

Bonding in 1,2,3-Triazoles. IV. The Crystal Structures of 2,3-Dimethyl- and 2-Phenyl-3-methyl-1,2,3-triazol-1-in-4-thione

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The crystal structures of the title compounds $C_4H_7N_3S$ and $C_9H_9N_3S$, have been investigated by X-ray diffraction technique. The crystals of the first compound are orthorhombic, space group $Pna2_1$, with $a=10.43(1)$ Å, $b=8.76(1)$ Å and $c=6.76(1)$ Å. The second compound is monoclinic, space group $P2_1/a$, with $a=7.72(2)$ Å, $b=11.73(1)$ Å, $c=10.61(1)$ Å and $\beta=105.2(3)^\circ$. The structures were refined by least-squares technique to R -values of 0.04 and 0.07. The angle between the phenyl ring and the triazole ring is 53.4° . The two triazole groups are compared on the basis of a normal probability plot. Atomic charges are obtained from semi-empirical MO-calculations.

The present structure analyses are parts of an investigation of substituted 1,2,3-triazoles.¹⁻³ The two compounds 2,3-dimethyl- and 2-phenyl-3-methyl-1,2,3-triazol-1-in-4-thione are henceforth referred to as MMTS and PMTS, respectively.

EXPERIMENTAL

Determination of the possible space groups and the data collections were carried out as described in Ref. 2. The dimensions of the crystals were $0.1 \times 0.1 \times 0.2$ mm and $0.3 \times 0.4 \times 0.5$ mm for MMTS

Table 1. Crystal data.

	MMTS	PMTS
Formula	$C_4H_7N_3S$	$C_9H_9N_3S$
M	129.2	191.3
$\mu(\text{MoK}\alpha)$ (cm^{-1})	4.0	2.8
Crystal system	orthorhombic	monoclinic
Melting point ($^\circ\text{C}$) ⁴	163–165	157
a (Å)	10.43(1)	7.72(2)
b (Å)	8.76(1)	11.73(1)
c (Å)	6.76(1)	10.61(1)
β ($^\circ$)		105.2(3)
Space group	$Pna2_1$ (No. 33)	$P2_1/a$ (No. 14)
D_c (g/cm^3)	1.39	1.37
Z	4	4
Total number of reflections	1528	4204
Number of independent observations ($I > 2\sigma(I)$)	633	1567
$R = \sum \ F_o - F_c \ / \sum F_o $	0.041	0.068
$R_w = \left(\frac{\sum w(F_o - F_c)^2}{\sum w F_o ^2} \right)^{\frac{1}{2}}$	0.049	0.101

Table 2. Final atomic coordinates $\times 10^4$. The estimated standard deviations $\times 10^4$ are given in parentheses. The values of the hydrogen atoms are multiplied by 10^3 .

Atom	MMTS			PMTS		
	x	y	z	x	y	z
S	0986(1)	13022(1)	1500(0)	6441(1)	5656(1)	3296(1)
N1	-0610(2)	8976(3)	1552(16)	5490(4)	7446(2)	6149(3)
N2	0620(2)	8646(2)	1492(18)	6645(3)	6670(2)	6770(2)
N3	1346(2)	9937(2)	1475(15)	7123(3)	5957(2)	5909(2)
C4	0541(2)	11166(3)	1527(18)	6229(4)	6269(2)	4684(2)
C5	-0687(2)	10490(3)	1513(19)	5205(4)	7208(3)	4894(3)
C6	2734(3)	9910(4)	1547(21)	8423(5)	5044(3)	6287(4)
C7	1117(4)	7106(4)	1509(40)	7475(4)	6728(2)	8136(3)
C8				7481(5)	5779(3)	8913(3)
C9				8259(6)	5873(4)	10245(4)
C10				8981(6)	6903(4)	10773(4)
C11				8943(5)	7844(3)	9979(4)
C12				8199(5)	7760(3)	8644(3)
H1	-152(4)	1100(4)	152(20)	433(7)	770(4)	426(5)
H2	302(9)	895(8)	232(13)	948(8)	528(5)	696(6)
H3	303(4)	1095(5)	107(7)	880(6)	487(4)	544(5)
H4	304(5)	945(7)	033(9)	821(8)	442(5)	670(6)
H5	058(6)	648(6)	233(9)	689(7)	514(4)	858(5)
H6	196(4)	707(4)	208(7)	830(9)	522(5)	1081(7)
H7	135(10)	694(10)	016(20)	950(7)	703(5)	1171(5)
H8				941(7)	860(5)	1032(5)
H9				811(3)	841(3)	806(4)

and PMTS, respectively. Both structures were solved by direct methods.⁵ The atomic scattering factors and the refinement technique are those used in Ref. 2. Crystal data and *R*-values are listed in Table 1. The final positional parameters with estimated standard deviations are listed in Table 2. The labelling of the atoms are shown in Fig. 1. Lists of thermal parameters as well as lists of observed and calculated structure factors may be obtained from the authors on request.

