

## Bonding in 1,2,3-Triazoles. III. The Crystal Structure of 1-Methyl-3-benzyl-4-(1,2,3-triazolio)sulfide

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The crystal structure of the title compound,  $C_{10}H_{11}N_3S$ , has been investigated by X-ray diffraction technique. The crystals are monoclinic, space group  $P2_1/n$ , with  $a=6.231(3)$  Å,  $b=8.008(2)$  Å,  $c=21.135(6)$  Å and  $\beta=94.95(4)^\circ$ . The structure was refined to  $R=0.063$ . Insertion of a  $CH_2$ -group between the triazole and the phenyl groups inverts the deformation of the endocyclic angle at the *ipso* position of the phenyl ring. A comparison of the geometry of the triazole group in several 1,3-substituted triazoliosulfides is carried out.

The present structure analysis is part of an investigation of substituted 1,2,3-triazole.<sup>1,2</sup>

### CRYSTAL DATA

$C_{10}H_{11}N_3S$ ,  $M=205.3$ .  $\mu(MoK\alpha)=2.58$  cm<sup>-1</sup>. Melting point 137–139 °C.<sup>3</sup> Monoclinic,  $a=6.231(3)$  Å,  $b=8.008(2)$  Å,  $c=21.135(6)$  Å,  $\beta=94.95(4)^\circ$ .  $Z=4$ .  $D_c=1.293$  g cm<sup>-3</sup>.  $D_o=1.291$  g cm<sup>-3</sup>. Space group:  $P2_1/n$  (No. 14).

### EXPERIMENTAL

The cell constants were determined from the optimum setting of 25 reflections on a four-circle diffractometer (CAD-4F). Determination of the possible space groups and the data collection were carried out as described in Ref. 2. However, Weissenberg photographs showed some splitting of the diffraction spots, indicating a crystal of poor quality.

Table 1. Atomic coordinates  $\times 10^4$ . Estimated standard deviations  $\times 10^4$  are given in parentheses. The values for hydrogen are multiplied by  $10^3$ .

Atom	x	y	z	Atom	x	y	z
S	1707(2)	1833(2)	4855(1)	H1	065(8)	579(6)	449(2)
N1	3527(9)	5962(5)	4116(2)	H2	231(16)	835(17)	403(7)
N2	5131(9)	5032(6)	3977(3)	H3	289(13)	786(11)	350(2)
N3	4662(7)	3539(4)	4227(2)	H4	445(9)	847(7)	416(3)
C4	2754(9)	3516(6)	4505(3)	H5	743(9)	246(6)	431(2)
C5	2027(11)	5156(6)	4424(3)	H6	571(9)	126(7)	446(3)
C6	3518(17)	7738(7)	3918(4)	H7	888(10)	059(7)	355(3)
C7	6135(11)	2139(8)	4156(3)	H8	858(12)	-080(9)	265(4)
C8	5903(9)	1359(6)	3510(3)	H9	524(11)	-089(8)	198(4)
C9	7662(12)	0520(8)	3299(4)	H10	258(12)	065(8)	223(3)
C10	7493(16)	-0273(10)	2721(5)	H11	286(9)	197(7)	330(3)
C11	5596(16)	-0246(9)	2350(4)				
C12	3848(13)	0588(8)	2536(3)				
C13	4022(10)	1389(7)	3118(3)				

A total of 4754 reflections was reduced to 1079 independent reflections with  $I \geq 2\sigma(I)$ . The dimensions of the crystal were  $0.2 \times 0.1 \times 0.1$  mm. The structure was solved by Patterson technique. The atomic scattering factors are those used in Ref. 2. The structure was refined by a full matrix least squares procedure,<sup>4</sup> and the final  $R$ -values are  $R=0.063$  and  $R_w=0.059$ . The weights employed were proportional to  $1.0/(\sigma^2(F) + 0.007 \times F^2)$ . During refinement the distances of the methyl hydrogen from the methyl carbon were kept fixed at 0.95 Å. The atomic coordinates are given in Table 1. Lists of thermal parameters and observed and calculated structure factors may be obtained from the authors on request.

## DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Bond lengths and bond angles with their estimated standard deviations are listed in Tables 2 and 3. The labelling of the atoms are shown in Fig. 1. The phenyl group is planar within experimental error. Analysis of the triazole ring (Table 4) shows a planar group, which includes the sulfur atom. The methyl- and methylene-carbon atoms are out of plane. The angle between the normals of the two planes is  $88.2^\circ$ . The angle between the normal of the triazole ring and the C7–C8–C11 line is  $26.7^\circ$ , not far from the  $23.6^\circ$  expected from the N3–C7–C8 angle ( $113.6^\circ$ ).

The deformations of the endocyclic angles in the phenyl group do not possess two-fold symmetry.

Table 2. Bond distances (Å) with estimated standard deviations.

Atoms	Distance	Atoms	Distance
S–C4	1.695(6)	C5–H1	1.02(5)
C4–C5	1.395(7)	C6–H2	0.95(12)
C5–N1	1.349(8)	C6–H3	0.95(5)
N1–N2	1.300(8)	C6–H4	0.95(6)
N2–N3	1.349(6)	C7–H5	0.88(5)
N3–C4	1.371(7)	C7–H6	1.00(6)
N1–C6	1.482(7)	C9–H7	0.89(6)
N3–C7	1.465(8)	C10–H8	0.82(8)
C7–C8	1.497(9)	C11–H9	0.95(7)
C8–C9	1.391(10)	C12–H10	0.98(7)
C9–C10	1.373(13)	C13–H11	0.97(6)
C10–C11	1.361(13)		
C11–C12	1.364(12)		
C12–C13	1.383(9)		
C13–C8	1.376(8)		

Table 3. Bond angles ( $^\circ$ ) with estimated standard deviations.

Atoms	Angle	Atoms	Angle
S–C4–C5	132.0(5)	N3–C7–C8	113.6(5)
S–C4–N3	125.3(4)	C7–C8–C9	118.5(6)
N3–C4–C5	102.7(5)	C7–C8–C13	123.5(5)
C4–C5–N1	106.2(5)	C9–C8–C13	118.0(6)
C5–N1–N2	114.4(4)	C8–C9–C10	120.4(7)
N1–N2–N3	102.8(5)	C9–C10–C11	120.1(9)
N2–N3–C4	113.9(4)	C10–C11–C12	121.1(8)
N2–N3–C7	118.6(5)	C11–C12–C13	118.7(7)
C4–N3–C7	127.4(4)	C8–C13–C12	121.6(6)
C5–N1–C6	127.6(6)		
N2–N1–C6	118.0(6)		

Table 4. Distances in Å of atoms from the least squares plane of triazole. Atoms marked with \* are those defining the plane. The standard deviation of the atoms from the plane is 0.0072 Å.

Atom	Distance
*N1	0.007
*N2	–0.009
*N3	0.008
*C4	–0.003
*C5	–0.003
S	0.001
C6	0.016
C7	–0.018
H1	–0.119

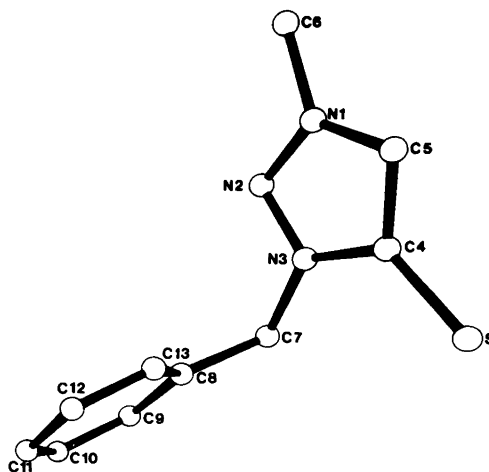


Fig. 1. The structure viewed along the  $a^*$ -axis.

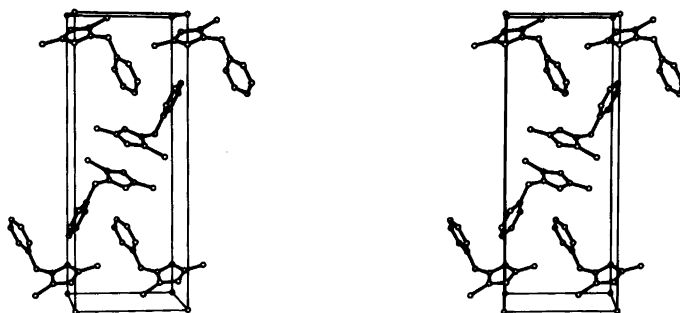


Fig. 2. Stereo view along the  $a^*$ -axis of the structure.

