

The Molecular and Crystal Structure of 2-Mercaptobenzothiazole

By JOHN P. CHESICK

Department of Chemistry, Haverford College, Haverford, Pa. 19041, U.S.A.

AND JERRY DONOHUE

Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pa. 19104, U.S.A.

(Received 10 August 1970)

The crystal structure of 2-mercaptobenzothiazole, $C_7H_5NS_2$ (Captax), has been redetermined. Crystals are monoclinic, space group $P2_1/c$, 4 molecules per unit cell, lattice constants $a=8.025$, $b=5.999$, $c=15.951$ Å, and $\beta=108.88^\circ$. Three-dimensional data out to $\sin \theta/\lambda=0.71$ were collected on an automated diffractometer using Mo $K\alpha$ radiation. Heavy atoms were located by three-dimensional Patterson synthesis. Fourier and least-squares refinement were used to obtain optimum values for positional and anisotropic thermal parameters of the 10 non-hydrogen atoms; hydrogen atoms were located in a difference synthesis. The final R value is 8.5%; the weighted R is 3.6%. Molecular packing in the crystal is quite different from that previously reported. No intermolecular nitrogen-sulfur distance is shorter than 3.35 Å, eliminating any consideration of unusual hydrogen bonding in this crystal structure. Non-hydrogen atoms are all within 0.027 Å of the plane defined by the benzene ring.

Introduction

Tashpulatov, Zvonkova & Zhdanov (1957) reported a crystal structure of Captax (2-mercaptobenzothiazole), $C_7H_5NS_2$, based on 672 reflections from a photographic study using Cu radiation. The crystals were monoclinic, space group $P2_1/c$, and the final R was 20%, based on refinements using fractional projections and linear sections of electron density. An intermolecular sulfur-nitrogen distance of 2.48 Å was reported, which implied a most unusual hydrogen bonding system with 'stronger intermolecular hydrogen bonds $N-H \cdots S$ than in thiopyridone, where the $N-H \cdots S$ distance equals 3.26 Å'. The unusual hydrogen-bond length prompted the structure redetermination reported here.

Experimental

K & K Laboratories 'Captax' was recrystallized from a mixture of toluene and chloroform. The crystal used in the final data collection was a plate of dimensions $0.06 \times 0.14 \times 0.22$ mm. The calculated linear-absorption coefficient was 6.62 cm^{-1} ; no absorption corrections were found necessary for this crystal.

Zero and first-level Weissenberg photographs taken with the crystal rotating about the b axis showed systematic absences in $h0l$ for l odd; precession photographs of the $hk0$ and $0kl$ zones showed systematic absences of $0k0$ reflections for k odd. The previous space group ($P2_1/c$) assignment was verified and the reported unit-cell parameter values were confirmed. These parameters agree with cell parameters reported earlier (Whitney, Corvin & McCrone, 1949; Jeffrey, 1949).

The crystal was transferred to a Picker Nuclear FACS I automated diffractometer equipped with a molybdenum tube and a graphite monochromator. Twelve reflections having 2θ values between 22 and 32° were used in a least-squares treatment to determine the lattice parameters, and to provide the orientation matrix for the data-collection mode. Various determinations of the lattice constants are presented in Table 1.

Data for this structure determination were collected using the moving-crystal moving-counter technique with a 2θ scan rate of $1^\circ/\text{minute}$ and 20-second background counts at both ends of the scan. The $00\bar{8}$, $4\bar{1}1$, and $0\bar{2}0$ reflections were measured as internal standards every 50 reflections. All reflections were measured out to $\sin \theta/\lambda=0.71$ for the $h\bar{k}l$ and $h\bar{k}\bar{l}$ octants of reciprocal space. Some additional equivalent reflections were checked during the alignment process;

Table 1. Lattice constants* of 2-mercaptobenzothiazole

a	b	c	β	Reference
7.995 Å	5.989 Å	15.899 Å	109°	Whitney <i>et al.</i> (1949)
8.04	6.01	15.91	109.8	Jeffrey (1949)
7.99	5.99	15.98	109.2	Tashpulatov <i>et al.</i> (1957)
8.025 (2)	5.999 (2)	15.951 (5)	108.88 (1)†	This work

* Previous work converted to $P2_1/c$ to bring all values on the same basis when necessary.

