862. *The Crystal and Molecular Structure of 3-Methylbenzothiazoline-2-thione.*

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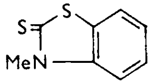
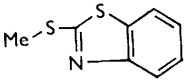
The crystal and molecular structure of 3-methylbenzothiazoline-2-thione has been determined by two-dimensional *X*-ray diffraction methods. The structure proposed previously on chemical and other physicochemical grounds is confirmed. The dimensions of the molecule have been determined and are compared with those in similar molecules.

THE structure of the 3-methylbenzothiazoline-2-thione molecule (I) was determined chemically by Mills, Clark, and Aeschlimann.[1] Their conclusions were confirmed and extended to the isomeric 2-methylthiobenzothiazole (II) by Morton and Stubbs.[2]

(I)





(II)

Nevertheless recent work on the other physical properties of these and related molecules has led to the belief that the earlier work should be checked. Accordingly a two-dimensional *X*-ray crystallographic study of the higher-melting isomer has been carried out. The earlier work is confirmed in every respect.

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	0·023	0·404	0·868	C_2	0·175	−0·021	0·569	C_6	0·535	0·522	0·754
S_2	−0·159	0·000	0·708	C_3	0·226	0·490	0·834	C_7	0·481	0·682	0·855
N	0·159	0·150	0·680	C_4	0·280	0·330	0·733	C_8	0·326	0·672	0·896
C_1	0·008	0·165	0·743	C_5	0·435	0·340	0·693				

EXPERIMENTAL

3-*Methylbenzothiazoline*-2-*thione*. $C_8H_7NS_2$. *M* 181·3. Monoclinic. $a = 8{\cdot}06_5$, $b = 5{\cdot}67_9$, $c = 9{\cdot}16_2$ Å, $\beta = 98°\ 36'$. $U = 415$ Å^3. $D_m = 1{\cdot}44$ (by flotation), $Z = 2$. $D_c = 1{\cdot}451$, $F(000) = 188$. Space group $P2_1$ (C_2^2, No. 4). Cu-K_α radiation (λ 1·542 Å), single-crystal rotation and Weissenberg photographs.

The lengths of the crystal axes exclude $P2_1/m$ as a possible space group. $P2_1$ was assumed and it is confirmed by the subsequent analysis. Multiple-film Weissenberg photographs were taken round [*b*] and [*a*]. Relative intensities were estimated visually by comparison with

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[1] Mills, Clark, and Aeschlimann, *J.*, 1923, 2362.

[2] Morton and Stubbs, *J.*, 1939, 1321.

standard strips prepared from the same crystals. No correction was made for absorption (μ = 52·1 cm.$^{-1}$). 135 *h*0*l* and 63 0*kl* 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 readily be located. Successive Fourier syntheses gave the positions of the lighter atoms, and each projection was then refined by difference syntheses. The scattering factors used were those of Berghuis *et al.*[3] for the carbon and nitrogen atoms, and that of Tomiie and Stam[4] for the sulphur atoms. Hydrogen atoms were ignored. An isotropic temperature factor B = 4·66 Å^2 proved satisfactory for each projection. The final agreement index was R = 10·7% for the *h*0*l* and R = 10·6% for the 0*kl* 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 *h*0*l* and 0*kl* projections, respectively. The molecule which is drawn in corresponds to the co-ordinates listed in Table 1. Fig. 2 shows the numbering of the atoms, the bond lengths and the bond angles. The whole molecule is planar within the limits of experimental

