	2188 (92)	2001 (81)	1585 (80)	1680 (78)	895 (69)	909 (65)
C(2)	1992 (88)	2089 (85)	2069 (87)	1470 (78)	1108 (73)	1031 (68)
C(3)	1886 (79)	1489 (65)	1691 (76)	1178 (66)	754 (62)	718 (56)
C(4)	1742 (76)	1395 (65)	1380 (73)	1125 (66)	619 (59)	575 (54)
C(5)	2448 (102)	1743 (82)	2977 (112)	1344 (84)	1275 (88)	1289 (77)
C(6)	1975 (89)	1825 (76)	2048 (90)	1368 (76)	906 (73)	838 (66)
C(7)	2514 (99)	1334 (69)	1631 (76)	1162 (76)	814 (70)	684 (56)
C(8)	3443 (120)	1892 (83)	2201 (96)	1959 (91)	1157 (89)	1064 (73)
C(9)	2859 (120)	1531 (81)	2718 (120)	1063 (88)	1091 (96)	978 (78)

To check the validity of the weighting scheme, the distribution of ($|\Delta|/\sigma$) was examined and it was found that 73% of the reflexions have ($|\Delta|/\sigma$) < 2·0. For three reflexions 100, 10$\bar{1}$ and 01$\bar{1}$ this ratio was greater than 3·0. The scattering factors used were those in *International Tables for X-ray Crystallography* (1962). The final atomic coordinates and temperature factors are listed in Tables 1 and 2.

Discussion

The structure of 3,6-dimethyl-5-thioformylpyrrolo[2,1-b]thiazole is the second in a series of stable thioaldehydes, known as pyrrolo[2,1-b]thiazoles, to have been determined. The preliminary structure of 6-methyl-5-thioformylpyrrolo[2,1-b]thiazole was determined by Cameron (1970) and its refinement (Cameron, Sharma, Lawrence & Killean, 1974) will be reported subsequently, as will the structure (Sharma, Lawrence & Killean, 1974) of 3-methyl-6-t-butyl-5-thioformylpyrrolo[2,1-b]thiazole which has already been initially reported by Sharma (1973). The structural interest in these compounds has centred on the configuration and the nature of the conjugation of the pyrrolo ring and the thioformyl group.

Tables 3 and 4 list the bond lengths and angles.
The best planes referred to the a^*, b', c orthogonal axis system with b' in the a^*b^* plane were calculated

Table 3. *Bond lengths* (Å) *and angles* (°)
with standard deviations

S(1)–C(1)	1·710 (2)	C(4)–N——C(7)	137·8 (2)
S(1)–C(8)	1·736 (4)	S(1)–C(1)–N	112·2 (2)
S(2)–C(6)	1·656 (2)	C(2)–C(1)–N	109·5 (2)
N——C(1)	1·358 (4)	S(1)–C(1)–C(2)	138·3 (2)
N——C(4)	1·418 (3)	C(1)–C(2)–C(3)	107·3 (2)
N——C(7)	1·396 (3)	C(2)–C(3)–C(4)	109·4 (2)
C(1)–C(2)	1·377 (3)	C(2)–C(3)–C(5)	124·6 (2)
C(2)–C(3)	1·380 (4)	C(4)–C(3)–C(5)	126·0 (2)
C(3)–C(4)	1·402 (4)	C(3)–C(4)–N	105·2 (2)
C(3)–C(5)	1·500 (3)	C(3)–C(4)–C(6)	131·8 (2)
C(4)–C(6)	1·394 (4)	N——C(4)–C(6)	123·0 (2)
C(7)–C(8)	1·338 (4)	C(4)–C(6)–S(2)	128·4 (2)
C(7)–C(9)	1·485 (6)	N——C(7)–C(8)	111·4 (2)
C(1)–S(1)–C(8)	89·5 (1)	N——C(7)–C(9)	123·1 (2)
C(1)–N——C(4)	108·6 (2)	C(8)–C(7)–C(9)	125·5 (2)
C(1)–N——C(7)	113·5 (2)	S(1)–C(8)–C(7)	113·4 (2)

Table 4. *Bond lengths* (Å) *and angles* (°)
involving hydrogen atoms

C(2)–H(4)	1·09	C(3)–C(5)–H(3)	109
C(5)–H(1)	1·09	H(1)–C(5)–H(2)	112
C(5)–H(2)	0·95	H(2)–C(5)–H(3)	98
C(5)–H(3)	0·95	H(3)–C(5)–H(1)	102
C(6)–H(5)	1·07	S(2)–C(6)–H(5)	121
C(8)–H(6)	1·03	C(4)–C(6)–H(5)	111
C(9)–H(7)	1·01	S(1)–C(8)–H(6)	111
C(9)–H(8)	0·90	C(7)–C(8)–H(6)	135
C(9)–H(9)	1·06	C(7)–C(9)–H(7)	111
C(1)–C(2)–H(4)	126	C(7)–C(9)–H(8)	117
C(3)–C(2)–H(4)	126	C(7)–C(9)–H(9)	108
C(3)–C(5)–H(1)	115	H(7)–C(9)–H(8)	117
C(3)–C(5)–H(2)	118	H(8)–C(9)–H(9)	110
		H(7)–C(9)–H(9)	108

by least-squares for the two five-membered rings. The equation of the best plane through the atoms of the pyrrolo ring, C(5) and C(6) is

$$0·3678x + 0·2208y + 0·9032z = 1·3595$$

and the deviations of all the atoms from this plane are insignificant except for S(2) of the thioformyl group which deviates by +0·04 Å.

