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Crystal and Molecular Structure Analysis of 1,2,4-Triazolo-N-amino-thiols

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The compound 4-amino-5-(4-methyl)-4H-[1,2,4]-triazole-3-thiol [AMT], $C_3H_6N_4S$, crystallizes in the orthorhombic space group $Pca2_1$ with cell parameters $a = 9.8130(3)$ Å, $b = 8.8600(5)$ Å, $c = 6.5400(5)$ Å, $V = 568.61(6)$ Å^3, and $Z = 4$. The structure was solved by direct methods using SHELXS-97 and refined using SHELXL-97. The final residual factor is $R1 = 0.0465$ for 1726 reflections and 75 parameters.

The compound 4-amino-5-(4-chlorophenyl)-4H-[1,2,4]-triazole-3-thiol[ACT], $C_8H_7ClN_4S$, crystallizes in the triclinic space group $P\bar{1}$ with cell parameters $a = 8.0440(8)$ Å, $b = 11.527(1)$ Å, $c = 11.7780(7)$ Å, $\alpha = 66.537(6)^\circ$, $\beta = 72.990(6)^\circ$, $\gamma = 76.001(3)^\circ$, $V = 948.1(1)$ Å^3, and $Z = 4$. The structure was solved by direct methods using SHELXS-97 and refined using SHELXL-97. The final residual factor is $R1 = 0.0644$ for 6805 reflections and 254 parameters.

Keywords: crystal structure, tautomerism; triazole complexes

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INTRODUCTION

Compounds of 1,2,4-triazole derivatives are found to possess diverse pharmacological activities [1] such as fungicidal, insecticidal, bactericidal, herbicidal, antitumor [2], anti-inflammatory [3], and central nervous system (CNS) stimulant properties [4]. They are also used in dyes and lubricants and as analytical reagents [5] and antiviral agents [6]. The complexes containing 1,2,4-triazole ligands possess specific magnetic properties [7].

Earlier, Ambalavanan et al. [8] reported the X-ray crystal structure studies of 4-amino-5-phenyl-4*H*-[1,2,4]-triazole-3-thiol and 4-amino-5-(4-methyl)-4*H*-[1,2,4]-triazole-3-thiols. The synthesis and characterization of AMT and ACT have been reported earlier [9]. Crystal structures of the compounds AMT and ACT are presented in this article. The schematic diagrams of the compounds AMT and ACT are shown in Fig. 1.

CRYSTAL STRUCTURE DETERMINATION

Single crystals of triazole complexes suitable for X-ray diffraction studies were mounted on a glass fiber. The measurements were made on a DIPLabo Imaging Plate system with graphite monochromated MoK_α radiation. Thirty-six frames of data were collected using the oscillation method. Image processing and data reduction were done using Denzo [10]. The structure was solved using SHELXS-97 [10]. The full-matrix least-squares refinement was done by using SHELXL-97 [11]. The $R1$ value of AMT for all reflections is 0.0465. The $R1$ value of ACT for all reflections is 0.0805. Table 1 gives the details of crystal data, data collection, and refinement.

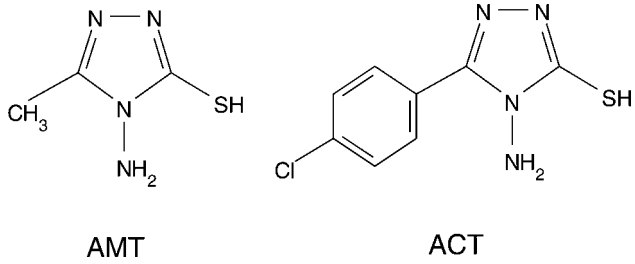

FIGURE 1 Schematic diagrams.