† Standard errors on the least significant figure are in parentheses.

no significant absorption effects were observed. The data collection also included the sets of equivalent reflection $h\bar{k}0$ and $h\bar{k}0$. The equivalent pairs from these sets were found to be identical to within the counting errors. In addition to the space-group extinctions, a total of 2111 unique reflections out to $\sin \theta/\lambda = 0.71$ was obtained. Of these, 1536 were considered as signi-

ficant (observed) when I_{obs} was greater than $2.33\sigma(I)$. Only these observed reflections are included in Table 2, which gives the observed and final calculated structure factors. Standard errors in the observed intensity, as obtained from counting statistics, and the Lorentz and polarization factors including the effects of the monochromator, were calculated by the usual methods.

Table 2. Observed and calculated structure factors

h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c
0 0 -2	10.0	9.9	0 1 -4	9.6	9.2	2 2 -2	54.0	53.1	2 2 -2	54.0	53.1	2 2 -2	54.0	53.1	2 2 -2	54.0	53.1
0 0 -4	14.8	14.7	0 1 -6	7.5	7.1	2 2 -4	31.4	31.4	2 2 -4	31.4	31.4	2 2 -4	31.4	31.4	2 2 -4	31.4	31.4
0 0 -6	19.6	19.5	0 1 -8	4.7	4.0	2 2 -6	18.0	17.9	2 2 -6	18.0	17.9	2 2 -6	18.0	17.9	2 2 -6	18.0	17.9
0 0 -8	24.4	24.3	0 1 -10	2.3	1.7	2 2 -8	10.0	9.9	2 2 -8	10.0	9.9	2 2 -8	10.0	9.9	2 2 -8	10.0	9.9
0 0 -10	29.2	29.1	0 1 -12	1.2	0.8	2 2 -10	5.5	5.4	2 2 -10	5.5	5.4	2 2 -10	5.5	5.4	2 2 -10	5.5	5.4
0 0 -12	34.0	33.9	0 1 -14	0.6	0.4	2 2 -12	3.0	2.9	2 2 -12	3.0	2.9	2 2 -12	3.0	2.9	2 2 -12	3.0	2.9
0 0 -14	38.8	38.7	0 1 -16	0.3	0.2	2 2 -14	1.8	1.7	2 2 -14	1.8	1.7	2 2 -14	1.8	1.7	2 2 -14	1.8	1.7
0 0 -16	43.6	43.5	0 1 -18	0.2	0.1	2 2 -16	1.0	0.9	2 2 -16	1.0	0.9	2 2 -16	1.0	0.9	2 2 -16	1.0	0.9
0 0 -18	48.4	48.3	0 1 -20	0.1	0.0	2 2 -18	0.6	0.5	2 2 -18	0.6	0.5	2 2 -18	0.6	0.5	2 2 -18	0.6	0.5
0 0 -20	53.2	53.1	0 1 -22	0.1	0.0	2 2 -20	0.4	0.3	2 2 -20	0.4	0.3	2 2 -20	0.4	0.3	2 2 -20	0.4	0.3
