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P. Ambalavanan^a, K. Palani^a, M. N. Ponnuswamy^a,
R. A. Thirumuruhan^a, H. S. Yathirajan^b, B.
Prabhuswamy^b, C. R. Raju^b, P. Nagaraja^b & K. N.
Mohana^b

^a Department of Crystallography and Biophysics,
University of Madras, Guindy Campus, Chennai, 600
025, India

^b Department of Studies in Chemistry, University of
Mysore, Manasagangotri, Mysore, 570 006, India

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CRYSTAL STRUCTURES OF TWO TRIAZOLE DERIVATIVES

*P. Ambalavanan, K. Palani, M. N. Ponnuswamy,
and R. A. Thirumuruhan*

*Department of Crystallography and Biophysics,
University of Madras, Guindy Campus,
Chennai–600 025, India*

*H. S. Yathirajan, B. Prabhswamy, C. R. Raju, P. Nagaraja,
and K. N. Mohana*

*Department of Studies in Chemistry, University of Mysore,
Manasagangotri, Mysore–570 006, India*

3-Phenyl-4-amino-5-mercapto-1,2,4-triazole(PAMT), $C_8H_8N_4S$, F.W. = 192.24, triclinic, $P \bar{1}$, $a = 6.1698(3) \text{ \AA}$, $b = 7.1765(1) \text{ \AA}$, $c = 9.9894(3) \text{ \AA}$, $\alpha = 81.87(1)^\circ$, $\beta = 84.97(2)^\circ$, $\gamma = 78.81(2)^\circ$, $V = 428.72(3) \text{ \AA}^3$, $Z = 2$, $D_{\text{cal}} = 1.489 \text{ Mg m}^{-3}$, $\mu = 0.330 \text{ mm}^{-1}$, $F_{000} = 200$, $\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$, final $R1$ and $wR2$ are 0.0871 and 0.2170, respectively. 3-(4-Methylphenyl)-4-amino-5-mercapto-1,2,4-triazole (MAMT), $C_9H_{10}N_4S$, F.W. = 206.27, triclinic, $P \bar{1}$, $a = 5.996(1) \text{ \AA}$, $b = 7.582(2) \text{ \AA}$, $c = 11.143(1) \text{ \AA}$, $\alpha = 73.16(1)^\circ$, $\beta = 89.65(2)^\circ$, $\gamma = 87.88(1)^\circ$, $V = 484.52(3) \text{ \AA}^3$, $Z = 2$, $D_{\text{cal}} = 1.414 \text{ Mg m}^{-3}$, $\mu = 2.674 \text{ mm}^{-1}$, $F_{000} = 216$, $\lambda(\text{CuK}\alpha) = 1.5418 \text{ \AA}$, final $R1$ and $wR2$ are 0.0656 and 0.1820, respectively. In both of the molecules the triazole rings are planar and oriented at angles of $5.7(1)^\circ$ and $1.4(2)^\circ$ with the respective phenyl rings in MAMT and PAMT. The molecules in the unit cell are stabilized by $N-H \dots N$ type hydrogen bonds in addition to van der Waals forces.

Keywords: crystal structure; conformation; hydrogen bonding; PAMT; MAMT

INTRODUCTION

Compounds of 1,2,4-triazole derivatives are found to be associated with diverse pharmacological activity. Recently, some new triazole derivatives have been synthesized as possible anticonvulsants, antidepressants,

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tranquilizers, and plant-growth regulators [1–3]. Some of the iron (II) complexes containing substituted 1,2,4-triazole ligands are spin-cross-over materials, which could be used as molecular-based memory devices, displays, and optical switches [4, 5]. The 1,2,4-triazole nucleus has recently been incorporated into a wide variety of therapeutically interesting drugs [6], including H1/H2 histamine receptor blocker, cholinesterase active agents, CNS stimulants, antianxiety agents, and sedatives.

Substituted 1,2,4-triazoles have been actively studied as bridging ligands coordinating through their vicinal N atoms. The complexes containing 1,2,4-triazole ligands possess specific magnetic properties [7–9]. On the other hand, some of the 1,2,4-triazole derivatives have anti-inflammatory activities [10] and some are antifungal agents [11].

