6-*tert*-Butyl-3-methyl-5-thioformylpyrrolo[2,1-*b*]thiazole

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Abstract. $C_{12}H_{15}NS_2$, monoclinic, $P2_1/n$, $a = 7\cdot195$ (3), $b = 13\cdot221$ (3), $c = 12\cdot832$ (3) Å, $\beta = 94\cdot65$ (5)°, $Z = 4$, $V = 1216\cdot4$ Å^3, $D_c = 1\cdot293$ (1) Mg m^{-3}, $R = 0\cdot031$ for 534 reflections. The thioformyl group is in an *anti* position. The bond lengths of the thioformyl group and the pyrrole ring indicate that the molecule resonates between the covalent and the partly ionic forms.

Introduction. The structure of 6-*tert*-butyl-3-methyl-5-thioformlypyrrolo[2,1-*b*]thiazole is the third in a series of stable thioaldehydes known as pyrrolo[2,1-*b*]thiazoles to be reported.

The other two structures, 3,6-dimethyl-5-thioformyl-pyrrolo[2,1-*b*]thiazole (Sharma & Killean, 1974) and 6-methyl-5-thioformylpyrrolo[2,1-*b*]thiazole (Killean, Lawrence, Cameron & Sharma, 1975), have been described.

The purple-red crystals of 6-*tert*-butyl-3-methyl-5-thioformylpyrrolo[2,1-*b*]thiazole were synthesized and grown by Webster (1972). A single crystal $0\cdot2 \times 0\cdot2 \times 0\cdot3$ mm was selected for X-ray investigations. The lattice constants were obtained from the orientation matrix on a Siemens four-circle diffractometer with Zr-filtered Mo $K\alpha$ radiation. Intensities of 534 independent reflections were recorded in the $\omega/2\theta$ scan mode with $0 \leq 2\theta \leq 46°$, and most of the intensities were measured within counting statistics of 2 to 7%. However, about 40 intensities were measured within counting statistics between 7 and 13%. Three standard reflections measured every 20 reflections showed no significant changes. The intensities were not corrected for absorption [μ(Mo $K\alpha$) = $0\cdot392$ mm^{-1}].

The structure was determined by the heavy-atom method from 285 reflections ($0 \leq \theta \leq 30°$). Full-matrix least-squares refinement with isotropic temperature factors and all observed data gave $R = \sum |F_o - |F_c||/\sum F_o = 0\cdot071$. Anisotropic refinement reduced R to $0\cdot058$. A difference synthesis revealed the positions of the 15 H atoms. In subsequent calculations, the parameters of the H atoms were not refined and the

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Table 1. *Atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3} \sum_i \sum_j \beta_{ij}\, \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
S(1)	0·2095 (3)	0·4888 (1)	0·7059 (1)	4·77 (5)
S(2)	0·2749 (3)	0·3485 (2)	0·2187 (1)	6·28 (6)
N	0·2468 (6)	0·4519 (4)	0·5125 (3)	2·97 (14)
C(1)	0·2259 (9)	0·4046 (5)	0·6049 (5)	3·74 (18)
C(2)	0·2232 (8)	0·3006 (5)	0·5920 (4)	3·87 (18)
C(3)	0·2414 (8)	0·2806 (4)	0·4862 (4)	3·48 (16)
C(4)	0·2555 (8)	0·3764 (4)	0·4330 (4)	3·00 (17)
C(5)	0·2456 (9)	0·1723 (4)	0·4424 (5)	4·09 (17)
C(6)	0·2742 (9)	0·4093 (4)	0·3316 (4)	4·07 (16)
C(7)	0·2479 (8)	0·5584 (4)	0·5219 (5)	3·34 (19)
C(8)	0·2315 (9)	0·5879 (5)	0·6191 (5)	4·16 (18)
C(9)	0·2714 (10)	0·6299 (5)	0·4315 (5)	4·64 (22)
C(10)	0·4281 (10)	0·1535 (5)	0·3911 (5)	5·35 (19)
C(11)	0·2353 (13)	0·0947 (5)	0·5310 (6)	5·93 (24)
C(12)	0·0721 (9)	0·1549 (5)	0·3644 (5)	4·93 (19)

isotropic temperature factor for each was chosen to be that of its attached C atom. Further refinement with absolute weights (Killean & Lawrence, 1969) gave a final R of $0\cdot031$ and $\sum wA^2/(m - n) = 0\cdot95$. Scattering factors were from *International Tables for X-ray Crystallography* (1962). The final atomic coordinates are listed in Table 1.‡

Discussion. The best planes referred to the a^*, b, c orthogonal axis system were calculated by least squares for the two five-membered rings. The equation of the best plane through the atoms of the pyrrole ring and C(5) and C(6) is $-0\cdot9948x + 0\cdot0243y - 0\cdot0980z = -2\cdot2326$, and the deviations of these atoms from the plane are insignificant. S(2) of the thioformyl group and C(10), C(11), C(12) of the *tert*-butyl deviate by $-0\cdot12$, $1\cdot24, 0\cdot07$ and $-1\cdot31$ Å respectively from this plane.