0 0 -22	58.0	57.9	0 1 -24	0.0	0.0	2 2 -22	0.3	0.2	2 2 -22	0.3	0.2	2 2 -22	0.3	0.2	2 2 -22	0.3	0.2
0 0 -24	62.8	62.7	0 1 -26	0.0	0.0	2 2 -24	0.2	0.1	2 2 -24	0.2	0.1	2 2 -24	0.2	0.1	2 2 -24	0.2	0.1
0 0 -26	67.6	67.5	0 1 -28	0.0	0.0	2 2 -26	0.1	0.0	2 2 -26	0.1	0.0	2 2 -26	0.1	0.0	2 2 -26	0.1	0.0
0 0 -28	72.4	72.3	0 1 -30	0.0	0.0	2 2 -28	0.1	0.0	2 2 -28	0.1	0.0	2 2 -28	0.1	0.0	2 2 -28	0.1	0.0
0 0 -30	77.2	77.1	0 1 -32	0.0	0.0	2 2 -30	0.0	0.0	2 2 -30	0.0	0.0	2 2 -30	0.0	0.0	2 2 -30	0.0	0.0
0 0 -32	82.0	81.9	0 1 -34	0.0	0.0	2 2 -32	0.0	0.0	2 2 -32	0.0	0.0	2 2 -32	0.0	0.0	2 2 -32	0.0	0.0
0 0 -34	86.8	86.7	0 1 -36	0.0	0.0	2 2 -34	0.0	0.0	2 2 -34	0.0	0.0	2 2 -34	0.0	0.0	2 2 -34	0.0	0.0
0 0 -36	91.6	91.5	0 1 -38	0.0	0.0	2 2 -36	0.0	0.0	2 2 -36	0.0	0.0	2 2 -36	0.0	0.0	2 2 -36	0.0	0.0
0 0 -38	96.4	96.3	0 1 -40	0.0	0.0	2 2 -38	0.0	0.0	2 2 -38	0.0	0.0	2 2 -38	0.0	0.0	2 2 -38	0.0	0.0
0 0 -40	101.2	101.1	0 1 -42	0.0	0.0	2 2 -40	0.0	0.0	2 2 -40	0.0	0.0	2 2 -40	0.0	0.0	2 2 -40	0.0	0.0
0 0 -42	106.0	105.9	0 1 -44	0.0	0.0	2 2 -42	0.0	0.0	2 2 -42	0.0	0.0	2 2 -42	0.0	0.0	2 2 -42	0.0	0.0
0 0 -44	110.8	110.7	0 1 -46	0.0	0.0	2 2 -44	0.0	0.0	2 2 -44	0.0	0.0	2 2 -44	0.0	0.0	2 2 -44	0.0	0.0
0 0 -46	115.6	115.5	0 1 -48	0.0	0.0	2 2 -46	0.0	0.0	2 2 -46	0.0	0.0	2 2 -46	0.0	0.0	2 2 -46	0.0	0.0
0 0 -48	120.4	120.3	0 1 -50	0.0	0.0	2 2 -48	0.0	0.0	2 2 -48	0.0	0.0	2 2 -48	0.0	0.0	2 2 -48	0.0	0.0
0 0 -50	125.2	125.1	0 1 -52	0.0	0.0	2 2 -50	0.0	0.0	2 2 -50	0.0	0.0	2 2 -50	0.0	0.0	2 2 -50	0.0	0.0
0 0 -52	130.0	129.9	0 1 -54	0.0	0.0	2 2 -52	0.0	0.0	2 2 -52	0.0	0.0	2 2 -52	0.0	0.0	2 2 -52	0.0	0.0
0 0 -54	134.8	134.7	0 1 -56	0.0	0.0	2 2 -54	0.0	0.0	2 2 -54	0.0	0.0	2 2 -54	0.0	0.0	2 2 -54	0.0	0.0
0 0 -56	139.6	139.5	0 1 -58	0.0	0.0	2 2 -56	0.0	0.0	2 2 -56	0.0	0.0	2 2 -56	0.0	0.0	2 2 -56	0.0	0.0
0 0 -58	144.4	144.3	0 1 -60	0.0	0.0	2 2 -58	0.0	0.0	2 2 -58	0.0	0.0	2 2 -58	0.0	0.0	2 2 -58	0.0	0.0
0 0 -60	149.2	149.1	0 1 -62	0.0	0.0	2 2 -60	0.0	0.0	2 2 -60	0.0	0.0	2 2 -60	0.0	0.0	2 2 -60	0.0	0.0
