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# A structural comparison of some amine- and thione-substituted triazoles

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#### Abstract

A series of amine- and thione-substituted triazoles have been synthesized and their structures determined by single-crystal X-ray diffraction methods. The compounds differ in the identity of the amine- and alkyl-substituents on the triazole ring. Crystal data for 4-furfuralideneamino-3-methyl-4,5-dihydro-1*H*-1,2,4-triazole-5-thione, C<sub>8</sub>H<sub>8</sub>N<sub>4</sub>OS: triclinic, space group *P*<sub>1</sub>, *Z*=2, *a*=10.490(2) Å, *b*=10.700(2) Å, *c*=4.2185(8) Å,  $\alpha$ =92.68(2)°,  $\beta$ =90.17(2)°,  $\gamma$ =92.61(1)°, *V*=472.5(1) Å<sup>3</sup>, *R*(*F*)=0.040 for 151 variables and 1056 observations (*I* > 3 $\sigma$ (*I*)); 4-furfuralideneamino-3-ethyl-4,5-dihydro-1*H*-1,2,4-triazole-5-thione, C<sub>9</sub>H<sub>10</sub>N<sub>4</sub>OS: triclinic, space group *P*<sub>1</sub>, *Z*=2, *a*=8.366(3) Å, *b*=9.296(2) Å, *c*=7.953(2) Å,  $\alpha$ =113.72(2)°,  $\beta$ =108.54(3)°,  $\gamma$ =84.94(3)°, *V*=536.3(3) Å<sup>3</sup>, *R*(*F*)=0.037 for 136 variables and 1126 observations (*I* > 3 $\sigma$ (*I*)); 4-furfuralideneamino-3-propyl-4,5-dihydro-1*H*-1,2,4-triazole-5-thione, C<sub>10</sub>H<sub>12</sub>N<sub>4</sub>OS: triclinic, space group *P*<sub>1</sub>, *Z*=2, *a*=9.149(3) Å, *b*=9.177(2) Å, *c*=8.045(4) Å,  $\alpha$ =110.11(2)°,  $\beta$ =114.52(3)°,  $\gamma$ =86.44(2)°, *V*=574.5(4) Å<sup>3</sup>, *R*(*F*)=0.040 for 145 variables and 1414 observations (*I* > 3 $\sigma$ (*I*)); 4-(2-acetylpyridyleneamino)-3-ethyl-4,5-dihydro-1*H*-1,2,4-triazole-5-thione, C<sub>11</sub>H<sub>13</sub>N<sub>5</sub>S: triclinic, space group *P*<sub>1</sub>, *Z*=2, *a*=7.736(3) Å, *b*=11.752(4) Å, *c*=7.219(2) Å,  $\alpha$ =93.68(3)°,  $\beta$ =106.26(3) Å,  $\gamma$ =91.04(3)°, *V*=628.3(4) Å<sup>3</sup>, *R*(*F*)=0.043 for 154 variables and 1224 observations (*I* > 3 $\sigma$ (*I*)). The molecules show substantial variations in conformation as well as in crystal packing. The differences in molecular structure are discussed in terms of the potential of the molecules to act as bidentate ligands towards metal ions. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Crystal structure; Triazoles; Amine-substituted triazoles; Thione-substituted triazoles

#### 1. Introduction

Metal complexes of compounds with S-C-N linkages display a wide range of biological activity

[1–4]. Molecules that possess an S–C–N–N linkage can potentially bind to a metal ion in a bidentate fashion through the S atom and the second N atom. One such molecule is 4-amino-3-methyl-4,5-dihydro-1*H*-1,2,4-triazole-5-thione [5] which has been found to coordinate to nickel(II) [6] and copper(I) [7] through the amine and thione substituents on the triazole ring. In crystals of the free ligand and its metal complexes, this triazole exists as the thione tautomer with the H

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Dedicated with affection and gratitude to Professor Abraham Clearfield on the occasion of his 70th birthday

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atom on the ring N atom adjacent to the thione. As a continuation of this study, we have synthesized and structurally characterized a series of amine- and thione-substituted triazoles. shown above in Scheme 1, that differ in the identity of the alkyl R group on the triazole ring and the R' group on the amine substituent. These molecules represent potential ligands for metal complexes that may also be biologically active. In this paper we report the crystal and molecular structures of this set of related compounds and examine the likelihood of their chelating metal ions given their observed conformations.