TABLE 1 Crystal Data and Structure Refinement for AMT and ACT

Parameter	AMT value	ACT value
Identification code	AMT	ACT
Empirical formula	$C_3H_6N_4S$	$C_8H_7ClN_4S$
Formula weight	130.18	226.69
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Triclinic
Space group	$Pca2_1$	$P\bar{1}$
Cell dimensions		
a	9.8130(3) Å	8.0440(8) Å
b	8.8600(5) Å	11.5270(11) Å
c	6.5400(5) Å	11.7780(7) Å
α	90°	66.537(6)°
β	90°	72.990(6)°
γ	90°	76.001(3)°
Volume	568.61(6) Å^3	948.13(14) Å^3
Z	4	4
Density(calculated)	1.521 Mg/m^3	1.588 Mg/m^3
Absorption coefficient	0.456 mm^{-1}	0.292 mm^{-1}
F_{000}	272	232
Crystal size	0.2 × 0.2 × 0.25 mm	0.15 × 0.2 × 0.25 mm
θ range for data collection	3.10° to 32.38°	2.21° to 28.28°
Index ranges	$-14 \le h \le 14$ $-13 \le k \le 13$ $-7 \le l \le 7$	$-10 \le h \le 10$ $-15 \le k \le 15$ $-13 \le l \le 13$
Reflections collected	1726	6805
Independent reflections	1726 [R(int) = 0.0000]	4152 [R(int) = 0.0268
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ parameters	1726/1/75	4152/0/254
Goodness of fit on F^2	1.054	1.108
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0437$, $wR2 = 0.1241$	$R1 = 0.0644$, $wR2 = 0.1915$
R indices (all data)	$R1 = 0.0465$, $wR2 = 0.1280$	$R1 = 0.0805$, $wR2 = 0.2154$
Absolute structure parameter	0.5(2)	0.3(2)
Extinction coefficient	0.23(3)	0.012(6)
Largest diff. peak and hole	0.482 and -0.529 e.Å^{-3}	0.633 and -0.766 e.Å^{-3}

RESULTS AND DISCUSSION

Tables 2–5 list coordinates, equivalent thermal parameters, bond lengths, and angles of AMT. Tables 6–8 list the coordinates, equivalent thermal parameters, bond lengths, and angles of ACT.

TABLE 2 Atomic Coordinates and Equivalent Thermal Parameters of the Nonhydrogen Atoms of AMT

Atom	x	y	z	U_{eq}
C1	0.1253(2)	1.0101(2)	0.912(2)	0.0556(5)
C2	0.1719(2)	0.8512(2)	0.907(1)	0.0374(3)
N3	0.2986(1)	0.8086(2)	0.9093(9)	0.0415(3)
N4	0.2919(1)	0.6534(1)	0.907(1)	0.0376(3)
C5	0.1646(1)	0.5994(1)	0.910(1)	0.0312(3)
S6	0.1139(3)	0.4185(4)	0.9098(2)	0.0376(2)
N7	0.0865(1)	0.7289(1)	0.9063(7)	0.0328(3)
N8	− 0.0561(1)	0.7369(2)	0.9156(8)	0.0421(4)

TABLE 3 Atomic Coordinates and Equivalent Thermal Parameters of the Hydrogen Atoms of AMT

Atom	x	y	z	U_{eq}
H1A	0.1939	1.0719	0.9749	0.083
H1B	0.0422	1.0171	0.9887	0.083
H1C	0.1096	1.0446	0.7746	0.083
H4	0.3629	0.5966	0.9049	0.045
H8A	− 0.0958	0.8234	0.9225	0.051
H8B	− 0.1038	0.6556	0.9143	0.051

TABLE 4 Bond Lengths of AMT (Å)

Atoms	Length	Atoms	Length
C1-C2	1.481(2)	N4-C5	1.338(2)
C2-N3	1.299(2)	C5-N7	1.380(2)
C2-N7	1.370(2)	C5-S6	1.678(1)
N3-N4	1.376(2)	N7-N8	1.403(2)

TABLE 5 Bond Angles of AMT (°)

Atoms	Angle	Atoms	Angle
N3-C2-N7	110.8(1)	N4-C5-S6	128.2(1)
N3-C2-C1	124.8(1)	N7-C5-S6	129.0(1)
N7-C2-C1	124.2(1)	C2-N7-C5	108.5(1)
C2-N3-N4	104.1(1)	C2-N7-N8	124.7(1)
C5-N4-N3	113.7(1)	C5-N7-N8	126.5(1)
N4-C5-N7	102.7(1)		

