

References

- BOKII, N. G., ZAKHAROVA, G. N. & STRUCHKOV, YU. T. (1972). *Zh. Strukt. Khim.* **13**, 291–297.
- CARLSTRÖM, D. & FALKENBERG, G. (1973). *Acta Chem. Scand.* **27**, 1203–1209.
- FINK, W. & WHEATLEY, P. J. (1967). *J. Chem. Soc. (A)*, pp. 1517–1519.
- GARZÓ, G. & ALEXANDER, G. (1971). *Chromatographia*, **4**, 554–560.
- GARZÓ, G., SZÉKELY, T., TAMÁS, J. & UJSZÁSZI, K. (1971). *Acta Chim. Acad. Sci. Hung.* **69**, 273–299.
- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 201–209. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
- LARSSON, K. (1960). *Ark. Kem.* **16**, 203–208.
- MAIN, P., GERMAIN, G. & WOOLFSON, M. M. (1970). *MULTAN*. Univs. of York and Louvain.
- PEYRONEL, G. (1954). *Atti Acad. Nazl. Lincei Rend. Classe Sci. Fis. Mat. Nat.* **16**, 231–236.
- ROTH, W. L. & HARKER, D. (1948). *Acta Cryst.* **1**, 34–42.
- SHKLOVER, V. E., BOKII, N. G., STRUCHKOV, YU. T., ANDRIANOV, K. A., ZAVIN, B. G. & SVISTUNOV, V. S. (1974). *Zh. Strukt. Khim.* **15**, 90–98.
- STEINFINK, H., POST, B. & FANKUCHEN, I. (1955). *Acta Cryst.* **8**, 420–424.

Acta Cryst. (1975). **B31**, 1217

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

BY R. C. G. KILLEAN, J. L. LAWRENCE, J. U. CAMERON* AND Aysel SHARMA†
School of Physical Sciences, University of St. Andrews, St. Andrews, Scotland

(Received 1 November 1974; accepted 13 January 1975)

Abstract. C₈H₇NS₂, monoclinic, space group *P*2₁/*c*, *a* = 9.350 (3), *b* = 12.130 (3), *c* = 7.216 (3) Å, β = 98.00 (4)°, *Z* = 4, *D*_c = 1.483 g cm⁻³, *R* = 0.032, 662 reflexions. The thioformyl group is in the *syn* configuration. The thioformyl group and the atoms of the pyrrole ring are planar, this plane being inclined at an angle of 1.6° to the plane of the thiazole ring.

Introduction. The crystals were dark red, elongated along *c*. The cell parameters were obtained from the best orientation matrix on a Siemens four-circle diffractometer.

The intensities of 662 independent reflexions were measured on the diffractometer with Mo *K*α radiation and a Zr filter. The five-point measuring cycle was employed and some 592 of the reflexions were measured within a counting statistics accuracy of between 2 and 6%, the remainder being measured to between 6 and 14%. The integrated intensities of three standard reflexions measured every 30 reflexions did not change significantly over the collection period. No absorption corrections were made (μ = 5.62 cm⁻¹). An earlier low-accuracy data set had been used to obtain the coordinates of the two S atoms from a Patterson synthesis. A Fourier summation phased on these atoms gave the positions of all the non-hydrogen atoms, but the subsequent least-squares refinement stopped at an *R* of 0.14. From these coordinates and the new data set, three cycles of least-squares refinement with iso-

tropic temperature factors (*R* = 0.089) were followed by three cycles with anisotropic temperature factors (*R* = 0.046). A difference map then clearly showed the positions of all seven H atoms. A final refinement of the non-hydrogen atoms was then carried out with absolute weights (Killean & Lawrence, 1969) with 0.0003 and 0.0012 for *c*² and *k*² respectively. This gave an *R* of 0.032 where

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

and a value

$$\frac{\sum w\Delta^2}{m-n} = 0.94.$$

Three reflexions, 102, 391, and 5,11,1 had large values of $|A|/\sigma$ {4.4, 3.9, and 4.1 respectively} suggesting that these reflexions are affected by some systematic error. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final atomic coordinates and temperature factors are listed in Tables 1 and 2.†

Discussion. The structures of two other pyrrolo[2,1-*b*]thiazoles, 3,6-dimethyl-5-thioformylpyrrolo[2,1-*b*]thiazole (Sharma & Killean, 1974) and 3-methyl-6-*t*-butyl-5-thioformylpyrrolo[2,1-*b*]thiazole (Sharma, Lawrence & Killean, 1975) have been determined to compare the

* Present address: The Manse, St Stephens Church, Broughty Ferry, Dundee.