#### 2. Experimental

#### 2.1. Synthesis of 3-CH<sub>3</sub>-4-(C<sub>4</sub>H<sub>3</sub>O)CHN-5-S-C<sub>2</sub>N<sub>3</sub>H (1)

A mixture of 10 g (0.094 mol) of thiocarbohydrazide in 60 ml of glacial acetic acid was heated under reflux for 4 h. Within 1 h of refluxing, a pale yellow solid started separating from the clear solution. The reaction mixture was allowed to stand overnight at room temperature, and the product of this reaction, 4-amino-3-methyl-4,5-dihydro-1*H*-1,2,4-triazole-5thione, was isolated with a yield of 80%, and recrystallized from ethanol (m.p., 204°C). The final product, 4-furfuralideneamino-3-methyl-4,5-dihydro-1*H*-1,2,-4-triazole-5-thione (1), was prepared by refluxing an equimolar mixture of 5.1 ml of furfuraldehyde and 8.0 g of 4-amino-3-methyl-4,5-dihydro-1*H*-1,2,4triazole-5-thione in ethanol. After 2 h of refluxing, a brown solid began to separate from the solution. The reaction mixture was cooled and the product isolated by filtration. The product was recrystallized from ethanol and light brown crystals of **1** were obtained with a yield of 75% (m.p., 225°C). Analysis (National Chemical Consulting, Tenafly, NJ): found, C (46.78); H (3.24); N (28.20); calculated, C (46.14); H (3.87); N (26.90).

### 2.2. Synthesis of $3-C_2H_5-4-(C_4H_3O)CHN-5-S-C_2N_3H$ (2)

A mixture of 10 g (0.094 mol) of thiocarbohydrazide in 60 ml of propionic acid was heated under reflux for 4 h. Within 1 h of refluxing, a pale yellow solid began to separate from the clear solution. The product of this reaction, 4-amino-3-ethyl-4,5-dihydro-1H-1,2,4-triazole-5-thione, was isolated with a 76% yield, and was recrystallized from water (m.p., 148°C). The final product, 4-furfuralideneamino-3ethyl-4,5-dihydro-1H-1,2,4-triazole-5-thione (2), was prepared by refluxing an equimolar mixture of furfuraldehyde and 4-amino-3-ethyl-4,5-dihydro-1H-1,2,4-triazole-5-thione in ethanol for 3-4 h. The solution was allowed to stand overnight at room temperature, during which time pale yellow crystals of 2 formed. The product was recrystallized from ethanol (m.p., 190°C). Analysis: found, C (48.57); H (4.05); N (25.24); calculated, C (48.64); H (4.54); N (25.21).

#### 2.3. Synthesis of $3-C_3H_7-4-(C_4H_3O)CHN-5-S-C_2N_3H$ (3)

A mixture of 10 g (0.094 mol) thiocarbohydrazide in 30 ml of butanoic acid was heated under reflux for 5-6 h. Within 1 h of refluxing, a cream-colored solid started separating from the solution. After the reflux, the excess butanoic acid was distilled off and the remaining liquid was allowed to stand overnight at room temperature. The solid that had crystallized was filtered, washed with ether and recrystallized from an equimolar solution of dioxane and water. Cream-colored crystals of 4-amino-3-propyl-4,5dihydro-1*H*-1,2,4-triazole-5-thione were isolated with a 74% yield (m.p., 104°C). The final product, 4-furfuralideneamino-3-propyl-4,5-dihydro-1*H*-1,2,-4-triazole-5-thione (**3**), was prepared by refluxing an equimolar mixture of furfuraldehyde and 4-amino-3-propyl-4,5-dihydro-1*H*-1,2,4-triazole-5-thione in ethanol for 2–3 h. The solution was concentrated and allowed to stand overnight at room temperature during which time cream-colored crystals of **3** formed. The product was recrystallized from ethanol (m.p., 155°C). Analysis: found, C (49.60); H (4.65); N, (23.24); calculated, C (50.83); H (5.12); N (23.71).