TABLE 6 Atomic Coordinates and Equivalent Thermal Parameters of the Nonhydrogen Atoms of ACT

Atom	x	y	z	U_{eq}
Cl1A	− 0.5133(1)	1.3082(7)	− 0.1091(8)	0.0561(3)
C2A	− 0.3839(3)	1.1617(2)	− 0.0568(3)	0.0404(6)
C3A	− 0.4194(4)	1.0877(3)	0.0698(3)	0.0479(7)
C4A	− 0.3241(4)	0.9675(3)	0.1117(3)	0.0446(6)
C5A	− 0.1900(3)	0.9216(2)	0.0268(3)	0.0359(5)
C6A	− 0.1532(3)	0.9996(3)	− 0.1003(3)	0.0419(6)
C7A	− 0.2507(4)	1.1200(3)	− 0.1425(3)	0.0446(6)
C8A	− 0.0902(3)	0.7961(2)	0.0777(3)	0.0367(5)
N9A	− 0.0849(3)	0.7405(2)	0.1984(2)	0.0455(6)
N10A	0.0252(3)	0.6277(2)	0.2063(2)	0.0468(6)
C11A	0.0909(3)	0.6106(3)	0.0954(3)	0.0401(6)
N12A	0.0152(3)	0.7187(2)	0.0117(2)	0.0369(5)
N13A	0.0352(4)	0.7403(2)	− 0.1166(2)	0.0526(7)
S14A	0.2331(1)	0.4925(7)	0.0561(8)	0.0507(3)
Cl1B	1.0245(1)	− 0.2987(7)	0.5985(8)	0.0537(3)
C2B	0.8879(3)	− 0.1547(2)	0.5489(3)	0.0399(6)
C3B	0.8502(4)	− 0.1112(3)	0.4309(3)	0.0471(7)
C4B	0.7475(4)	0.0065(3)	0.3896(3)	0.0432(6)
C5B	0.6818(3)	0.0806(2)	0.4673(3)	0.0355(5)
C6B	0.7188(4)	0.0328(3)	0.5871(3)	0.0453(6)
C7B	0.8215(4)	− 0.0847(3)	0.6280(3)	0.0464(7)
C8B	0.5759(3)	0.2039(2)	0.4170(3)	0.0370(6)
N9B	0.5510(3)	0.2499(2)	0.3006(2)	0.0477(6)
N10B	0.4403(3)	0.3622(2)	0.2924(2)	0.0490(6)
C11B	0.3931(3)	0.3881(3)	0.3988(3)	0.0389(6)
N12B	0.4838(3)	0.2876(2)	0.4793(2)	0.0357(5)
N13B	0.4756(3)	0.2740(2)	0.6035(2)	0.0461(6)
S14B	0.2515(1)	0.5063(7)	0.4381(7)	0.0469(3)

The ORTEP, packing diagram and intermolecular hydrogen bonds of the molecules of AMT and ACT are shown in Figures 3–8. The compound AMT is planar, but ACT is not. This deviation can be ascribed to the presence of the bulky chlorophenyl group, which is ideally situated with a torsion angle of -19.4°. Both AMT and ACT show strong tautomerism. They tautomerize from N-amino thiol A to B as shown in Fig. 2.

The compounds AMT and ACT show intermolecular H-bonds between the thiol and the N-H group. ACT shows a strong intramolecular H-bond between the thiol and N-amino group. AMT does not exhibit this type of bond, possibly because of the steric effect of the chlorophenyl ring, which pushes the N-amino group toward the thiol moiety.