† Present address: Physics Department, University of Benin, Benin City, Nigeria.

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30859 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic coordinates and standard deviations

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
S(1)	-0.0072 (1)	0.3872 (1)	0.1486 (2)
S(2)	0.2664 (1)	-0.0213 (1)	0.0543 (2)
N	0.1649 (4)	0.2334 (3)	0.0907 (5)
C(1)	0.1557 (5)	0.3452 (3)	0.0929 (7)
C(2)	0.2854 (5)	0.3901 (4)	0.0550 (7)
C(3)	0.3739 (5)	0.3042 (3)	0.0269 (7)
C(4)	0.3010 (4)	0.2031 (3)	0.0477 (6)
C(5)	0.5266 (5)	0.3130 (4)	-0.0116 (8)
C(6)	0.3497 (5)	0.0976 (4)	0.0295 (7)
C(7)	0.0409 (4)	0.1789 (4)	0.1314 (6)
C(8)	-0.0600 (5)	0.2509 (4)	0.1656 (7)
H(1)	0.535	0.361	-0.115
H(2)	0.580	0.240	-0.020
H(3)	0.592	0.346	0.110
H(4)	0.445	0.105	-0.022
H(5)	0.017	0.105	0.150
H(6)	-0.165	0.235	0.220
H(7)	0.308	0.470	0.050

configuration and nature of conjugation of the pyrrole ring and the thioformyl group in the three compounds. A detailed comparison will be given in the report of the latter structure.

The numbering of the atoms in 6-methyl-5-thioformylpyrrolo[2,1-*b*]thiazole is shown in Fig. 1. Unlike the other two compounds, the thioformyl group is in the *syn* configuration due to the absence of a methyl group attached to C(7). The atoms of the pyrrole ring and the thioformyl group are planar, but C(5) of the methyl group attached to the pyrrole ring is significantly out of this plane (0.06 Å). The thiazole ring is also planar and the angle between the two planes is 1.6°.

The bond lengths and angles are listed in Tables 3 and 4. The lengths in the thiazole ring do not differ significantly from those of the thiazole ring in 3,6-dimethyl-5-thioformylpyrrolo[2,1-*b*]thiazole but differences of 0.024 ($\Delta/\sigma = 3.33$), 0.019 ($\Delta/\sigma = 2.92$) and 0.17 Å ($\Delta/\sigma = 2.97$) occur between C(4)–C(6), C(4)–C(3) and N–(4) in the two structures owing to the different geometries of the thioformyl groups and the absence of a methyl group attached to C(7) in this structure. The angles C(3)–C(4)–C(6) and N–(4)–C(6) also differ significantly ($\Delta/\sigma > 7.0$) for the two structures.

The molecular packing viewed down *c* is shown in Fig. 2. The molecules lie mainly parallel to the *ab* plane

and are stacked along *b*. A short contact (3.25 Å) exists between the negatively charged S atom of the thioformyl group and the positively charged N atom in the molecule, the van der Waals radii for S and N being 1.85 and 1.50 Å respectively (Pauling, 1960). The shortest S...S intermolecular contact, S(1)...S¹(1), is 3.49 Å (*cf.* 3.70 Å, Pauling, 1960). The shortest methyl contacts are C(5)...C(4) and C(5)...C(6), 3.57 and

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

S(1)–C(1)	1.707 (5)	C(1)–S(1)–C(8)	90.2 (2)
S(1)–C(8)	1.734 (5)	C(1)–N–C(4)	109.0 (3)
S(2)–C(6)	1.661 (5)	C(1)–N–C(7)	114.4 (3)
N–C(1)	1.358 (5)	C(4)–N–C(7)	136.6 (3)
N–C(4)	1.401 (5)	S(1)–C(1)–N	111.1 (2)
N–C(7)	1.400 (5)	C(2)–C(1)–N	109.3 (4)
C(1)–C(2)	1.391 (6)	S(1)–C(1)–C(2)	139.5 (3)
C(2)–C(3)	1.363 (6)	C(1)–C(2)–C(3)	107.1 (3)
C(3)–C(4)	1.421 (5)	C(2)–C(3)–C(4)	109.6 (4)
C(3)–C(5)	1.497 (7)	C(2)–C(3)–C(5)	126.0 (3)
C(4)–C(6)	1.370 (6)	C(4)–C(3)–C(5)	124.4 (4)
C(7)–C(8)	1.333 (6)	C(3)–C(4)–N	105.1 (4)
		C(3)–C(4)–C(6)	128.7 (3)
		N–C(4)–C(6)	126.2 (4)
		C(4)–C(6)–S(2)	129.3 (2)
		N–C(7)–C(8)	110.9 (4)
		S(1)–C(8)–C(7)	113.3 (2)