# 2.4. Synthesis of $3-C_2H_5-4-(C_5H_4N)C(CH_3)N-5-S-C_2N_3H$ (4)

An equimolar mixture of 4-amino-3-ethyl-4,5dihydro-1*H*-1,2,4-triazole-5-thione and 2-acetylpyridine in dry methanol was refluxed for 6 h. The solution was cooled and kept undisturbed for 5–6 days in the refluxing flask. During this time, large colorless block-shaped crystals of **4** were obtained with a 75% yield (m.p., 190°C). Analysis: found, C (54.53); H (5.05); N 29.04; calculated, C (53.42); H (5.30); N (28.32).

#### 2.5. Crystallographic studies

All the single-crystal X-ray diffraction measurements were performed at room temperature on a Rigaku AFC6S four-circle diffractometer (graphitemonochromated 2.0 kW Mo K $\alpha$  X-ray source;  $\lambda = 0.71069$  Å) operated by MSC-AFC diffractometer control software [8]. All crystals were cut from larger fragments and were mounted on glass fibers with silicone cement. Unit cell parameters were obtained by indexing 25 reflections found during a search of reciprocal space and were refined by a least-squares analysis of the setting angles of 20-24 high-angle reflections ( $19^{\circ} < 2\theta$ (Mo K $\alpha$ )  $< 42^{\circ}$ ). Intensity data in the range  $3-50^{\circ}2\theta$  were collected with  $\omega$  scans of  $4^{\circ} \min^{-1}$  (1 and 4) or  $8^{\circ} \min^{-1}$  (2 and 3). Reflections were measured at a constant scan rate with up to four scans for weaker data (those with  $I < 10\sigma(I)$ ). The intensities of three standard reflections measured after every 150 data showed no significant variations in any of the experiments. All crystallographic calculations were performed on a VAXStation 3100/76 computer with the TEXSAN [9] series of programs. Atomic scattering factors [10] and anomalous

dispersion terms [11] were from standard sources. Data were corrected for Lorentz and polarization effects. An absorption correction based on  $\psi$  scans [12] of three reflections was applied to the data of **2**. The space group was assigned in each case as  $P\overline{1}$ based on intensity statistics and the overall likelihood of the centrosymmetric space group. Successful refinements confirmed the space group selection. The S atoms were located on E-maps generated by the direct methods program MITHRIL [13], while the lighter non-hydrogen (O, N and C) atom positions were obtained by difference Fourier methods (DIR-DIF [14]). The hydrogen atoms were located on difference electron density maps following least-squares refinement. The H atom positions of 1 were refined while those of the other compounds were kept fixed. The  $B_{iso}$  value of each H atom was set at 1.2 times the  $B_{eq}$  value of the attached atom at the time of its inclusion. Final refinements included anisotropic displacement parameters for all non-hydrogen atoms and were performed on those data having  $I > 3\sigma(I)$ . There were no unusual variations in  $F_{0} - F_{c}$  as a function of  $(\sin \theta)/\lambda$ , Miller indices, or  $F_0$ . Crystallographic data for the four compounds are summarized in Table 1. Final positional and equivalent isotropic displacement parameters are listed in Table 2.