Bhargava and coworkers [12] synthesized and studied the anti-inflammatory activity of some 3-(O-substituted phenyl)-4-substituted phenyl-5-alkyl/alkenyl mercapto-1H-1,2,4-triazoles. The compound 2,4-dihydro-1,2,4-triazole-3-thiones was prepared and used as bactericides, fungicides, and pesticides [13]. Insecticidal and ascaricidal properties of 4-methyl-3-(trifluoromethyl)- Δ^2 -1,2,4-triazoline-5-thiones were also reported [14]. A series of 3-(2,4-dichlorophenyl)-4-aryl-5-mercapto-1,2,4-triazoles compounds possess good fungitoxic properties [15]. Several 3-aryloxy methyl-1,2,4-triazoles have been synthesized and screened for their antifungal activities [16].

A survey on the triazole derivatives reveals that these compounds possess biological activities, and the synthetic utility of substituted groups depend on their stereochemistry. To understand the conformation and packing features of the compounds, the crystal structure determination of these triazole derivatives was carried out. The chemical diagrams of 3-Phenyl-4-amino-5-mercapto-1,2,4-triazole (PAMT) and 3-(4-Methylphenyl)-4-amino-5-mercapto-1,2,4-triazole (MAMT) are shown in Figure 1.

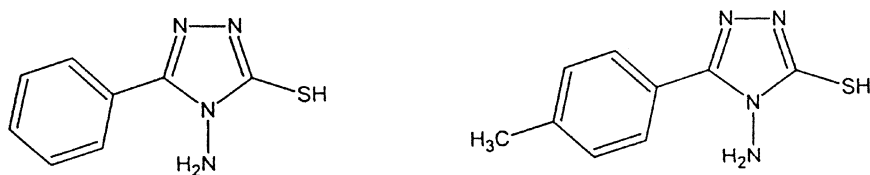


FIGURE 1 Chemical diagrams of PAMT and MAMT.

X-RAY DATA COLLECTION, STRUCTURE SOLUTION, AND REFINEMENT

Data Collection

Intensity data were collected from a Siemens SMART CCD [17] area detector diffractometer with graphite monochromated MoK α radiation for PAMT. The entire data collection was covered over a hemisphere of reciprocal space by a combination of three sets of exposures, each having a different ϕ angle (0, 88, and 180°) for the crystal, and each exposure time of 10 s covered 0.3° in ω . The crystal-to-detector distance was 4 cm and the detector swing angle was -35°. Data was complete by over 99%. Crystal decay, monitored by repeating thirty initial frames at the end of the data collection and analyzing the duplicate reflections, was found to be negligible.

For MAMT, the data were collected on a CAD4 diffractometer [18] using graphite monochromated CuK α radiation. Accurate unit cell parameters were derived from least-squares analysis using 25 reflections. In order to check the intensity deterioration due to the radiation or crystal degradation, three standard reflections were monitored for every 1 h and for every hundred reflections.

Both the structures were solved using direct methods in SHELXS 97 [19] and refined in SHELXL97 [20]. The nonhydrogen atoms were treated with anisotropic thermal parameters. Hydrogen atoms were fixed at chemically acceptable positions but not refined. The geometrical parameters were calculated using PARST [21], and the molecular graphics were drawn through ZORTEP [22].

RESULTS AND DISCUSSION

The crystal and refinement data are given in Table I. Figures 2 and 3 show the ZORTEP plot of the molecules of PAMT and MAMT with thermal ellipsoids at 30% probability level.

The bond lengths and bond angles of PAMT and MAMT are comparable with the values reported in the literature [23]. The bonds N2-C3 (1.308(5); 1.312(3) Å) and N1-C5 (1.338(5); 1.341(3) Å) show double bond character. The other N-C bonds in both the structures assume intermediate character, indicating the delocalization of the electron cloud. The bond lengths (C5-S13=) 1.668(4) Å in PAMT and 1.675(3) Å in MAMT are shorter than the reported values [24] due to the zwitterionic form (Figure 4).