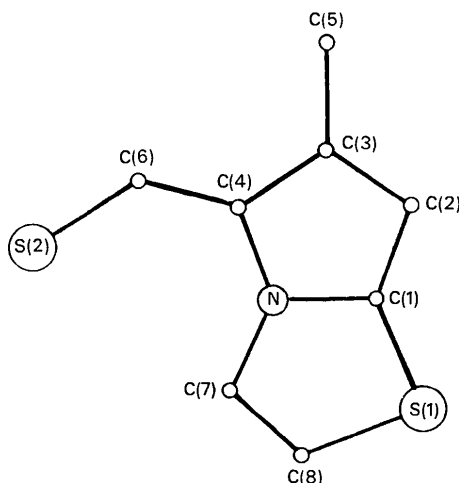


Fig. 1. Schematic diagram of the molecule showing the numbering used.

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

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S(1)	1072 (16)	550 (8)	2072 (31)	185 (10)	426 (17)	-7 (13)
S(2)	994 (15)	380 (6)	2962 (38)	-9 (9)	399 (19)	54 (14)
N	647 (37)	383 (21)	1421 (77)	0 (23)	125 (43)	-66 (33)
C(1)	917 (54)	403 (26)	1427 (105)	64 (30)	209 (59)	-32 (41)
C(2)	1041 (55)	393 (24)	1686 (106)	-161 (33)	153 (63)	-36 (46)
C(3)	832 (53)	424 (27)	1561 (104)	-120 (30)	122 (59)	-24 (43)
C(4)	650 (47)	406 (26)	1418 (94)	-28 (25)	92 (55)	6 (40)
C(5)	955 (66)	596 (36)	2436 (129)	-169 (38)	275 (75)	-26 (55)
C(6)	724 (48)	483 (28)	1769 (109)	-42 (31)	222 (59)	71 (46)
C(7)	722 (48)	515 (29)	1372 (99)	-56 (32)	106 (57)	69 (43)
C(8)	886 (54)	609 (32)	1737 (112)	72 (36)	262 (61)	54 (49)

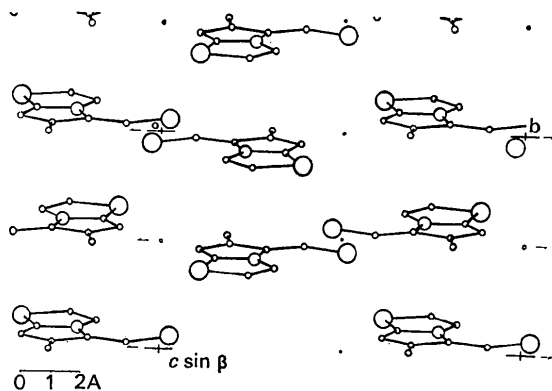


Fig. 2. Molecular packing viewed down the a axis.

3.65 Å respectively, and indicate a possible reason for the deviation of the methyl carbon from the plane of the pyrrole ring.

Calculations were performed on the IBM 360/44 computer at the Computer Centre of the University of St. Andrews.

The authors thank Professor D. H. Reid and Dr D. F. Grant for useful discussions.

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

C(2)–H(7)	0.99	C(6)–H(4)	1.02
C(5)–H(1)	0.96	C(7)–H(5)	0.94
C(5)–H(2)	1.02	C(8)–H(6)	1.12
C(5)–H(3)	1.07		
C(1)–C(2)–H(7)	128	H(3)–C(5)–H(1)	106
C(3)–C(2)–H(7)	125	S(2)–C(6)–H(4)	124
C(3)–C(5)–H(1)	112	S(4)–C(6)–H(4)	106
C(3)–C(5)–H(2)	118	N—C(7)–H(5)	136
C(3)–C(5)–H(3)	110	C(8)–C(7)–H(5)	113
H(1)–C(5)–H(2)	112	S(1)–C(8)–H(6)	117
H(2)–C(5)–H(3)	99	C(7)–C(8)–H(6)	129

References

- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- KILLEAN, R. C. G. & LAWRENCE, J. L. (1969). *Acta Cryst.* **B25**, 1750–1752.
- PAULING, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.
- SHARMA, A. & KILLEAN, R. C. G. (1974). *Acta Cryst.* **B30**, 2869–2872.
- SHARMA, A., LAWRENCE, J. L. & KILLEAN, R. C. G. (1975). To be published.