

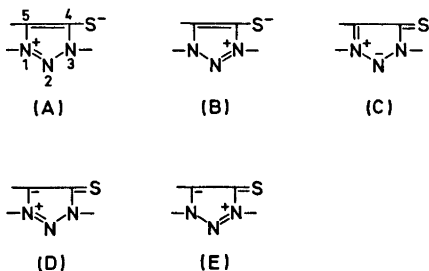
The Crystal Structure of 1,3-Dimethyl-4-(1,2,3-triazolio)sulfide

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The crystal structure of 1,3-dimethyl-4-(1,2,3-triazolio)sulfide, $C_4H_7N_3S$, has been investigated by X-ray crystallographic methods. The crystals are monoclinic, space group $P2_1/a$, with $a = 7.75 \pm 0.02$ Å, $b = 10.56 \pm 0.03$ Å, $c = 8.30 \pm 0.02$ Å and $\beta = 114.3 \pm 0.2^\circ$. Three-dimensional data were collected using an automatic equi-inclination diffractometer and $MoK\alpha$ -radiation. The structure was refined by the method of least squares to an R -value of 0.034.

The molecular structure of the mesoionic compound 1,3-dimethyl-4-(1,2,3-triazolio)sulfide can be regarded as a resonance hybrid of the forms (A)–(E).



^{13}C -NMR spectra¹ indicate a localization of charge on N1 corresponding to a dominant contribution from either (A), (C), or (D). In order to confirm this result an X-ray investigation was carried out. The preparation and the discussion of the chemical aspects of the compound have been published by Begtrup,² who also provided suitable single crystals.

EXPERIMENTAL

Lattice type and space group were established from Weissenberg and precession photographs using Cu- and Mo -radiation. Three-dimensional data between a cylinder of radius

$Y = 5.4^\circ$ and a hemisphere with $\sin \theta/\lambda < 0.6$ Å⁻¹ were measured on an automatic equi-inclination diffractometer (Stoe & Cie, Darmstadt, DBR) using $MoK\alpha$ -radiation from a graphite monochromator and ω -scan technique. Higher order contamination was reduced by means of pulse height discrimination.

The diffractometer output was processed using a program, which takes into account the polarization of the incident beam. This leaves 960 sets of symmetry related reflections with $I > 2\sigma(I)$. No correction for absorption was made.

The remaining calculations were performed using THE X-RAY SYSTEM.³ All calculations were carried out on the IBM 370/165 at NEUCC, Technical University of Denmark.

CRYSTAL DATA

Crystal system: monoclinic (b unique).

Unit cell: $a = 7.75 \pm 0.02$ Å
 $b = 10.56 \pm 0.03$ Å,
 $c = 8.30 \pm 0.02$ Å,
 $\beta = 114.3 \pm 0.2^\circ$.

$d_{\text{calc}} = 1.39$ g/cm³.

4 mol of $C_4H_7N_3S$ per unit cell.

Systematic absences: $h0l$ for h odd,
 $0k0$ for k odd

Space group: $P2_1/a$.

STRUCTURE DETERMINATION

The sulfur atoms were found from the Harker section in the three-dimensional Patterson function, and the remaining atoms, except hydrogen, were then found in a Fourier map phased from these positions. The structure was refined by a full-matrix least squares procedure, using first isotropic and later anisotropic tem-

perature factor parameters. Convergence was reached at $R=0.055$.

A difference Fourier synthesis was calculated after refinement was ended, and it clearly showed the hydrogen atoms in the expected positions. A few cycles of least squares refinement were computed with the positional parameters and the isotropic temperature factors of the hydrogen atoms included. Agreement factors $R=0.034$ and $R_w=0.046$ were obtained. The standard deviations $\sigma(F)$, derived from counting statistics, were modified for use as weights in the least squares refinement. The weighting function used, $w=(0.3+2.0\sigma^2(F)+0.025F+0.02/F-0.6\sin\theta/\lambda)^{-1}$, was found to give an average of $w|F_o-F_c|^2$ which is nearly independent of the magnitude of F and $\sin\theta/\lambda$.

The scattering factors for C, N, and S were taken from *International Tables*.⁴ For the hydrogen atoms, the scattering factors calculated by Stewart, Davidson and Simpson⁵ were used. No correction for anomalous dispersion was made.