TABLE 7 Bond Lengths of ACT (Å)

Atoms	Length	Atoms	Length
Cl1A-C2A	1.735(3)	Cl1B-C2B	1.739(3)
C2A-C3A	1.374(4)	C2B-C3B	1.376(4)
C2A-C7A	1.379(4)	C2B-C7B	1.380(4)
C3A-C4A	1.383(4)	C3B-C4B	1.388(4)
C4A-C5A	1.400(4)	C4B-C5B	1.402(4)
C5A-C6A	1.391(4)	C5B-C6B	1.390(4)
C5A-C8A	1.458(3)	C5B-C8B	1.461(3)
C6A-C7A	1.393(4)	C6B-C7B	1.386(4)
C8A-N9A	1.316(4)	C8B-N9B	1.316(4)
C8A-N12A	1.385(3)	C8B-N12B	1.385(3)
N9A-N10A	1.370(3)	N9B-N10B	1.368(3)
N10A-C11A	1.333(4)	N10B-C11B	1.330(4)
C11A-N12A	1.378(3)	C11B-N12B	1.376(3)
C11A-S14A	1.677(3)	C11B-S14B	1.677(3)
N12A-N13A	1.396(4)	N12B-N13B	1.391(3)

TABLE 8 Bond Angles of ACT (°)

Atoms	Angle	Atoms	Angle
C3A-C2A-C7A	121.1(2)	C3B-C2B-C7B	121.0(2)
C3A-C2A-Cl1A	119.0(2)	C3B-C2B-Cl1B	119.7(2)
C7A-C2A-Cl1A	119.9(2)	C7B-C2B-Cl1B	119.3(2)
C2A-C3A-C4A	119.7(3)	C2B-C3B-C4B	119.4(3)
C3A-C4A-C5A	120.6(3)	C3B-C4B-C5B	120.5(3)
C6A-C5A-C4A	118.7(2)	C6B-C5B-C4B	118.7(2)
C6A-C5A-C8A	123.3(2)	C6B-C5B-C8B	123.8(2)
C4A-C5A-C8A	117.9(2)	C4B-C5B-C8B	117.5(2)
C5A-C6A-C7A	120.5(2)	C7B-C6B-C5B	120.6(3)
C2A-C7A-C6A	119.4(3)	C2B-C7B-C6B	119.7(3)
N9A-C8A-N12A	109.3(2)	N9B-C8B-N12B	109.4(2)
N9A-C8A-C5A	122.9(2)	N9B-C8B-C5B	122.5(2)
N12A-C8A-C5A	127.8(2)	N12B-C8B-C5B	128.1(2)
C8A-N9A-N10A	104.8(2)	C8B-N9B-N10B	104.7(2)
C11A-N10A-N9A	113.9(2)	C11B-N10B-N9B	113.9(2)
N10A-C11A-N12A	103.1(2)	N10B-C11B-N12B	103.3(2)
N10A-C11A-S14A	131.6(2)	N10B-C11B-S14B	131.5(2)
N12A-C11A-S14A	125.3(2)	N12B-C11B-S14B	125.1(2)
C11A-N12A-C8A	108.8(2)	C11B-N12B-C8B	108.6(2)
C11A-N12A-N13A	124.5(2)	C11B-N12B-N13B	124.1(2)
C8A-N12A-N13A	126.6(2)	C8B-N12B-N13B	127.3(2)

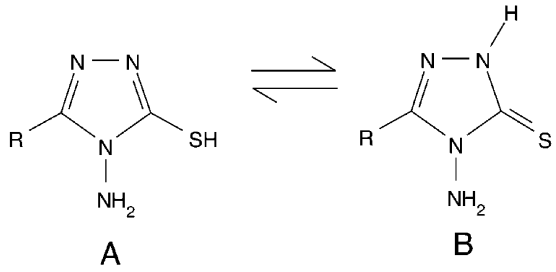

FIGURE 2 Schematic representation of tautomerism of triazoles.

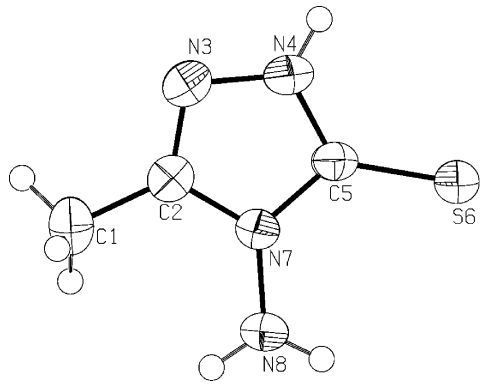

FIGURE 3 ORTEP of AMT at 50% probability.