The equation of the best plane through the atoms of the thiazole ring and C(9) is $-0\cdot9935x + 0\cdot0238y - 0\cdot1106z = -2\cdot3255$, and again the deviations of these

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

S(1)—C(1)	1·719 (6)	C(3)—C(4)	1·446 (7)
S(1)—C(8)	1·735 (6)	C(3)—C(5)	1·539 (7)
S(2)—C(6)	1·658 (5)	C(4)—C(6)	1·388 (7)
N—C(1)	1·359 (7)	C(5)—C(10)	1·534 (9)
N—C(4)	1·433 (7)	C(5)—C(11)	1·537 (9)
N—C(7)	1·413 (7)	C(5)—C(12)	1·554 (9)
C(1)—C(2)	1·384 (9)	C(7)—C(8)	1·321 (8)
C(2)—C(3)	1·400 (7)	C(7)—C(9)	1·516 (8)

C(1)—S(1)—C(8)	89·4 (3)	N—C(4)—C(6)	117·5 (4)
C(1)—N—C(4)	108·3 (4)	C(10)—C(5)—C(3)	110·4 (4)
C(1)—N—C(7)	112·6 (4)	C(11)—C(5)—C(3)	110·3 (5)
C(4)—N—C(7)	139·0 (4)	C(12)—C(5)—C(3)	109·6 (5)
S(1)—C(1)—N	112·2 (4)	C(10)—C(5)—C(11)	107·6 (5)
C(2)—C(1)—N	110·8 (5)	C(10)—C(5)—C(12)	111·8 (5)
S(1)—C(1)—C(2)	137·0 (4)	C(11)—C(5)—C(12)	107·1 (5)
C(1)—C(2)—C(3)	107·6 (4)	C(4)—C(6)—S(2)	132·4 (4)
C(2)—C(3)—C(4)	107·9 (4)	N—C(7)—C(8)	112·0 (5)
C(2)—C(3)—C(5)	122·5 (4)	N—C(7)—C(9)	123·8 (5)
C(4)—C(3)—C(5)	129·6 (4)	C(8)—C(7)—C(9)	124·2 (5)
C(3)—C(4)—N	105·4 (4)	S(1)—C(8)—C(7)	113·7 (5)
C(3)—C(4)—C(6)	137·1 (4)		

Fig. 2. Molecular packing viewed down a.

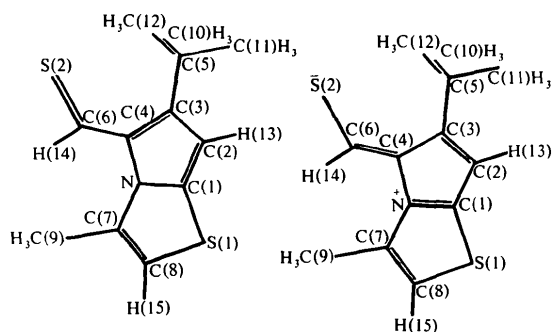Fig. 1. Canonical forms of the molecule.

atoms from the plane are insignificant. The angle between the two planes is 1·4°. Table 2 lists the bond lengths and angles. The bond lengths would appear to indicate that the bonds are covalent with partial ionic character. Resonance structures are shown in Fig. 1.

Fig. 2 illustrates the molecular packing viewed down a. The molecules lie nearly parallel to the *bc* plane and are stacked along the diagonal of this plane. Most of the short contacts are between the parallel planes along the diagonal. All the contacts between the molecules are of the van der Waals type and fall within the expected range.
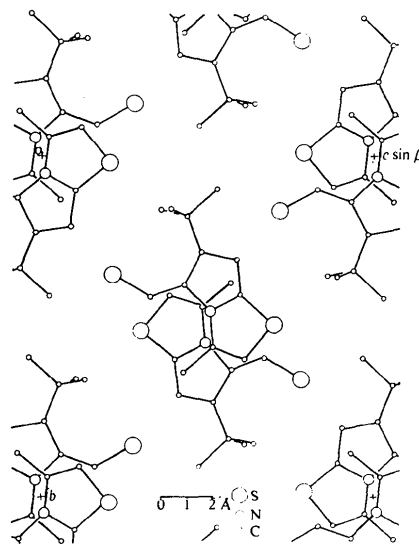
The shortest intermolecular contact is S(2)···C(9), 3·47 Å, a shortening of about 0·4 Å [van der Waals radii for S and methyl group being 1·85 and 2·00 Å respectively (Pauling, 1960)] due to S···H interaction. The other short contacts are S(1)···C(11) 3·65; C(1)···C(9) 3·60; C(1)···C(7) 3·69; C(2)···C(9) 3·66; C(4)···C(8) 3·55; C(6)···C(8) 3·56 and C(4)···C(7) 3·68 Å.

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