The final positional and thermal parameters and their estimated standard deviations are listed in Tables 1 and 2. A list of observed and calculated structure factors may be obtained from the author on request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Bond lengths and bond angles and their estimated standard deviations are listed in Tables 3 and 4. The standard deviations are

Table 1. Final atomic coordinates and their standard deviations $\times 10^4$. For hydrogen isotropic U -values ($\times 10^3 \text{ \AA}^2$) are given.

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	U	$\sigma(U)$
S	0.3490	(1)	0.4108	(1)	0.1585	(1)		
N1	0.3735	(2)	0.2519	(2)	0.5906	(2)		
N2	0.3746	(3)	0.1493	(2)	0.5007	(2)		
N3	0.3673	(2)	0.1951	(2)	0.3472	(2)		
C4	0.3607	(3)	0.3247	(2)	0.3368	(3)		
C5	0.3655	(3)	0.3592	(2)	0.5010	(3)		
C6	0.3848	(4)	0.2380	(3)	0.7718	(3)		
C7	0.3597	(4)	0.1067	(2)	0.2085	(3)		
H1	0.3641	(39)	0.4400	(26)	0.5531	(36)	4.8	(0.7)
H2	0.3299	(65)	0.3129	(44)	0.8013	(57)	10.6	(1.4)
H3	0.5155	(63)	0.2183	(37)	0.8541	(54)	9.1	(1.2)
H4	0.3042	(55)	0.1638	(38)	0.7751	(47)	8.4	(1.1)
H5	0.4456	(62)	0.1388	(40)	0.1580	(54)	9.6	(1.2)
H6	0.2251	(73)	0.0968	(41)	0.1252	(63)	11.2	(1.5)
H7	0.4027	(52)	0.0228	(39)	0.2633	(49)	8.6	(1.1)

Table 2. Anisotropic temperature factor parameters in units of 10^{-4} \AA^2 with their estimated standard deviations in parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	649 (4)	386 (3)	318 (3)	-34 (3)	214 (3)	44 (2)
N1	383 (8)	390 (9)	252 (8)	20 (7)	132 (7)	-6 (7)
N2	486 (10)	344 (10)	322 (9)	45 (8)	176 (8)	26 (7)
N3	383 (9)	310 (8)	265 (8)	16 (7)	131 (7)	-14 (7)
C4	348 (10)	320 (10)	303 (10)	-3 (8)	110 (8)	-5 (8)
C5	489 (12)	324 (11)	345 (10)	7 (9)	189 (9)	-25 (8)
C6	557 (13)	666 (16)	285 (11)	-7 (13)	212 (10)	15 (10)
C7	651 (15)	391 (13)	391 (12)	33 (11)	238 (11)	-78 (10)

Table 3. Interatomic distances in Å. Standard deviations $\times 10^3$ in parentheses.

Atoms	Distance	σ
S-C4	1.707	(4)
C4-C5	1.396	(5)
N1-C5	1.343	(4)
N3-C4	1.370	(5)
N1-C6	1.478	(5)
N3-C7	1.464	(4)
N1-N2	1.317	(4)
N2-N3	1.342	(4)
C5-H1	0.959	(29)
C6-H2	0.976	(51)
C6-H3	0.983	(40)
C6-H4	1.009	(43)
C7-H5	0.982	(54)
C7-H6	0.992	(46)
C7-H7	0.988	(39)

Table 4. Bond angles in degrees with their estimated standard deviations.

Atoms	Angle	σ
N3-C4-C5	102.3	0.2
S-C4-C5	132.7	0.2
S-C4-N3	125.0	0.2
C4-N3-C7	126.8	0.2
C4-N3-N2	113.9	0.2
C7-N3-N2	119.3	0.3
N3-N2-N1	103.5	0.2
N2-N1-C6	118.9	0.2
N2-N1-C5	112.9	0.3
C6-N1-C5	128.1	0.2
N1-C5-C4	107.3	0.2
N1-C5-H1	120.5	1.9
C4-C5-H1	132.2	1.9
N1-C6-H2	109.0	2.8
N1-C6-H3	109.9	3.1
N1-C6-H4	109.1	2.2
H2-C6-H3	115.4	3.3
H2-C6-H4	106.5	4.0
H3-C6-H4	106.8	3.2
N3-C7-H5	107.5	2.5
N3-C7-H6	107.8	3.3
N3-C7-H7	108.2	2.4
H5-C7-H6	116.2	4.0
H5-C7-H7	110.3	3.7
H6-C7-H7	106.6	3.3

derived from the standard deviations of the cell dimensions and the standard deviations of the coordinates of the atoms in question. An analysis of the planarity of the molecule shows (Table 5) that this is almost planar, the

Table 5. Analysis of the planarity in the 1,3-dimethyl-4-(1,2,3-triazolio)-sulfide molecule. The equation for the plane is $m_1x + m_2y + m_3z = d$, where x, y, z are fractional coordinates, and d is the origin to plane distance in Å. Atoms marked with * are those defining the plane.