0 0 -62	154.0	153.9	0 1 -64	0.0	0.0	2 2 -62	0.0	0.0	2 2 -62	0.0	0.0	2 2 -62	0.0	0.0	2 2 -62	0.0	0.0
0 0 -64	158.8	158.7	0 1 -66	0.0	0.0	2 2 -64	0.0	0.0	2 2 -64	0.0	0.0	2 2 -64	0.0	0.0	2 2 -64	0.0	0.0
0 0 -66	163.6	163.5	0 1 -68	0.0	0.0	2 2 -66	0.0	0.0	2 2 -66	0.0	0.0	2 2 -66	0.0	0.0	2 2 -66	0.0	0.0
0 0 -68	168.4	168.3	0 1 -70	0.0	0.0	2 2 -68	0.0	0.0	2 2 -68	0.0	0.0	2 2 -68	0.0	0.0	2 2 -68	0.0	0.0
0 0 -70	173.2	173.1	0 1 -72	0.0	0.0	2 2 -70	0.0	0.0	2 2 -70	0.0	0.0	2 2 -70	0.0	0.0	2 2 -70	0.0	0.0
0 0 -72	178.0	177.9	0 1 -74	0.0	0.0	2 2 -72	0.0	0.0	2 2 -72	0.0	0.0	2 2 -72	0.0	0.0	2 2 -72	0.0	0.0
0 0 -74	182.8	182.7	0 1 -76	0.0	0.0	2 2 -74	0.0	0.0	2 2 -74	0.0	0.0	2 2 -74	0.0	0.0	2 2 -74	0.0	0.0
0 0 -76	187.6	187.5	0 1 -78	0.0	0.0	2 2 -76	0.0	0.0	2 2 -76	0.0	0.0	2 2 -76	0.0	0.0	2 2 -76	0.0	0.0
0 0 -78	192.4	192.3	0 1 -80	0.0	0.0	2 2 -78	0.0	0.0	2 2 -78	0.0	0.0	2 2 -78	0.0	0.0	2 2 -78	0.0	0.0
0 0 -80	197.2	197.1	0 1 -82	0.0	0.0	2 2 -80	0.0	0.0	2 2 -80	0.0	0.0	2 2 -80	0.0	0.0	2 2 -80	0.0	0.0
0 0 -82	202.0	201.9	0 1 -84	0.0	0.0	2 2 -82	0.0	0.0	2 2 -82	0.0	0.0	2 2 -82	0.0	0.0	2 2 -82	0.0	0.0
0 0 -84	206.8	206.7	0 1 -86	0.0	0.0	2 2 -84	0.0	0.0	2 2 -84	0.0	0.0	2 2 -84	0.0	0.0	2 2 -84	0.0	0.0
0 0 -86	211.6	211.5	0 1 -88	0.0	0.0	2 2 -86	0.0	0.0	2 2 -86	0.0	0.0	2 2 -86	0.0	0.0	2 2 -86	0.0	0.0
0 0 -88	216.4	216.3	0 1 -90	0.0	0.0	2 2 -88	0.0	0.0	2 2 -88	0.0	0.0	2 2 -88	0.0	0.0	2 2 -88	0.0	0.0
0 0 -90	221.2	221.1	0 1 -92	0.0	0.0	2 2 -90	0.0	0.0	2 2 -90	0.0	0.0	2 2 -90	0.0	0.0	2 2 -90	0.0	0.0
0 0 -92	226.0	225.9	0 1 -94	0.0	0.0	2 2 -92	0.0	0.0	2 2 -92	0.0	0.0	2 2 -92	0.0	0.0	2 2 -92	0.0	0.0
0 0 -94	230.8	230.7	0 1 -96	0.0	0.0	2 2 -94	0.0	0.0	2 2 -94	0.0	0.0	2 2 -94	0.0	0.0	2 2 -94	0.0	0.0
0 0 -96	235.6	235.5	0 1 -98	0.0	0.0	2 2 -96	0.0	0.0	2 2 -96	0.0	0.0	2 2 -96	0.0	0.0	2 2 -96	0.0	0.0
0 0 -98	240.4	240.3	0 1 -100	0.0	0.0	2 2 -98	0.0	0.0	2 2 -98	0.0	0.0	2 2 -98	0.0	0.0	2 2 -98	0.0	0.0
0 0 -100	245.2	245.1	0 1 -102	0.0	0.0	2 2 -100	0.0	0.0	2 2 -100	0.0	0.0	2 2 -100	0.0	0.0	2 2 -100	0.0	0.0