The least-squares plane calculation shows that the triazole rings are planar and the atoms N12 & S13 also lie in the plane of the ring in both the

TABLE I Crystal Data for PAMT and MAMT

Parameters	PAMT	MAMT
Empirical formula	C ₈ H ₈ N ₄ S	C ₉ H ₁₀ N ₄ S
Formula weight	192.24	206.27
Temperature (K)	293(2)	293(2)
Wavelength	0.71073 Å	1.5418 Å
Crystal system	Triclinic	Triclinic
Space group	P $\bar{1}$	P $\bar{1}$
Unit cell dimensions	a = 6.1698(3) Å b = 7.1765(1) Å c = 9.9894(3) Å α = 81.87(1)° β = 84.97(2)° γ = 78.81(2)°	a = 5.996(1) Å b = 7.582(2) Å c = 11.143(1) Å α = 73.16(1)° β = 89.65(1)° γ = 87.88(1)°
Volume	428.72(3) Å ³	484.52(3) Å ³
Z	2	2
Calculated density	1.489 Mg/m ³	1.414 Mg/m ³
Absorption coefficient	0.330 mm ⁻¹	2.674 mm ⁻¹
F(000)	200	216
Crystal size	0.16 × 0.10 × 0.04 mm	0.25 × 0.30 × 0.08 mm
θ -range for data collection	2.06 to 25.99°	4.15 to 72.41°
Index ranges	-7 ≤ h ≤ 7 -5 ≤ k ≤ 8 -11 ≤ l ≤ 12	-7 ≤ h ≤ 7 0 ≤ k ≤ 9 -13 ≤ l ≤ 13
Reflections collected	2672	2077
Independent reflections	1655 [R(int) = 0.0479]	1921 [R(int) = 0.0749]
Observed reflections [I > 2σ(I)]	1087	1684
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Goodness of fit on F ²	1.002	1.048
Final R-indices [I > 2σ(I)]	R ₁ = 0.0871, wR ₂ = 0.2170	R ₁ = 0.0656, wR ₂ = 0.1820

molecules. The phenyl ring is planar (maximum deviation is 0.009(5) Å for atom C9) and lies slightly out of plane of the triazole ring in MAMT, whereas the ring in PAMT lies in the plane of the triazole ring. The corresponding orientation angles subtended by phenyl and triazole groups in MAMT and PAMT are 5.7(1)° and 1.4(2)°, respectively. The substituted methyl group C14 also lies in the plane of the phenyl ring (deviation: 0.007(4) Å). The exocyclic bond angles, (C10-C9-C14 =) 122.1(3)° and (C8-C9-C14 =) 121.3(3)°, show slight variation from the normal value of 120°. The bond angles involving atoms N4-C3-C6 (127.1(3)° for PAMT and 128.3(2)° for MAMT) and N2-C3-C6 (123.0(3)° for PAMT and 122.2(2)° for MAMT) are expanded and contracted due to the steric hindrance between N12 and phenyl group.

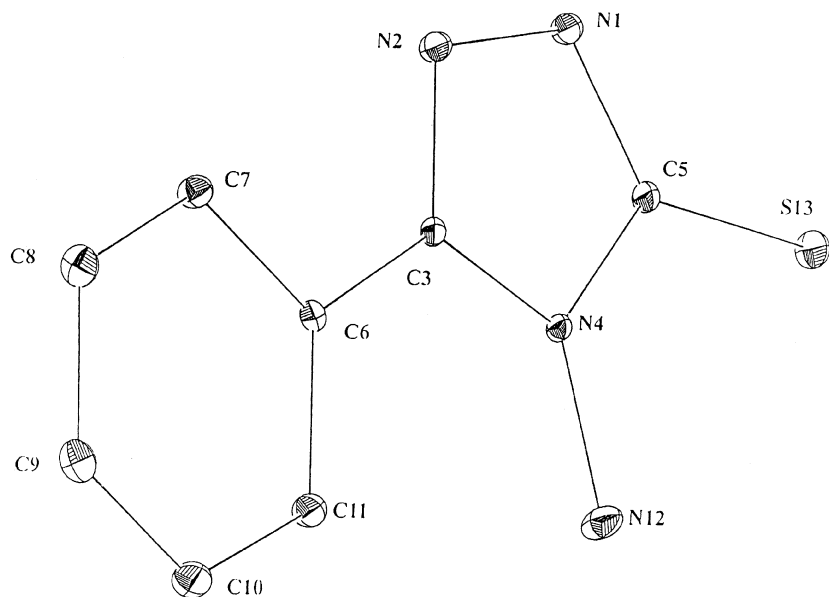


FIGURE 2 ORTEP diagram of PAMT.