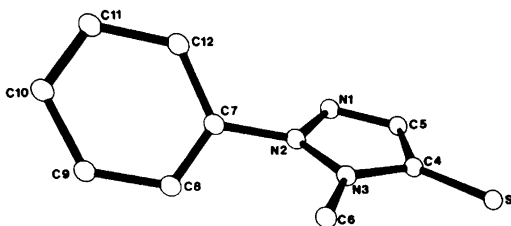


Fig. 1. PMTS viewed along the a^* -axis.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Bond lengths and bond angles with estimated standard deviations are listed in Tables 3 and 4. The triazole groups in the two molecules are planar (Table 5). In PMTS the sulfur atom and the methyl carbon atom are significantly out of plane. In MMTS the two methyl carbons are out of plane, while the sulfur atom lies in the plane. The deviations from the least squares plane in MMTS are rather large. This may be attributed to the orientation of the molecule in the polar space group $Pna2_1$. The normal to the molecular plane almost coincides with the *c*-axis, which is the polar axis. The origin in this direction was fixed by constraining the *z*-coordinate of sulfur to 0.15 rather than keeping the molecular center of gravity fixed. As a result, the standard deviations in the *z*-coordinates for the non-sulfur atoms are large. In contrast to similar compounds^{2,3} there is a pronounced anisotropy in the thermal parameters which have their largest value along c^* .

A normal probability plot^{6,7} of the weighted difference in distances between the two triazole

Table 3. Bond distances (Å) with estimated standard deviations.

Atoms	MMTS Distance	Atoms	PMTS Distance
S-C4	1.691(3)	S-C4	1.685(4)
C4-C5	1.411(4)	C4-C5	1.408(5)
C5-N1	1.329(4)	C5-N1	1.321(5)
N1-N2	1.316(4)	N1-N2	1.322(5)
N2-N3	1.361(3)	N2-N3	1.360(4)
N3-C4	1.365(3)	N3-C4	1.352(7)
N3-C6	1.449(4)	N3-C6	1.450(5)
N2-C7	1.445(4)	N2-C7	1.424(7)
		C7-C8	1.385(4)
		C8-C9	1.386(8)
		C9-C10	1.386(6)
		C10-C11	1.384(6)
		C11-C12	1.384(7)
		C12-C7	1.382(5)
C5-H1	0.97(3)	C5-H1	1.00(5)
C6-H2	1.03(8)	C6-H2	0.98(5)
C6-H3	1.01(4)	C6-H3	1.04(6)
C6-H4	0.96(6)	C6-H4	0.88(6)
C7-H5	0.96(6)	C8-H5	0.90(5)
C7-H6	0.96(5)	C9-H6	0.96(7)
C7-H7	0.96(13)	C10-H7	0.98(5)
		C11-H8	0.99(6)
		C12-H9	0.97(4)

Table 4. Bond angles (°) with estimated standard deviations.

Atoms	MMTS Angle	Atoms	PMTS Angle
S-C4-C5	130.7(2)	S-C4-C5	131.3(2)
S-C4-N3	126.1(2)	S-C4-N3	125.6(2)
N4-C4-C5	103.2(2)	N3-C4-C5	103.0(3)
C4-C5-N1	111.3(2)	C4-C5-N1	111.9(3)
C5-N1-N2	106.1(2)	C5-N1-N2	105.6(3)
N1-N2-N3	111.1(2)	N1-N2-N3	110.9(2)
N2-N3-C4	108.2(2)	N2-N3-C4	108.6(2)
N2-N3-C6	122.8(2)	N2-N3-C6	124.0(2)
C4-N3-C6	128.8(2)	C4-N3-C6	127.4(3)
N1-N2-C7	123.7(3)	N1-N2-C7	122.6(2)
N3-N2-C7	125.2(3)	N3-N2-C7	125.7(2)
		N2-C7-C12	117.8(3)
		N2-C7-C8	119.8(2)
		C12-C7-C8	122.3(3)
		C7-C8-C9	118.4(3)
		C8-C9-C10	120.1(3)
		C9-C10-C11	120.5(3)
		C10-C11-C12	120.2(3)
		C11-C12-C7	118.5(3)

Table 5. Distances in Å of atoms from the least squares planes of triazole. Atoms marked with * are those defining the planes. The estimated standard deviations are 0.0133 Å for MMTS and 0.0060 Å for PMTS.

Atom	MMTS	PMTS
*N1	0.014	0.008
*N2	-0.005	-0.006
*N3	-0.006	0.002
*C4	0.013	0.003
*C5	-0.017	-0.006
S	-0.001	0.059
C6	0.067	0.043
C7	0.019	0.182
H1	-0.029	-0.022

groups leads to a slope of 0.827 and a median correlation coefficient of 0.983. Although some of the distances are redundant, all have been included in the plots. The value of the median correlation coefficient is well above the 5% critical value (0.937) for rejecting the hypothesis of normality.⁸ However, the intercept is -0.631, indicating that the distances in MMTS are systematically larger than the corresponding distances in PMTS. This feature may be explained by the larger deviations from the least squares plane in MMTS, which lead to systematically larger molecular distances, provided the x and y coordinates are unaffected by this deviation. A calculation of a scale factor between the two sets of distances gave 0.9969(8), and this fully accounts for the displacement of the intercept from zero. Thus the two triazole groups are possibly identical, the systematic differences being due to the larger deviations from the least-squares plane for MMTS. A half normal probability plot of the original differences resulted in a slope of 0.963, an intercept of 0.080 and a correlation coefficient of 0.961. In contradiction to the full normal probability plot this indicates absence of systematic differences between the two triazole groups. This illustrates the danger of using only the half normal probability plot, when comparing identical groups.

