708. *The Crystal and Molecular Structure of 2-Methylthiobenzothiazole.*

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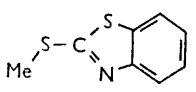
The crystal and molecular structure of 2-methylthiobenzothiazole has been determined by two-dimensional *X*-ray diffraction methods. The dimensions of the molecule have been obtained, and are compared with those of comparable molecules.

Recently the structure of 3-methylbenzothiazoline-2-thione was described.[1] The present paper reports the structure of the isomeric 2-methylthiobenzothiazole (I).



(I)

Experimental.—*2-Methylthiobenzothiazole.* $C_8H_7NS_2$. $M = 181{\cdot}3$. Monoclinic. $a = 13{\cdot}57_2$, $b = 5{\cdot}49_1$, $c = 11{\cdot}52_0$ Å, $\beta = 102°\ 52'$. $U = 837$ Å^3. $D_m = 1{\cdot}44$ (by flotation), $Z = 4$. $D_c = 1{\cdot}439$, $F(000) = 376$. Space group $P2_1/c$ (C_{2h}^5, No. 14). Cu-K_α radiation (λ 1·542 Å), single-crystal rotation and Weissenberg photographs.

Multiple-film Weissenberg photographs were taken round [*b*] and [*c*]. Relative intensities were estimated visually by comparison with standard strips. No correction was made for absorption ($\mu = 51{\cdot}6$ cm.$^{-1}$). 147 *h*0*l* and 60 *hk*0 reflexions were observed to be non-zero. Each projection was solved from a sharpened Patterson synthesis from which the positions of the two sulphur atoms could be

Table 1.

Fractional atomic co-ordinates.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	Atom	*x*/*a*	*y*/*b*	*z*/*c*	Atom	*x*/*a*	*y*/*b*	*z*/*c*
S_1	0·200	−0·163	0·122	C_2	0·179	−0·067	0·262	C_6	0·416	−0·686	0·350
S_2	0·095	0·182	0·256	C_3	0·288	−0·367	0·199	C_7	0·359	−0·519	0·396
N	0·234	−0·169	0·352	C_4	0·344	−0·539	0·152	C_8	0·297	−0·357	0·322
C_1	0·089	0·154	0·412	C_5	0·407	−0·696	0·227				

Table 2.

Observed and calculated structure factors for one asymmetric unit.