The equation of the best plane through the thiazole ring is

$$0·3786x + 0·2708y + 0·8850z = 1·2423$$

and C(9) deviates by 0·02 Å from the thiazole ring plane. This may be just significant. The angle between the two planes is 3·2°. However, the non-coplanarity of the two rings was expected, as both five-membered rings are in a strained state.

The non-coplanarity of the pyrrolo ring with the thioformyl group arises from the steric hindrance between the atoms in the side chain and the ring atoms *ortho* to the side chain as suggested by Takano, Sasada & Kakudo (1966). In the molecule an *ortho* non-bonded contact of 3·27 Å was observed between the sulphur atom of the thioformyl group and the C(5) of the methyl group. This indicates that sulphur and hydrogen atoms interact, with a shortening of the van der Waals distance of about 0·6 Å due to the negatively charged sulphur atom.

C(9) of the methyl group has short intermolecular

contacts of 3·74 and 3·78 Å for the pairs C(9)C(7) and C(9)C(2) respectively. This may be the cause of the deviation of C(9) from the thiazole ring plane.

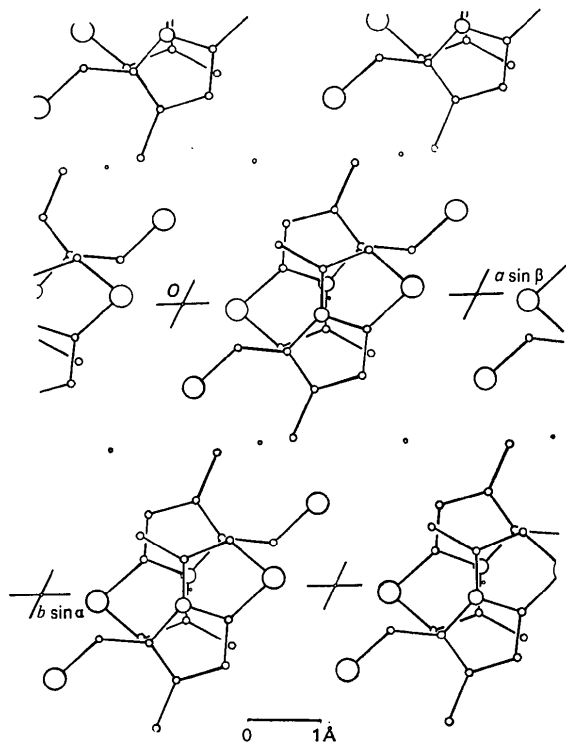N.m.r. spectroscopy (Webster, 1972) indicates that

Fig. 1. Molecular packing viewed down c.

the *syn* configuration is the preferred geometry of 5-thioformylpyrrolo[2,1-*b*]thiazoles. However, in this molecule the C(9) methyl group is large enough to prevent the thioformyl group from taking up the *syn* geometry and thus the thioformyl group points away from the thiazole ring in an *anti* configuration.

The observed bond lengths indicate that the electron configuration contains contributions from the covalent as well as from the ionic form of the compound. The thioformyl sulphur–carbon bond length shows significant shortening from the formal single-bond length. In other resonating molecules the exocyclic carbon–sulphur bond lengths are 1·660 (5) and 1·653 (5) Å (Lin & Sundaralingam, 1971); 1·657 Å (Downie, Harrison, Raper & Hepworth, 1972); 1·650 Å (Karle & Karle, 1965) and 1·666 Å (Form, Raper & Downie, 1973). These show good agreement with the value 1·656 (2) Å for this molecule. The carbon–carbon bond lengths in the thioformyl group and in the pyrrolo ring have a mean value of 1·388 (8) Å. These bond lengths are comparable with those in other conjugated molecules, *e.g.* 1·386 (4), 1·379 (4), 1·391 (4), 1·387 (4), 1·368 (5), 1·396 (4) Å (Kruger & Gafner, 1971) and 1·394 (18), 1·395 (13), 1·375 (13), 1·392 (5), 1·385 (9), 1·369 (16), 1·397 (18) Å (Kruger & Gafner, 1972). Karle & Karle (1965) give the values 1·355 and 1·437 Å for carbon–nitrogen bond lengths which compare well with 1·358 (4) Å for N–C(1), 1·418 (3) Å for N–C(4), and 1·396 (3) Å for N–C(7).