#### 3. Results

#### 3.1. 3-CH<sub>3</sub>-4-(C<sub>4</sub>H<sub>3</sub>O)CHN-5-S-C<sub>2</sub>N<sub>3</sub>H

The molecular structure of **1** is shown in Fig. 1 and a packing diagram with the unit cell outline is provided in Fig. 2. Selected bond distances and angles for all four compounds are presented in Table 3. The molecule exists in the thione tautomeric form with an S-C distance of 1.681(4) Å which indicates substantial double bond character [5]. All the bond distances and angles of the triazole moiety are within four estimated standard deviations of those reported for 4-amino-3-methyl-4,5-dihydro-1H-1,2,4-triazole-5-thione [5], except the angles involving the amine substituent. The angles in 1 are approximately 5° larger (C1–N1–N4 =  $133.7(3)^\circ$ ) and smaller  $(C2-N1-N4 = 118.7(3)^{\circ})$  than those in the parent triazole. This distortion may be the result of nonbonded interactions between the S atom and H2, the

Table 1 Crystallographic data for new amine- and thione-substituted triazoles

Parameter	(1)	(2)	(3)	(4)
Empirical formula	C <sub>8</sub> H <sub>8</sub> N <sub>4</sub> OS	$C_9H_{10}N_4OS$	C <sub>10</sub> H <sub>12</sub> N <sub>4</sub> OS	C <sub>11</sub> H <sub>13</sub> N <sub>5</sub> S
Formula weight	208.24	222.26	236.29	247.32
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
a (Å)	10.490(2)	8.366(3)	9.149(3)	7.736(3)
<i>b</i> (Å)	10.700(2)	9.296(2)	9.177(2)	11.752(4)
<i>c</i> (Å)	4.2185(8)	7.953(2)	8.045(4)	7.219(2)
$\alpha$ (°)	92.68(2)	113.72(2)	110.11(2)	93.69(3)
β (°)	90.17(2)	108.54(3)	114.52(3)	106.27(3)
$\gamma$ (°)	92.61(1)	84.94(3)	86.44(2)	91.05(3)
$V(Å^3)$	472.5(1)	536.3(3)	574.5(4)	628.3(4)
Space group	<i>P</i> 1 (no. 2)	<i>P</i> 1 (no. 2)	<i>P</i> 1 (no. 2)	<i>P</i> 1 (no. 2)
Z value	2	2	2	2
$D_{\text{calc}} (\text{g cm}^{-3})$	1.464	1.376	1.366	1.307
F(000)	216	232	248	260
$\mu$ (cm <sup>-1</sup> )	2.99	2.68	2.54	2.32
Transmission factors	None	0.93-1.00	None	None
$2\theta$ range for data (°)	3-50	3-50	3-50	3-50
Data collected	$+h, \pm k, \pm l$	$+h, \pm k, \pm l$	$+h, \pm k, \pm l$	$+h, \pm k, \pm l$
Total data	1738	2012	2151	2386
Number of unique data	1640	1874	2012	2206
R int	0.034	0.014	0.012	0.030
Number of data $I > 3\sigma(I)$	1056	1126	1414	1224
Number of variables	151	136	145	154
$R(F); R_w(F) \ (I > 3\sigma(I))$	0.040; 0.039	0.037; 0.036	0.040; 0.039	0.043; 0.040
Goodness of fit	2.05	2.00	2.43	2.10
Peaks in final $\Delta F (e^{-} Å^{-3})$	0.27, -0.19	0.17, -0.16	0.20, -0.25	0.18, -0.25



Fig. 1. ORTEP diagram of the molecular structure of **1** showing the atom labelling scheme. In this and subsequent figures, the displacement ellipsoids are shown at the 50% probability level except for those of the hydrogen atoms, which are shown as spheres of arbitrary size.

latter of which is not present in the parent. Overall, the molecule is fairly flat, with a dihedral angle of  $14.3^{\circ}$  between the essentially planar triazole and furfuralidene rings. The torsion angle C1–N1–N4–C3 is  $11.2^{\circ}$  so that the furfuralidene group is rotated towards the viewer relative to the triazole ring. The packing diagram



Fig. 2. ORTEP packing diagram of 1 showing the outline of the unit cell. View is approximately along the *c* axis. The S, O and N atoms are shown with octant shading.