0 0 -102	250.0	249.9	0 1 -104	0.0	0.0	2 2 -102	0.0	0.0	2 2 -102	0.0	0.0	2 2 -102	0.0	0.0	2 2 -102	0.0	0.0
0 0 -104	254.8	254.7	0 1 -106	0.0	0.0	2 2 -104	0.0	0.0	2 2 -104	0.0	0.0	2 2 -104	0.0	0.0	2 2 -104	0.0	0.0
0 0 -106	259.6	259.5	0 1 -108	0.0	0.0	2 2 -106	0.0	0.0	2 2 -106	0.0	0.0	2 2 -106	0.0	0.0	2 2 -106	0.0	0.0
0 0 -108	264.4	264.3	0 1 -110	0.0	0.0	2 2 -108	0.0	0.0	2 2 -108	0.0	0.0	2 2 -108	0.0	0.0	2 2 -108	0.0	0.0
0 0 -110	269.2	269.1	0 1 -112	0.0	0.0	2 2 -110	0.0	0.0	2 2 -110	0.0	0.0	2 2 -110	0.0	0.0	2 2 -110	0.0	0.0
0 0 -112	274.0	273.9	0 1 -114	0.0	0.0	2 2 -112	0.0	0.0	2 2 -112	0.0	0.0	2 2 -112	0.0	0.0	2 2 -112	0.0	0.0
0 0 -114	278.8	278.7	0 1 -116	0.0	0.0	2 2 -114	0.0	0.0	2 2 -114	0.0	0.0	2 2 -114	0.0	0.0	2 2 -114	0.0	0.0
0 0 -116	283.6	283.5	0 1 -118	0.0	0.0	2 2 -116	0.0	0.0	2 2 -116	0.0	0.0	2 2 -116	0.0	0.0	2 2 -116	0.0	0.0
0 0 -118	288.4	288.3	0 1 -120	0.0	0.0	2 2 -118	0.0	0.0	2 2 -118	0.0	0.0	2 2 -118	0.0	0.0	2 2 -118	0.0	0.0
0 0 -120	293.2	293.1	0 1 -122	0.0	0.0	2 2 -120	0.0	0.0	2 2 -120	0.0	0.0	2 2 -120	0.0	0.0	2 2 -120	0.0	0.0
0 0 -122	298.0	297.9	0 1 -124	0.0	0.0	2 2 -122	0.0	0.0	2 2 -122	0.0	0.0	2 2 -122	0.0	0.0	2 2 -122	0.0	0.0
0 0 -124	302.8	302.7	0 1 -126	0.0	0.0	2 2 -124	0.0	0.0	2 2 -124	0.0	0.0	2 2 -124	0.0	0.0	2 2 -124	0.0	0.0
0 0 -126	307.6	307.5	0 1 -128	0.0	0.0	2 2 -126	0.0	0.0	2 2 -126	0.0	0.0	2 2 -126	0.0	0.0	2 2 -126	0.0	0.0
0 0 -128	312.4	312.3	0 1 -130	0.0	0.0	2 2 -128	0.0	0.0	2 2 -128	0.0	0.0	2 2 -128	0.0	0.0	2 2 -128	0.0	0.0
0 0 -130	317.2	317.1	0 1 -132	0.0	0.0	2 2 -130	0.0	0.0	2 2 -130	0.0	0.0	2 2 -130	0.0	0.0	2 2 -130	0.0	0.0
0 0 -132	322.0	321.9	0 1 -134	0.0	0.0	2 2 -132	0.0	0.0	2 2 -132	0.0	0.0	2 2 -132	0.0	0.0	2 2 -132	0.0	0.0
0 0 -134	326.8	326.7	0 1 -136	0.0	0.0	2 2 -134	0.0	0.0	2 2 -134	0.0	0.0	2 2 -134	0.0	0.0	2 2 -134	0.0	0.0
0 0 -136	331.6	331.5	0 1 -138	0.0	0.0	2 2 -136	0.0	0.0	2 2 -136	0.0	0.0	2 2 -136	0.0	0.0	2 2 -136	0.0	0.0
0 0 -138	336.4	336.3	0 1 -140														