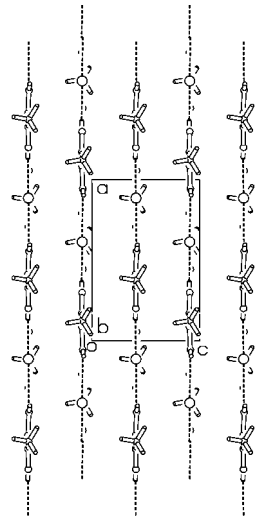

FIGURE 4 Packing of the AMT molecules down the **b** axis.

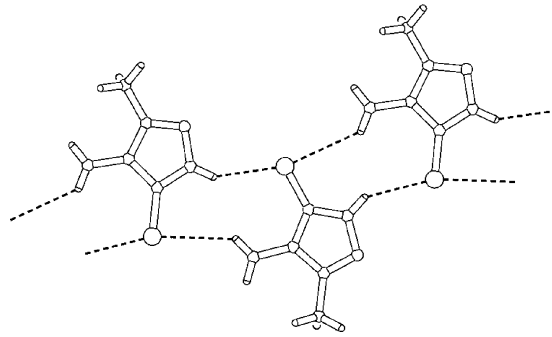

FIGURE 5 Hydrogen bonds in AMT.

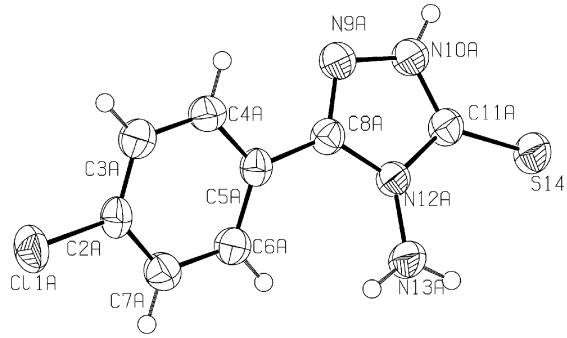

FIGURE 6 ORTEP of ACT at 50% probability.

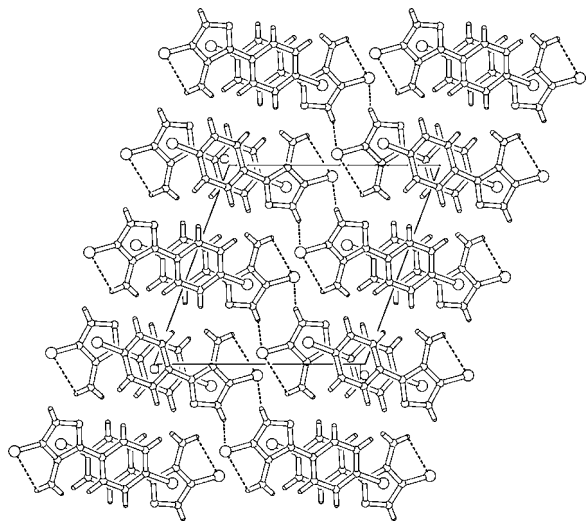

FIGURE 7 Packing of the ACT molecules down the **a** axis.

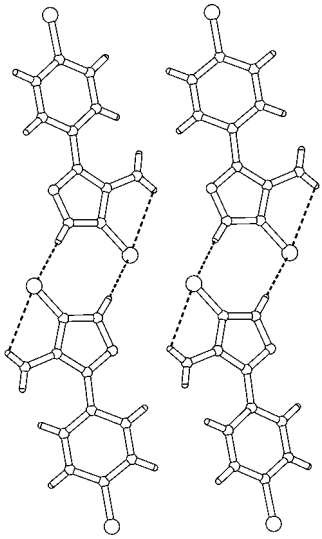

FIGURE 8 Hydrogen bonds in ACT.

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