*h*0*l*	F_o	F_c	*h*0*l*	F_o	F_c	*h*0*l*	F_o	F_c	*h*0*l*	F_o	F_c	*hk*0	F_o	F_c
0.0.2	33·36	−32·02	3	8·96	−8·14	11	2·97	3·32	11	2·29	2·00	0.2.0	11·24	−11·48
1	5·28	−5·81	4	5·25	−5·93	12	2·73	2·91	12	2·29	−2·68	1	6·14	−6·65
2	0·87	−1·34	5	6·00	5·66	13	2·71	2·53	13	1·41	−1·18	2	1·30	−1·13
3	12·64	10·56	7	4·64	−4·86	14	1·69	−2·35				3	8·32	7·05
4	12·87	14·11	9	1·49	1·33	15	2·39	−3·30	1.0.$\bar{12}$	2·14	2·29	4	1·17	−0·78
5	8·80	9·66	10	3·05	3·40	16	1·36	−1·69	2	4·74	4·48	6	9·80	10·27
6	1·95	1·12	11	2·01	2·03				4	3·96	−3·59	8	1·44	1·75
7	8·26	−8·08				1.0.$\bar{6}$	14·54	−13·10	5	2·42	−2·66	9	1·91	−1·85
8	3·48	3·05	0.0.10	2·98	−3·16	2	15·78	−15·40	6	1·73	−2·30	10	6·29	−6·27
9	2·94	2·46	1	4·96	−4·22	3	10·07	9·72	11	1·16	1·52			
10	4·47	−4·93	2	1·79	−0·99	4	13·99	13·23	12	1·90	2·22			
11	4·84	−5·46	3	3·35	2·74	5	6·37	6·46				1.3.0	4·07	−3·96
12	3·84	−3·72	4	3·81	3·67	8	4·60	5·32	1.0.$\bar{14}$	3·04	−3·19	2	2·23	−2·49
14	3·13	3·91				9	3·06	2·87	2	1·50	−1·68	4	1·65	1·16
15	1·35	1·63	3.0.12	1·66	1·23	10	2·46	−3·48	3	1·01	0·65	6	1·32	1·33
			5	3·34	−3·48				4	1·72	1·30	8	1·28	−1·53
0.0.4	8·57	−8·20	6	1·45	−1·06				6	0·81	−0·53	9	1·92	2·79
1	7·95	7·45				11.0.$\bar{6}$	6·94	−8·60	8	1·68	1·43	11	1·94	−1·21
2	9·09	8·52	0.0.14	1·28	−1·01	12	4·21	−4·91						
3	4·91	3·52	1	1·23	0·81	13	1·29	0·87	*hk*0			0.4.0	5·29	−5·44
4	3·34	−2·82				14	3·33	3·11	1.0.0	5·92	5·99	1	2·33	−2·43
5	11·77	−13·28	1.0.$\bar{2}$	3·11	−2·98	15	1·27	1·72	2	20·61	−21·36	2	3·35	3·32
6	4·21	−4·80	2	8·81	9·21	16	1·04	−0·71	3	3·59	−3·80	3	2·00	2·51
7	3·79	4·15	3	10·65	−9·67				4	11·02	−11·09	4	2·81	−2·44
12	3·06	3·20	4	2·61	−1·74	1.0.$\bar{8}$	4·69	4·20	5	1·79	1·71	6	2·54	1·84
13	1·42	1·25	6	14·83	13·75	3	3·89	−3·23	6	8·63	−8·85	8	2·72	2·28
14	1·84	−2·22	7	6·39	7·71	4	1·19	0·89	7	9·05	−9·51	10	3·08	−3·12
15	0·85	−1·01	8	1·31	0·54	5	1·79	0·34	8	6·04	−6·14			
			9	3·28	−4·04	6	1·99	−1·98	10	10·13	10·35			
0.0.6	7·28	−5·93	10	6·97	−6·46	7	6·85	−6·23	11	5·31	5·07	1.5.0	2·77	3·10
1	5·51	−5·45	13	1·45	−1·97	8	6·36	−6·51	13	2·35	−2·16	2	1·81	−1·77
2	2·65	2·75	14	2·71	−2·43	9	4·51	4·87	16	1·67	−1·97	3	5·84	−5·36
3	1·68	1·42	16	3·73	3·96	10	1·98	1·94				4	1·32	−1·40
4	3·26	3·39				11	1·67	1·71	1.1.0	9·09	−11·04	6	1·10	1·09
6	5·44	6·15	1.0.$\bar{4}$	7·07	8·27	12	3·62	3·45	3	33·98	35·68	7	2·52	2·40
7	6·80	7·39	2	17·50	18·11	13	1·42	−1·35	4	10·42	11·00	10	0·95	0·53
8	2·30	−3·22	3	5·50	−5·33				6	6·68	−6·59	11	1·40	1·06
9	3·76	−3·65	4	13·53	−12·97	1.0.$\bar{10}$	1·68	1·09	7	11·44	−11·72			
10	2·81	−3·09	5	12·63	−10·93	3	1·45	−0·60	8	2·56	−2·21			
11	1·41	−1·48	6	5·79	−6·55	4	1·68	−1·83	9	1·17	−1·46	0.6.0	5·64	5·42
			7	5·26	6·87	5	1·33	1·60	11	3·69	−3·12	1	1·23	1·09
0.0.8	11·24	9·91	8	1·89	2·97	6	5·17	5·22	13	5·22	4·95	2	0·99	−1·11
1	5·81	5·01	9	4·08	−3·65	7	3·87	2·72	14	1·58	1·82	6	1·51	−1·66
2	3·73	−3·79	10	2·94	3·36	9	4·33	−4·94	15	1·17	1·31	7	1·36	−1·63

[1] Wheatley, *J.*, 1961, 4379.

located. Successive Fourier syntheses gave the positions of the lighter atoms, and each projection was refined by difference syntheses. The scattering factors used were those of Berghuis *et al.*[2] for the carbon and nitrogen atoms, and that of Tomiie and Stam [3] for the sulphur atoms. Hydrogen atoms were ignored. An isotropic temperature factor $B = 4{\cdot}47$ Å^2 proved adequate for each projection. The final agreement index was $R = 10{\cdot}2\%$ for the $h0l$