Determination of the structure

A three-dimensional sharpened and origin-removed Patterson function was calculated for sections in the uw plane computed at fractional intervals of 0.05 in v . Sulfur coordinates of the previous work were not compatible with the three-dimensional Patterson function computed here. The section ($u\frac{1}{2}w$) contains the peaks from the equivalent positions which differ by $b/2$; the x and y coordinates of the two unique sulfur atoms were readily assigned from the section at $v=\frac{1}{2}$, and the locations of other sulfur-sulfur peaks provided the y coordinates and checked the x and z assignments. A three-dimensional electron density function was calculated with about 450 reflections phased with the sulfur contributions. This showed clear maxima at positions for the other 8 unique non-hydrogen atoms expected on the basis of the known chemical structure, with a few extraneous peaks of intensity comparable to the weakest of the probable atomic peaks. A second Fourier synthesis was calculated, using the two sulfur atoms and three additional atoms located from the most intense peaks in the first Fourier synthesis, to assign phases. This second synthesis, calculated with 715 reflections, showed clearly the locations of all 10 nonhydrogen atoms with no spurious peaks of comparable magnitude. Block-diagonal least-squares refinement was performed using observed reflections out to $\sin \theta/\lambda=0.64$ (1251 reflections). This refinement, starting with atomic coordinates taken from the second Fourier synthesis as input, yielded an R of 12% for isotropic refinement.

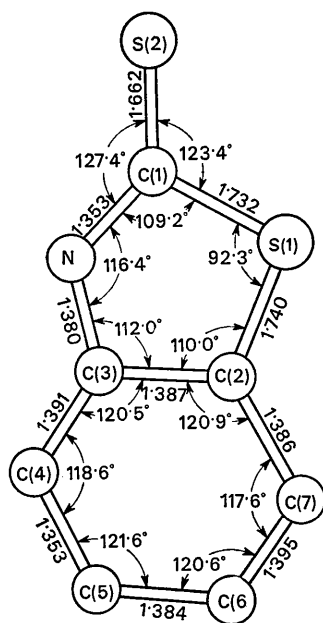


Fig. 1. Bond lengths and bond angles in the 2-mercaptobenzothiazole molecule. Standard errors on C-S bonds are 0.004 Å, on other bonds 0.006 Å; standard errors on bond angles are in the range 0.2–0.4°.

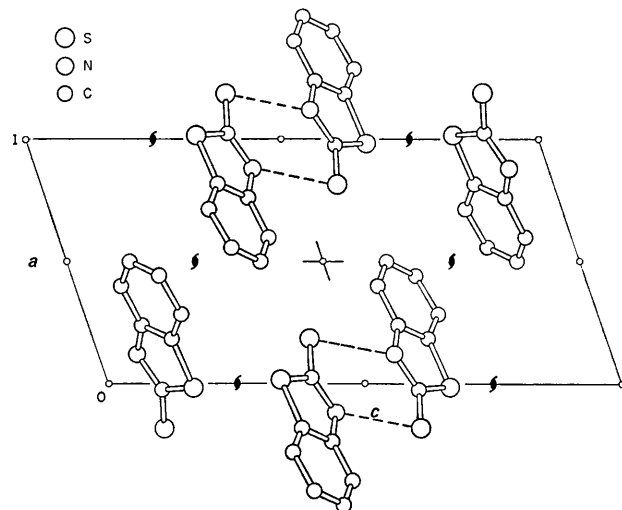


Fig. 2. View of the structure along the b axis. The dashed lines represent hydrogen bonds.