Also the C—C distances are shorter than expected, especially those involving the carbon atom in the *para* position. This may be explained by the strong anisotropy in the thermal parameters of this atom. Furthermore, the values of the thermal parameters increase with the distance from C8, the carbon atom at the *ipso* position. The deviation of the C9—C8—C13 angle from  $120^\circ$  is  $-2.0^\circ$ , and compare well to the value of  $-1.9^\circ$  expected for a  $\text{CH}_3$ -substitution. Thus insertion of the  $\text{CH}_2$ -group between the triazole ring and the phenyl ring cancels the effect of the electronegative triazole group. The intermolecular distances are of the order expected from the corresponding van der Waals distances.

The distance between the triazole groups  $(x,y,z)$  and  $(1-x,1-y,1-z)$ , related by a center of symmetry (Fig. 2) is  $\sim 3.6$  Å. The shortest distance between these two groups involving sulfur is the S—C6 distance of 3.79 Å.

The S—S  $(-x,-y,1-x)$  distance of 3.71 Å is unusually short compared to S—S distances in the compounds reported in Refs. 1, 2 and 6. In these compounds the shortest S—S distances lie between 4.58 (Ref. 1) and 5.80 Å (PMTS, Ref. 6).

#### COMPARISON OF 1,3-SUBSTITUTED TRIAZOLIO-SULFIDES

In order to compare the geometry of the triazole groups of the five 1,3-substituted triazolio-sulfides an ideal planar molecule was constructed. The five triazole groups were projected onto their least squares planes, and the  $x$  and  $y$  coordinates of the atoms were calculated in a coordinate system with origin at the centroid of the equally weighted atoms. Keeping one group fixed, the remaining four groups

were allowed to rotate and translate in the  $x,y$ -plane, in order to minimize the sum of the squared differences in atomic coordinates between each pair of groups. The weights of the groups in this sum were chosen in accordance with the average variance of the bond distances in the groups. The result showed a coincidence of the origins, the maximum translation being 0.0001 Å. The coordinates of the atoms in the average group were then found as weighted averages of the atomic coordinates in the five groups. The variance,  $\sigma^2$ , of the weighted mean was calculated from  $\sigma^2 =$

$$\frac{1}{n-1} \frac{\sum w_i \Delta_i^2}{\sum w_i}, \text{ where } \Delta_i \text{ are the residuals, and } w_i \text{ the}$$

weights. The resulting coordinates are listed in Table 5, and the bond distances and the bond angles are shown in Fig. 3. The  $R$ -value between the average structure and one of the projected structures is defined as  $R = (\sum (x_i - \langle x_i \rangle)^2 / \sum x_i^2)^{\frac{1}{2}}$ , where the summation is carried out over both coordinates of the five atoms, and  $\langle x_i \rangle$  is the corresponding coordinate in the average structure. The  $R$ -values

Table 5. Atomic coordinates (Å) with estimated standard deviations for the average triazole group in 1,3-substituted-4-(1,2,3-triazolio)sulfides.

Atom	$x$	$y$
N1	0.5531(17)	0.9538(24)
N2	1.1677(11)	-0.2073(22)
N3	0.1550(11)	-1.0874(14)
C4	-1.0913(18)	-0.5072(19)
C5	-0.7846(34)	0.8484(20)

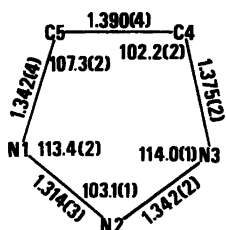


Fig. 3. Bond lengths and bond angles with estimated standard deviations for the average triazole group in 1,3-substituted-4-(1,2,3-triazolio)sulfides.

were 0.0055 for PMTS, 0.0028 for MPTS-P, 0.0083 for MPTS-C,<sup>2</sup> 0.0038 for the 1,3-dimethyl compound,<sup>1</sup> and 0.0058 for the present compound. This indicates that the five triazole groups are identical.

From the average structure it may be concluded that methyl and phenyl substituents can be interchanged with negligible effect on the geometry of the triazole ring. Furthermore, the almost identical values of the angles at N1 and N3 show that these are almost unaffected by the asymmetry in the carbon substituents.

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