$m_1 = 7.1637$	$m_1 = 7.1575$
$m_2 = 0.3340$	$m_2 = 0.3197$
$m_3 = -0.2808$	$m_3 = -0.2626$
$d = 2.5957$	$d = 2.5986$

Atom	Distance (Å)	Atom	Distance (Å)
*N1	-0.0019	*N1	0.0000
*N2	-0.0028	*N2	-0.0011
*N3	0.0035	*N3	0.0018
*C4	0.0021	*C4	-0.0016
*C5	0.0022	*C5	0.0010
*S	-0.0030	S	-0.0111
C6	0.0239	C6	0.0292
C7	-0.0416	C7	-0.0445
H1	0.0049	H1	0.0035

two methyl carbon atoms being significantly out of plane. However, a subsequent calculation shows that the sulfur atom lies 0.011 Å away from the best plane through the triazole ring only, indicating that the sulfur atom is slightly out of plane.

The temperature factors of the atoms attached to the ring are strongly anisotropic,

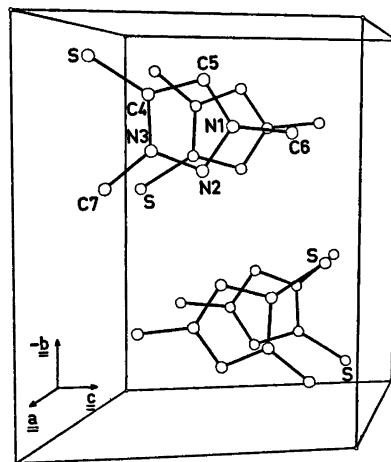


Fig. 1. The content of a unit cell. The numbering of the atoms is shown on one molecule. On the remaining molecules only the sulfur atoms are marked.

with their highest value along the α^* -axis, which is almost perpendicular to the plane of the triazole ring. The angle between the normal to the plane and the α^* -axis is 2.7° . As expected, the temperature factor of the hydrogen atom bonded to C5 is considerably smaller than those of the hydrogen atoms in the methyl groups.

The only interatomic distance less than the van der Waals distance is 3.48 \AA , and is found between the methyl carbon atom, C7, and the sulfur atom in molecules related by the operation of the screw axis. The deviations from the plane of the triazole ring of the two atoms are in this direction. The shortest distance between the sulfur atom and the methyl hydrogen atoms is 2.98 \AA . The remaining contact distances are approximately equal to the sum of the van der Waals radii of the atoms in question. Several of these are found between the almost parallel molecules related by the operation of the glide plane. The distances range from 3.65 to 3.98 \AA , and the average distance between the planes of the molecules is approximately equal to the van der Waals distance between aromatic molecules. The C4-S bond distance of 1.707 \AA is a representative of C-S distances found in similar compounds containing the group N-CS-X, where X is either C or N.⁶⁻¹³ The C-S bond is predominantly a single bond, which is seen from the bond character of 1.28, calculated from the formula given by Pauling¹⁴ with the C-S distance equal to 1.81 \AA , corrected by 0.03 \AA for the negatively charged sulfur atom.¹⁵ The C=S distance is equal to 1.59 \AA . The C4-N3 distance of 1.370 \AA is somewhat longer than would be expected from theoretical calculations on 1,2,3-triazole itself.¹⁶ This may be due to the decrease of π -electrons in the ring in presence of the sulfur atom.

In order to distinguish between the canonical forms (A) to (E), the bond characters for the N1-C5, N1-N2, and N2-N3 bonds were calculated, using idealized single bond and double bond distances of 1.46 and 1.26 \AA , respectively, for N-N bonds,¹⁷ and 1.475 and 1.265 \AA , respectively, for the C-N bonds. From a bond character of 1.36 for the N1-C5 bond and the bond character for the C4-S bond it is concluded that the forms (D) and (E) only give a minor contribution to the total structure. For the N1-N2 bond the bond

character is 1.46, and for the N2-N3 bond it is 1.32, leading to the conclusion that the resonance hybrid is made up predominantly of form (A), and almost equal amounts of the forms (B) and (C).

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