Anisotropic block-diagonal least-squares refinement using all observed reflections yielded an R of 10.4%. Three cycles of full-matrix least-squares refinement effected minor changes in the parameters and R value. Hydrogen atoms were located from a three-dimensional difference Fourier synthesis. A hydrogen atom was found to be covalently bonded to N rather than to S(2), giving the expected tautomer. Thus, the compound is more properly named benzothiazole-2-thione. These coordinates of the hydrogen atoms, with isotropic temperature factors arbitrarily set at 3.5 Å², were used in 3 more cycles of full-matrix least-squares refinement for final adjustment in coordinates and anisotropic thermal parameters of the 10 nonhydrogen atoms. These parameters are shown, with their estimated standard deviations, in Tables 3 and 4. The final R is 8.5% and the weighted R is 3.6%. A second difference Fourier synthesis was calculated in an attempt to improve the hydrogen-atom locations. All hydrogen peaks in this difference map were well above background noise, and no other peaks of comparable intensities were seen.

Table 3. Final coordinates and estimated standard deviations (in parentheses) (all values $\times 10^4$)

	x	y	z
S(1)	-162 (1)	5062 (2)	1621 (1)
S(2)	-1852 (1)	823 (2)	780 (1)
N	1233 (4)	2589 (5)	753 (2)
C(1)	-226 (5)	2675 (6)	1001 (2)
C(2)	1851 (4)	5876 (7)	1526 (2)
C(3)	2416 (4)	4319 (6)	1035 (2)
C(4)	4024 (5)	4579 (7)	891 (2)
C(5)	4995 (5)	6418 (8)	1216 (3)
C(6)	4437 (5)	8011 (7)	1694 (2)
C(7)	2856 (5)	7744 (7)	1870 (2)
H(N)	1200	1700	500
H(4)	4200	3600	600
H(5)	6000	6650	1250
H(6)	5000	9050	2000
H(7)	2400	8800	2000

Table 4. Final anisotropic temperature factors and estimated standard deviations (in parentheses) (all values $\times 10^4$)

The form of the temperature factor is $\exp [-(h^2b_{11}\dots + 2hkb_{12}\dots)]$.

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
S(1)	166 (2)	281 (4)	52 (1)	-24 (5)	99 (2)	-62 (3)
S(2)	184 (2)	274 (4)	55 (1)	-85 (5)	94 (2)	-28 (3)
N	166 (7)	204 (11)	40 (2)	-11 (14)	63 (5)	-33 (7)
C(1)	150 (7)	206 (13)	35 (2)	23 (17)	52 (6)	4 (8)
C(2)	127 (7)	263 (14)	35 (2)	22 (18)	41 (6)	-2 (9)
C(3)	134 (7)	221 (14)	33 (2)	36 (17)	38 (6)	13 (8)
C(4)	174 (8)	300 (17)	43 (2)	26 (20)	81 (7)	-26 (10)
C(5)	120 (8)	380 (19)	50 (2)	-24 (20)	38 (7)	31 (11)
C(6)	175 (9)	286 (16)	40 (2)	-62 (20)	12 (7)	-19 (10)
C(7)	177 (9)	248 (15)	47 (2)	29 (19)	61 (7)	-19 (10)

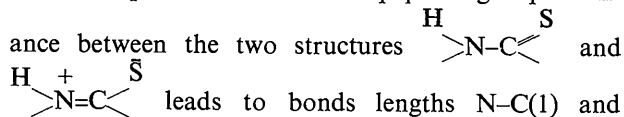
Results

Intramolecular angles and bond lengths are presented in Fig. 1. Deviations of the atoms from the plane determined by a least-squares fit to the 6 carbon atoms in the benzene ring are presented in Table 5. A similar calculation to determine the deviations from the plane defined by the 2 sulfur atoms, the nitrogen atom, and C(1) shows that this group of 4 atoms is coplanar to within 0.005 Å.