The carbon–sulphur bond lengths in the thiazole ring, although shorter than the well-established value of 1·81 Å (Kitaigorodskii, 1961), are quite common for a number of resonating structures. Values in similar
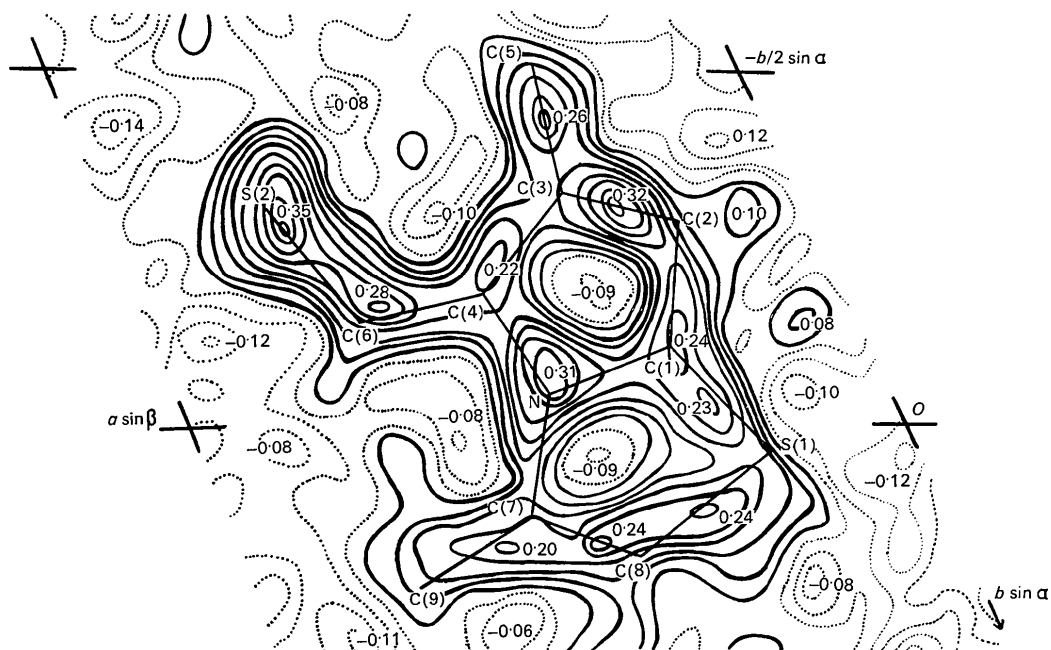

Fig. 2. Section of difference Fourier synthesis.

heterocyclic compounds are 1·720 (5), 1·742 (3) Å (Kruger & Gafner, 1971) and 1·728 (14), 1·738 (9) Å (Kruger & Gafner, 1972). These agree well with the present values 1·710 (2) and 1·736 (4) Å. The C(7)–C(8) length [1·338 (4) Å] in the thiazole ring shows double-bond character.

The carbon to methyl lengths are 1·500 (3) and 1·485 (6) Å and are shorter than the usual value of 1·54 Å. However, they agree well with the rationalization of C–CH$_3$ bond lengths on the basis of secondary-substituted carbon atoms (Kehl & Jeffrey, 1958). The carbon–hydrogen distances vary from 0·90 to 1·09 Å with a mean of 1·02 Å.

The bond angle at S(1) is 89·5 (1)° and is close to the corresponding values of 91·1 (2) and 91·1 (8)° in similar thiazole ring systems investigated by Kruger & Gafner (1971, 1972). The thiazole ring internal angles are also in good agreement.

Fig. 1 illustrates the molecular packing viewed down c. The packing diagram shows layers of molecules lying mainly parallel to the ab plane and stacked in the b direction. Most of the short contacts are between the parallel planes. All the contacts between the molecules are of the van der Waals type and fall within the expected range of values. The shortest intermolecular contacts are: C(9)···C(1) 3·61; C(9)···C(7) 3·74; C(9)···C(2) 3·74; C(7)···C(7) 3·55; C(5)···C(8) 3·71 Å.

In a least-squares refinement with a complete data set and conventional scattering factors no allowance is made for electron concentration in bonds and consequently the temperature factors tend to be falsified. A method (Jeffrey & Cruickshank, 1953) of minimizing this difficulty is to determine the anisotropic temperature factors from only high-order reflexions. In order to determine the anisotropic temperature factors from the high-order reflexions (2 sin $\theta/\lambda \geq 0.9$ Å^{-1}), three cycles of full-matrix least-squares refinement were carried out. This reduced R to 0·025. The scale factor obtained from the least-squares refinement with only high-order reflexions was not significantly different from the one obtained from all the reflexions. A difference synthesis was then computed with all the observed and calculated structure factors from the last cycle of the least-squares refinement. Fig. 2 shows a

section of this difference synthesis which almost coincides with the plane of the molecule. The maximum electron density is 0·35 e Å^{-3} and is located on the S(2)–C(6) bond, 0·44 Å away from the S(2) atom. Two peaks with heights 0·23 and 0·24 e Å^{-3} appear on the bonds S(1)–C(1) and S(1)–C(8) respectively.

The least-squares and Fourier calculations were performed on the IBM 360/44 computer at the Computer Centre of the University of St Andrews.

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