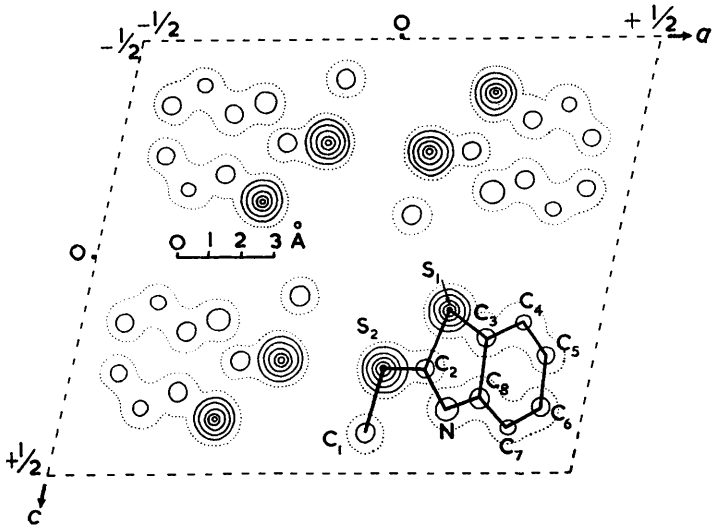


FIG. 1a.

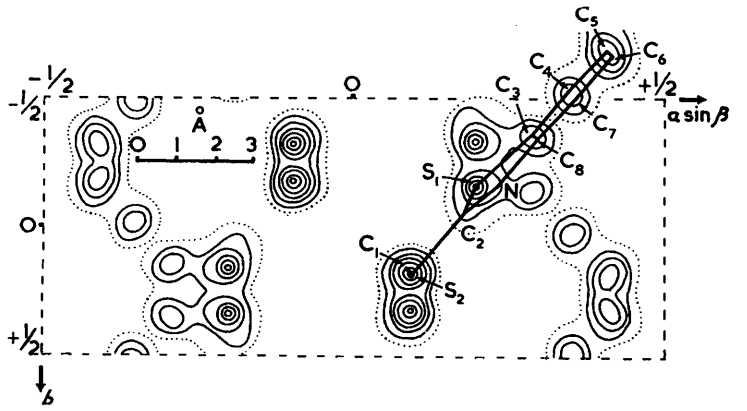


FIG. 1b.

FIG. 1. (a) Projection of the contents of the unit cell down [b].
(b) Projection of the contents of the unit cell down [c].
(Contours are drawn at equal arbitrary intervals.)

and $R = 7{\cdot}2\%$ for the $hk0$ projection. These agreement indices refer to the observed terms only.

Results.—The co-ordinates of the atoms are given in Table 1, and the observed and calculated structure factors in Table 2. Figs. 1 (a and b) show the final Fourier maps of the $h0l$ and the $hk0$ projection, respectively. Fig. 2 shows the numbering of the atoms, the bond lengths, and the bond angles. For two-dimensional analyses the usual methods

[2] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.
[3] Tomiie and Stam, *Acta Cryst.*, 1958, **11**, 126.

for assessing accuracy are unreliable, especially when one of the projections is poorly resolved; but it is felt that the C–S distances are valid to ±0·03 Å and the others to ±0·05 Å. The bond lengths agree well with expected values [4] and with those found in 3-methylbenzothiazoline-2-thione.[1] There are four C–S bonds in the molecule, all of which are formally single bonds. They show, however, some interesting differences, though these differences probably lie within the limits of the experimental error. The bond C_1–S_2 is a true single bond with a length (1·824 Å) agreeing with the estimates by Huggins [5] and Abrahams.[6] The other C–S bonds are all shortened by conjugation, strain, and possibly other effects, but the lengths agree well with those listed by Abrahams,[6] and those found in 4-methyl-1,2-dithiacyclopentene-3-thione.[7]

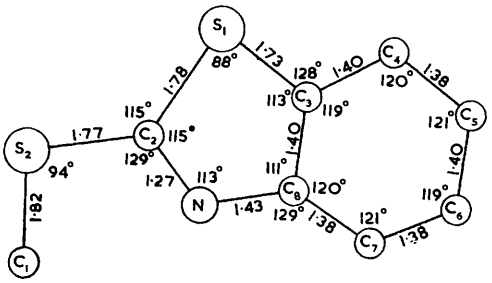


FIG. 2. The numbering of the atoms, the bond lengths, and the interatomic angles.

The molecule is planar within the limits of experimental error, with the exception of the *S*-methyl group, which lies 0·19 Å out of the molecular plane. The intermolecular distances are normal and there are no close approaches.

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ZÜRICH 3/45, SWITZERLAND. [*Received, March 14th*, 1962.]

[4] Sutton *et al.*, "Tables of Interatomic Distances," *Chem. Soc. Special Publ.*, No. 11.
[5] Huggins, *J. Amer. Chem. Soc.*, 1953, **75**, 4126.
[6] Abrahams, *Quart. Rev.*, 1956, **10**, 407.
[7] Jeffrey and Shiono, *Acta Cryst.*, 1959, **12**, 447.