Table 2 Fractional atomic coordinates and equivalent isotropic displacement parameters

Atom	x	у	z	$B_{eq}^{a}$
3-CH3-	4-(C <sub>4</sub> H <sub>3</sub> O)CH	$N-5-S-C_2N_3H$		
S	0.6749(1)	0.49327(9)	0.3475(3)	4.15(5)
0	0.9771(2)	0.8610(2)	1.0232(6)	3.9(1)
N1	0.6893(3)	0.7540(3)	0.3970(7)	3.0(1)
N2	0.5414(3)	0.6746(3)	0.0957(8)	3.7(2)
N3	0.5309(3)	0.8027(3)	0.0841(7)	3.6(1)
N4	0.7875(3)	0.7871(3)	0.6089(7)	3.1(1)
C1	0.6356(3)	0.6402(3)	0.2794(8)	3.2(2)
C2	0.6225(3)	0.8475(3)	0.2683(9)	3.3(2)
C3	0.8616(3)	0.7046(4)	0.6999(9)	3.3(2)
C4	0.9652(3)	0.7392(3)	0.9101(9)	3.0(2)
C5	1.0636(4)	0.6764(4)	1.017(1)	4.4(2)
C6	1.1417(4)	0.7612(4)	1.203(1)	4.6(2)
C7	1.0866(4)	0.8707(4)	1.200(1)	4.4(2)
C8	0.6559(4)	0.9823(4)	0.334(1)	4.0(2)
3-C <sub>2</sub> H <sub>5</sub>	-4-(C <sub>4</sub> H <sub>3</sub> O)CH	$IN-5-S-C_2N_3H$		
S	0.2998(1)	0.2944(1)	0.3265(1)	5.00(4)
õ	0.1394(3)	-0.2303(3)	0.4243(3)	5.0(1)
N1	0.4081(3)	0.1902(3)	0.6261(3)	3.1(1)
N2	0.5301(3)	0.4015(3)	0.6812(4)	4.2(1)
N3	0.6046(3)	0.3705(3)	0.8438(4)	4.1(1)
N4	0.3207(3)	0.0461(3)	0.5550(4)	3.5(1)
C1	0.4111(4)	0.2945(4)	0.5436(4)	3.6(1)
C2	0.5286(4)	0.2407(4)	0.8070(4)	3.4(1)
C3	0.1866(4)	0.0162(4)	0.4118(5)	3.7(1)
C4	0.0911(4)	-0.1297(4)	0.3337(4)	3.4(1)
C5	-0.0467(4)	-0.1909(4)	0.1784(5)	4.6(1)
C6	-0.0869(5)	-0.3382(4)	0.1709(5)	5.3(2)
C7	0.0261(5)	-0.3564(4)	0.3199(6)	5.8(2)
C8	0.5598(4)	0.1562(4)	0.9369(5)	4.3(1)
C9	0.7105(5)	0.2228(5)	1.1130(5)	5.9(2)
3-C 3H	-4-(C (H 20)CF	$IN_{2}S_{2}C_{2}N_{2}H$		
s s	0.7201(1)	0.1879(1)	0.6819(1)	4.32(3)
0	1.2500(2)	0.3453(3)	0.5985(3)	5.24(9)
N1	0.8120(3)	0.0898(2)	0.3744(3)	2 98(8)
N2	0.5981(3)	-0.0318(3)	0.3194(3)	3 66(9)
N3	0.5701(3)	-0.0910(3)	0.5171(3) 0.1520(3)	3.00(2)
N4	0.0224(3) 0.9624(3)	0.0731(3) 0.1738(3)	0.1520(3) 0.4510(3)	3 30(9)
C1	0.701(3)	0.0822(3)	0.4589(4)	3.1(1)
$C^2$	0.7545(3)	-0.022(3)	0.1897(4)	3.1(1) 3.3(1)
C3	0.9837(3)	0.0229(3)	0.1057(1)	3.4(1)
C4	1 1335(3)	0.3090(3) 0.4045(3)	0.5701(4) 0.6581(4)	3.7(1)
C5	1.1333(3) 1.1842(4)	0.5500(3)	0.0301(4) 0.7898(4)	4.6(1)
C6	1.3415(4)	0.5300(3)	0.8136(5)	4 9(1)
C7	1.3759(4)	0.4610(4)	0.6976(6)	6.2(2)
C8	0.8349(4)	-0.0431(3)	0.0567(4)	4.3(1)
C9	0.7573(4)	-0.1787(4)	-0.1373(4)	4.7(1)
C10	0.7876(4)	-0.3345(4)	-0.1163(5)	5.7(1)