The charge distribution (atomic units) in the triazole thione group, as calculated by the CNDO method,⁹ show a negative sulfur atom (-0.44 and -0.43 for MMTS and PMTS, respectively) and a positive C4 (0.24, 0.25) indicating that the C-S bonds (1.692 Å, 1.685 Å) predominantly are single bonds. The charge on the remaining atoms ranges

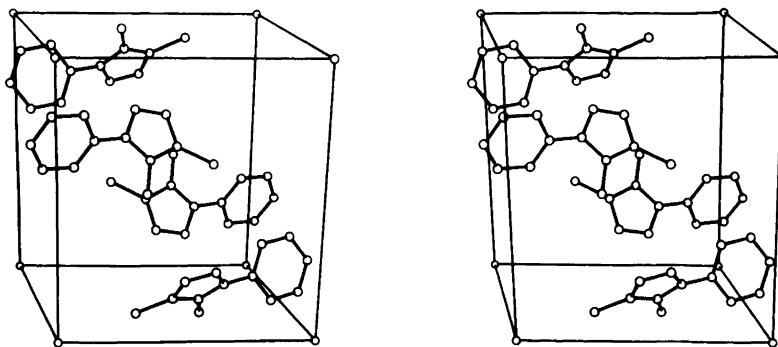


Fig. 2. Stereo view along the a^* -axis of the structure of PMTS.

from -0.09 to 0.04 . The replacement of the methyl group with a phenyl group changes the charge of N2 from 0.04 to -0.03 in agreement with what was found in Ref. 2. The CNDO calculations also indicate that the molecules possess large dipole moments.

A general discussion of substitution effects on the geometry of the triazole ring is given in a subsequent paper.¹⁰

The phenyl group in PMTS is planar, and the angle between the normal to this group and the normal to the triazole ring is 53.4° . In isotropic phase the ^{13}C NMR data also indicate a large angle.⁴ The rotation of the two planes is mainly around the N2–C7–C10 line, the angles between this line and the normal to the triazole group and the phenyl group being 82.6 and 89.4° , respectively. The deformations of the endocyclic angles in the phenyl group are symmetric around the C7–C10 line with an angle of 122.3° at C7. This indicates a highly electronegative substituent (*cf.* Norrestam and Schepper^{11,12}). The intramolecular distances from C8 and C12 to N1 and N3 range from 2.93

to 3.52 Å. In agreement with what was found in Ref. 2, the charges on the phenyl carbon atoms are alternating with a value of 0.13 at the *ipso* position (C7).

The intermolecular contact distances are in both compounds of the order expected from the corresponding van der Waals radii. However the relatively high melting point of PMTS, as compared to the 1-methyl-3-phenyl substituted compounds,² indicates an electrostatic interaction between the molecules. The shortest distances in PMTS (Fig. 2) from the sulfur atom are found to N2($1-x, 1-y, 1-z$) (3.61 Å) and N3($1-x, 1-y, 1-z$) (3.62 Å). Other intermolecular distances are found between the molecules (x, y, z) and ($x - \frac{1}{2}, 3/2 - y, z$). Thus the distances from N1 to N2, N3 and C6 are 3.16 Å, 3.37 and 3.37 Å, respectively.

In MMTS the almost parallel molecules are stacked along the c -axis (Fig. 3). The molecules are related by the operation of the two-fold screw axis, giving an average distance between the molecular planes of 3.38 Å. The melting point (163 – 165°C) of this compound is higher than the melting point

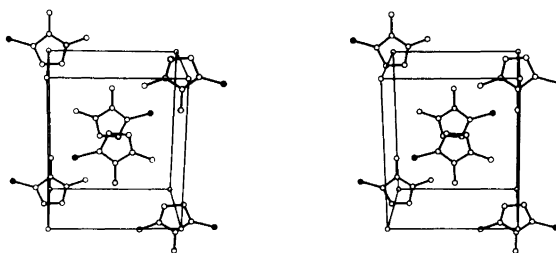


Fig. 3. Stereo view along the c^* -axis of the structure of MMTS. The sulfur atoms are shown as black spheres.

(125–127 °C) of the 1,3-dimethyl isomer.³ In the latter compound, the average distance between almost parallel molecules is 3.53 Å.¹ In MMTS the shortest distances between atoms in the two triazole rings are found between C4 and N1 (3.36 and 3.40 Å). Distances less than 3.70 Å between molecules related by other symmetry elements are N1–C7($x - \frac{1}{2}, 3/2 - y, z$) (3.54 Å) and S–C7($x, y + 1, z$) (3.58 Å).

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