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	*h*0*l*	F_o	F_c
0.0.1	4·88	6·39	7	0·85	1·26	6	1·11	−1·56	9	0·85	−0·57	8	2·67	−3·49
2	30·33	−32·93	8	3·12	2·54	7	1·35	1·81	10	2·95	−3·65			
3	0·92	−1·31	9	2·40	2·89				11	0·84	−0·80	$\bar{6}$.0.1	2·64	−2·50
4	3·43	−3·17				7.0.3	6·29	6·09				2	7·27	−6·75
5	14·28	−15·05	3.0.1	10·70	10·92	5	4·11	−4·41	$\bar{3}$.0.1	14·87	14·23	3	0·82	−0·68
7	10·56	11·26	2	8·00	8·51	6	1·10	−1·26	2	7·97	6·97	5	3·11	−3·59
8	2·12	1·42	3	5·28	−5·97				3	15·32	−15·83	6	1·95	0·93
11	1·13	−0·96	4	3·51	−4·59	8.0.1	2·04	1·48	4	8·61	−8·64	7	4·25	4·74
			5	2·69	−2·07				5	5·29	5·40	9	0·96	−0·71
1.0.0	17·66	15·80	6	3·56	−3·17	9.0.1	1·67	1·61	7	2·22	−2·58			
2	6·49	6·83	7	0·87	−1·34	2	1·99	2·46	8	7·27	6·48	$\bar{7}$.0.1	1·50	−2·00
3	8·99	−7·90	8	3·57	4·21				9	1·46	1·51	2	7·52	−7·61
4	7·71	6·82				10.0.1	1·75	1·78	10	2·77	−2·90	3	2·12	−1·89
5	6·63	6·32	4.0.1	13·69	13·65				11	0·79	−0·78	4	2·61	3·08
6	10·29	10·19	2	2·98	2·87	$\bar{1}$.0.1	9·34	−9·72				5	0·86	−1·16
7	6·71	5·66	3	11·54	−11·78	2	9·76	−10·21	$\bar{4}$.0.1	2·67	1·79	6	1·44	1·03
10	0·92	−0·87	5	3·23	2·46	3	12·18	−10·45	2	7·42	−7·39	7	3·31	3·19
			6	3·12	−3·14	4	0·78	0·78	3	8·29	−7·66			
1.0.1	10·78	11·00	7	1·48	−1·52	5	2·64	−2·02	4	8·20	−7·93	$\bar{8}$.0.2	2·24	−1·53
2	2·32	3·00	8	3·49	4·12	6	1·79	1·03	6	3·55	3·94	3	2·79	−2·78
3	7·21	7·07				7	5·39	5·44	7	6·32	5·63	7	2·05	1·48
4	7·24	−8·39	5.0.1	8·60	7·38	8	2·29	2·55	8	4·33	3·55	8	1·72	1·78
5	7·59	−7·38	3	3·41	−3·22	10	1·08	−1·09	9	2·00	−1·04			
7	4·00	4·42	5	2·45	−3·23				10	2·09	−2·09	$\bar{9}$.0.1	0·73	0·98
11	1·59	−1·66	6	2·58	−3·14	$\bar{2}$.0.1	13·08	16·83	11	1·57	−1·80	2	1·27	−1·36
			7	1·77	2·34	2	6·33	−4·43				3	3·05	−3·19
2.0.1	4·19	3·61	8	1·91	2·35	3	16·60	−16·13	$\bar{5}$.0.1	8·25	−8·07	5	2·37	2·65
3	2·42	−1·75				4	2·38	3·70	2	5·03	−4·65	6	1·35	0·63
4	12·84	−12·65	6.0.1	3·76	3·47	6	2·35	−3·58	4	4·36	−4·70			
5	3·21	−2·86	4	2·30	−2·13	7	1·84	1·74	6	7·19	6·98	$\bar{1}\bar{0}$.0.1	1·10	−1·05
6	3·09	3·86	5	4·06	−4·14	8	6·31	7·19	7	3·79	2·30	3	1·36	−1·03
												4	0·84	−0·92

0*kl*	F_o	A_c	B_c	$\|F_c\|$	0*kl*	F_o	A_c	B_c	$\|F_c\|$	0*kl*	F_o	A_c	B_c	$\|F_c\|$
0.2.0	12·75	13·47	−3·43	13·90	7	5·75	4·23	−3·19	5·30	7	1·82	0·71	−1·55	1·70
4	6·11	0·65	−5·61	5·65	8	2·61	−1·16	−1·33	1·76	8	1·96	−1·87	−1·06	2·15
6	4·07	3·82	0·79	3·90	9	1·14	−1·09	0·03	1·09	9	1·58	−1·26	−0·65	1·42
0.1.1	12·71	15·37	4·32	15·97	0.3.1	9·40	5·49	−7·31	9·13	0.5.1	4·55	−2·26	−3·14	3·87
2	28·37	−6·29	26·41	27·15	2	7·90	6·34	0·86	6·89	2	2·95	3·00	0·44	3·04
3	10·02	−7·88	7·28	10.73	3	4·17	3·48	−1·49	3·79	3	2·22	2·36	−0·28	2·38
4	7·92	5·17	−7·97	9·51	4	3·59	0·03	−4·15	4·15	4	2·18	−1·18	−1·50	1·90
5	7·51	−0·28	−7·47	7·48	5	5·45	−4·85	−0·20	4·86	5	1·74	−1·52	0·40	1·57
6	4·47	−3·47	0·67	3·53	6	6·97	−3·48	6·31	7·20	6	2·72	0·32	2·87	2·88
7	3·05	0·12	−3·27	3·27	7	1·23	−0·60	0·08	0·60					
8	1·51	1·21	−1·06	1·60	8	1·66	0·77	−2·26	2·39	0.6.1	1·96	−1·50	1·11	1·86
9	4·62	0·78	4·11	4·18	9	1·84	1·30	1·39	1·90	2	2·70	−3·07	−0·37	3·09
10	1·37	0·75	1·26	1·47	10	1·48	0·95	0·03	0·95	3	2·42	2·28	−0·81	2·42
										4	2·02	2·11	−0·49	2·17
0.2.1	4·88	−2·83	−2·41	3·72	0.4.1	4·94	−3·42	−3·28	4·74	5	1·37	−1·37	−0·43	1·43
2	5·69	−5·75	−0·67	5·79	2	1·87	−2·07	−0·72	2·20					
3	5·11	−0·26	4·25	4·26	3	4·31	2·43	3·86	4·56	0.7.1	1·24	−0·54	−1·21	1·32
4	5·03	1·64	3·53	3·90	4	6·75	4·13	4·58	6·17	2	1·19	−1·34	0·45	1·42
5	2·06	−1·94	1·24	2·31	5	1·85	0·63	1·12	1·29	3	1·19	−1·24	0·19	1·26
6	1·13	−0·10	0·91	0·91	6	1·06	−0·98	−0·69	1·20					