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Atom	x	у	z	$B_{eq}^{a}$
$3-C_2H_2$	$5-4-(C_5H_4N)C$	$C(CH_3)N-5-S-C_2$	N₃H	
S	0.7420(2)	0.1289(1)	0.0544(2)	4.61(5)
N1	0.6070(4)	0.1958(3)	-0.3145(4)	3.4(1)
N2	0.4462(4)	0.0654(3)	-0.2485(5)	3.7(1)
N3	0.3592(4)	0.0901(3)	-0.4341(5)	3.6(1)
N4	0.7294(4)	0.2904(3)	-0.2944(5)	3.8(1)
N5	1.1854(4)	0.3381(3)	-0.2674(5)	4.7(2)
C1	0.5981(5)	0.1289(3)	-0.1682(5)	3.3(2)
C2	0.4580(5)	0.1720(3)	-0.4703(6)	3.5(2)
C3	0.8857(5)	0.2639(3)	-0.3042(5)	3.2(2)
C4	0.4227(5)	0.2341(4)	-0.6471(6)	4.7(2)
C5	0.2510(6)	0.1954(4)	-0.7932(7)	7.0(3)
C6	0.9490(5)	0.1478(3)	- 0.3386(6)	4.6(2)
C7	1.0171(5)	0.3635(3)	-0.2730(5)	3.3(2)
C8	0.9636(5)	0.4738(4)	-0.2525(6)	4.6(2)
C9	1.0942(7)	0.5627(4)	-0.2159(7)	5.6(2)
C10	1.2671(6)	0.5374(4)	-0.2051(7)	5.4(2)
C11	1.3083(5)	0.4250(4)	- 0.2343(7)	5.6(2)

 ${}^{a}B_{eq} = (4/3)[a^{2}\beta_{11} + b^{2}\beta_{22} + c^{2}\beta_{33} + (2ab\cos\gamma)\beta_{12} + (2ac\cos\beta) \times \beta_{13} + (2bc\cos\alpha)\beta_{23}]$ 

shows that the molecules are arranged in staggered rows running parallel to the *a* axis with the molecules in adjacent rows in opposite orientations. The main intermolecular interaction is a hydrogen bond between H1 and S (N2–H1···S, 0.97(3); 2.37(3) Å; 173(3)°) on each side of the center of inversion.

# $3.2. \ 3-C_2H_5-4-(C_4H_3O)CHN-5-S-C_2N_3H$

The molecular structure of 2 is depicted in Fig. 3, while a packing diagram and unit cell outline are shown in Fig. 4. The bond distances and angles in the triazole moiety (Table 3) are not substantially different from those in 1; however the conformation of the molecule is different. The dihedral angle of 13.3° between the triazole and furfuralidene rings is similar to that in 1, indicating that 2 is also approximately planar; however, the furfuralidene ring is rotated in the opposite direction to 1, away from the viewer relative to the triazole (torsion angle C1–N1–N4–C3 =  $-22.3^{\circ}$ ). The molecules also pack differently. As in 1, there are staggered rows of molecules, in this case running parallel to the c axis, with adjacent rows related by the center of inversion. The molecules in 2 are standing upright in their rows



Fig. 3. ORTEP diagram of the molecular structure of **2** showing the atom labelling scheme.

while those in **1** are lying on their sides. Despite the different orientations, the N2–H1 $\cdots$ S hydrogen bonding interaction is preserved in **2** (1.02; 2.30 Å; 172°).