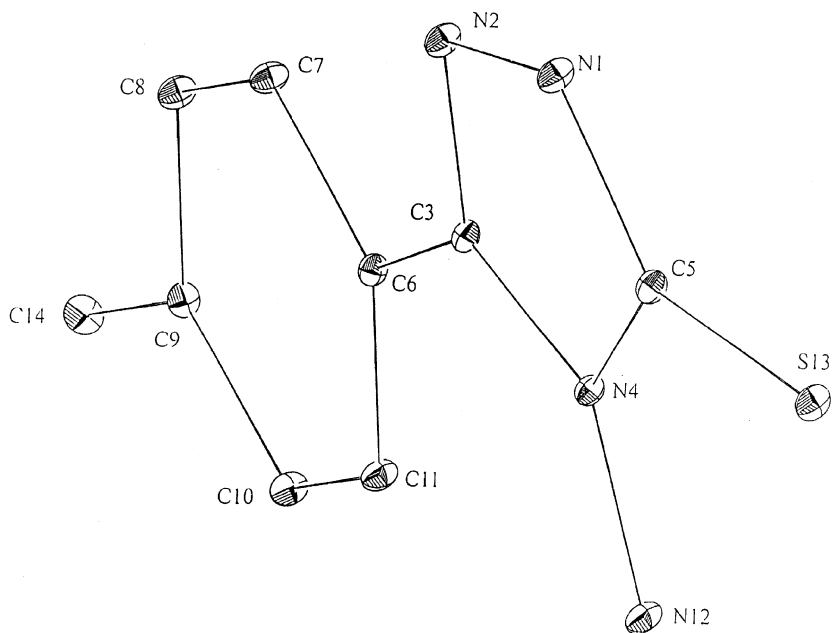


FIGURE 3 ORTEP diagram of MAMT.

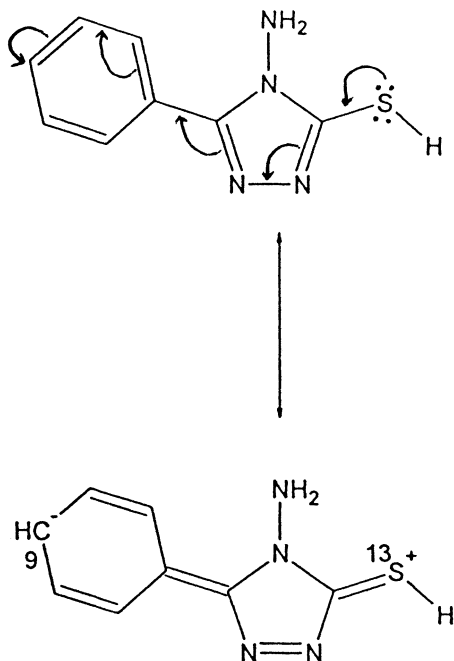


FIGURE 4 Zwitterionic formation in PAMT and MAMT.

Interestingly, the translationally related molecules along a direction form hydrogen bonds $\text{N12-H12A} \dots \text{N2}$ ($x+1$, y , z) for PAMT and $\text{N12-H12A} \dots \text{N2}$ ($x-1$, y , z) for MAMT. The details are: **PAMT**: $\text{N12} \dots \text{N2} = 3.161(6) \text{ \AA}$, and $\text{N12-H12A} \dots \text{N2} = 122.3(3)^\circ$. **MAMT**: $\text{N12} \dots \text{N2} = 3.206(3) \text{ \AA}$, and $\text{N12-H12A} \dots \text{N2} = 119.0(2)^\circ$.

PREPARATION OF PAMT AND MAMT

The values mentioned in square brackets correspond to the sample MAMT.

A mixture of potassium salt of β -aryldithiocarbazinate (0.1 mol, 25.0 g)[0.1 mol, 26.4 g] and hydrazinen hydrate (80%, 0.25 mol, 12.5 ml)[80%, 0.25 ml, 12.5 ml] was heated on an oil-bath at 150°C for 5 h (evolution of H_2S gas). The reaction mixture was then cooled and poured into cold water (130 ml)[200 ml], acidified with conc. HCl, filtered, washed with cold water ($2 \times 50 \text{ ml}$)[$3 \times 250 \text{ ml}$] and recrystallized from aqueous ethanol to get the product in 83%[90%]yield.

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