Table 5. Deviations of atoms from plane of benzene ring

S(1)	0.020 Å	C(3)	-0.012 Å
S(2)	0.027	C(4)	0.011
N	-0.020	C(5)	0.001
C(1)	0.001	C(6)	-0.011
C(2)	0.001	C(7)	0.010

Bond lengths in the mercaptothiazole moiety are close to expectation. In the 'thiopeptide' group resonance



C(1)-S(2) which are intermediate between pure single and double bonds. The contribution of the second structure is less than that occurring in the peptide group itself because of the smaller electronegativity of sulfur compared with oxygen, leading to a longer C-N bond in the thio compound [1.353 Å compared with 1.325 Å (Marsh & Donohue, 1967)].

Bond angles in the 5-membered ring are also normal. Angles at sulfur atoms in such compounds are generally observed to be slightly larger than 90°, e.g. 91.3° in thiophene (Bak, Christensen, Rastrup-Andersen & Tannenbaum, 1956), 92.02° in bithienyl (Almenningen, Bastiansen & Svendsås, 1958), and 91.2° in 1,4-thiophthen (Cox, Gillot & Jeffrey, 1949).

The benzene ring also exhibits expected bond distances, except for C(4)-C(5), which is apparently highly significantly shorter than the other five. No obvious explanation is apparent for this anomaly; perhaps it is due to the Hughes (1968) effect.

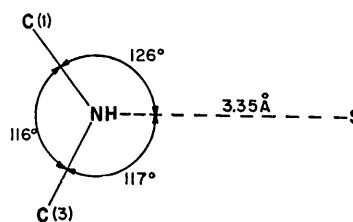


Fig. 3. Some details of the NH...S hydrogen-bond system.

The shortest intermolecular sulfur-nitrogen distance found is 3.347 Å. Thus, no unusually short hydrogen bond exists; this distance is characteristic of NH...S systems (Donohue, 1969). Projection of the structure along the b axis is presented in Fig. 2. The molecules form centrosymmetric hydrogen-bonded dimers, a feature tentatively suggested by Jeffrey (1949) for this crystal. Some details of the hydrogen bond are presented in Fig. 3.

This work was supported by the National Science Foundation, Haverford College Faculty Research Fund and Computer Center, and the Advanced Research Projects Agency, Office of the Secretary of Defense.

Reference

- ALMENNINGEN, A., BASTIANSEN, O. & SVENDSÅS, P. (1958). *Acta Chem. Scand.* **12**, 1671.
 BAK, B., CHRISTENSEN, D., RASTRUP-ANDERSEN, J. & TANNENBAUM, E. (1956). *J. Chem. Phys.* **25**, 892.
 COX, E. G., GILLOT, R. J. J. H. & JEFFREY, G. A. (1949). *Acta Cryst.* **2**, 356.
 DONOHUE, J. (1969). *J. Mol. Biol.* **45**, 231.
 HUGHES, E. W. (1968). In *Structural Chemistry and Molecular Biology*, p. 628. Edited by A. RICH & N. DAVIDSON, San Francisco: Freeman.
 JEFFREY, G. A. (1949). In KOCH, H. P. (1949). *J. Chem. Soc.* p. 401.
 MARSH, R. E. & DONOHUE, J. (1967). *Advanc. Protein Chem.* **22**, 235.
 TASHPULATOV, I., ZVONKOVA, Z. V. & ZHDANOV, G. S. (1957). *Kristallografiya*, **2**, 38.
 WHITNEY, J., CORVIN, I. & MCCRONE, W. C. (1949). *Anal. Chem.* **21**, 757.