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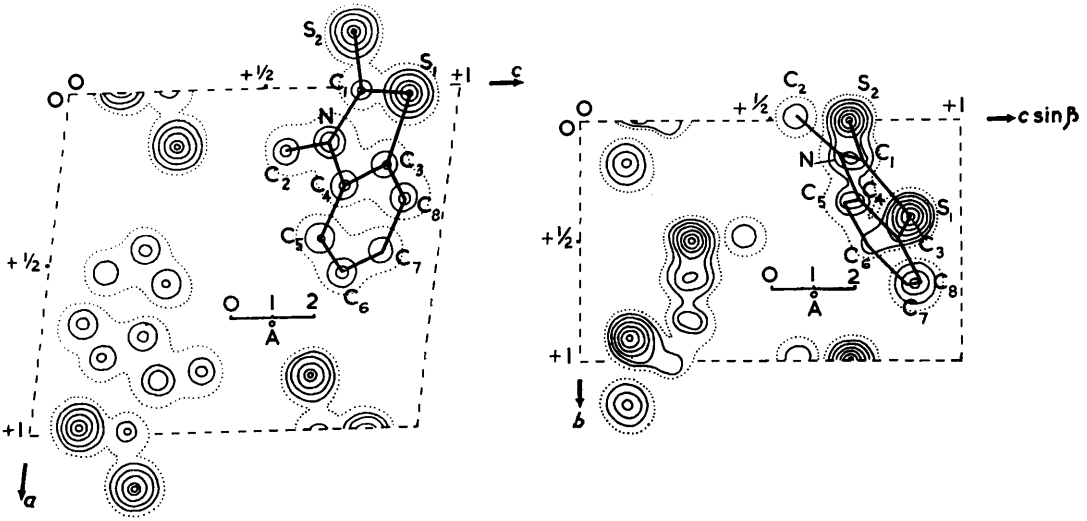
[3] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

[4] Tomiie and Stam, *Acta Cryst.*, 1958, **11**, 126.

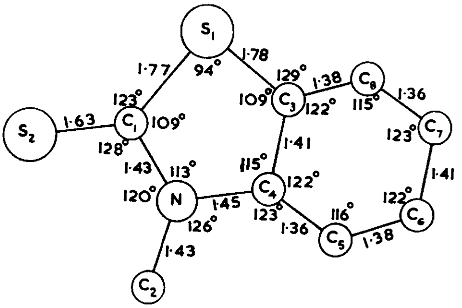
error. The bond lengths and angles in general agree well with the expected values.[5] There are, however, some considerable differences between the present lengths and those found for the parent benzothiazoline-2-thione.[6] These differences occur round the nitrogen atom and lead to what appear to be more reasonable lengths and angles in the five-membered ring. The present results are not in accord with the curve relating C–S and C–N bond lengths in molecules of this type.[7] It is doubtful, however, whether the proposed relationship could have a very wide validity, particularly as it ignores the accurate refinement of thiourea by Kunchur and Truter.[8] There will clearly be some connection between the lengths of the C–N and C–S bonds, but several factors will probably play a part. The most important influence is whether the carbon atom $C_{(1)}$ is attached to one or to two nitrogen atoms, but even this can be affected if the nitrogen atoms are involved in the formation of a ring. There appear to be at present too few structure determinations to enable the effect of the different factors to be sorted out.



(*a*) (*b*)

FIG. 1. (*a*) Projection of the contents of the unit cell down [*b*]. (*b*) Projection of the contents of the unit cell down [*a*]. (The contours are drawn at equal arbitrary intervals with some of the higher contours in the sulphur atoms omitted.

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



One strange similarity between the results of the present work and those for benzothiazoline-2-thione[6] is the distortion of the benzene ring. The difference between

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[5] " Tables of Interatomic Distances," *Chem. Soc. Special Publ.*, No. 11.

[6] Tashpulatov, Zvonkova, and Zhdanov, *Kristallographiya*, 1957, **2**, 33.

[7] Zvonkova, Astakhova, and Glushkova, *Kristallographiya*, 1960, **5**, 547.

[8] Kunchur and Truter, *J.*, 1958, 2551.

dimensions of the benzene ring shown in Fig. 2 and a regular hexagon are probably within the limits of experimental error, but the results of the two analyses agree so well in this respect that it is tempting to believe that the distortion is real.

The intermolecular distances are normal, and there are no close approaches.

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