## 3.3. 3-C<sub>3</sub>H<sub>7</sub>-4-(C<sub>4</sub>H<sub>3</sub>O)CHN-5-S-C<sub>2</sub>N<sub>3</sub>H

The molecular structure of 3 appears in Fig. 5, and a packing diagram with unit cell outline is present in Fig. 6. The bond distances and angles are mostly

Table 3 Selected bond distances (Å), bond angles (°), and torsion angles (°)



Fig. 4. ORTEP packing diagram of 2 showing the outline of the unit cell. View is approximately along the *a* axis. The S, O and N atoms are shown with octant shading.

consistent with those in 1 and 2, although a small but significant lengthening of the N1–N4 bond and contraction of the N1–N4–C3 angle are evident in Table 3. As was the case with 1 and 2, the most substantial change is in the conformation of the molecule. There is a much larger deviation from coplanarity between the rings (dihedral angle,  $30.5^{\circ}$ ) and the furfuralidene moiety is rotated further away from

	(1)	(2)	(3)	(4)	
S-C1	1.681(4)	1.681(3)	1.687(3)	1.679(4)	
N1-C1	1.387(4)	1.377(4)	1.379(3)	1.372(4)	
N1-N4	1.385(3)	1.396(3)	1.403(3)	1.420(4)	
N1-C2	1.379(4)	1.388(4)	1.385(3)	1.376(4)	
N3-C2	1.295(4)	1.296(4)	1.297(3)	1.303(4)	
N2-N3	1.383(4)	1.378(3)	1.379(3)	1.373(4)	
N2-C1	1.330(4)	1.335(4)	1.332(3)	1.343(4)	
N4-C3	1.273(4)	1.274(4)	1.268(3)	1.274(4)	
S-C1-N1	130.1(3)	131.1(2)	129.9(2)	128.0(3)	
S-C1-N2	127.0(3)	126.6(2)	127.4(2)	129.6(3)	
N3-N2-C1	114.6(3)	114.4(2)	114.3(2)	113.8(3)	
N2-N3-C2	103.1(3)	104.1(2)	104.1(2)	104.5(3)	
N1-C2-N3	111.9(3)	110.3(3)	110.5(2)	109.9(3)	
C1-N1-C2	107.6(3)	108.8(2)	108.5(2)	109.3(3)	
N4-N1-C2	118.7(3)	118.7(2)	119.4(2)	124.6(3)	
N4-N1-C1	133.7(3)	132.2(3)	131.6(2)	124.9(3)	
N1-C1-N2	102.8(3)	102.4(3)	102.7(2)	102.4(3)	
N1-N4-C3	120.2(3)	118.3(3)	117.0(2)	114.4(3)	
C1-N1-N4-C3	11.2(5)	- 22.3(5)	- 36.5(4)	82.3(5)	
C2-N1-N4-C3	- 170.8(3)	164.6(3)	153.0(3)	- 111.5(4)	



Fig. 5. ORTEP diagram of the molecular structure of **3** showing the atom labelling scheme.

the viewer than in 2 (torsion angle C1–N1–N4–C3 =  $-36.5^{\circ}$ ). The positioning of the propyl group results in a further deviation from overall planarity for 3 compared to 1 and 2. The molecules of 3 pack in a manner similar to 1, with adjacent rows of molecules on their sides (running parallel to the *b* axis) related by the center of inversion. The same intermolecular hydrogen bonding interaction is present in 3 (N2–H1…S, 1.00; 2.34 Å; 165°).

#### 3.4. $3 - C_2H_5 - 4 - (C_5H_4N)C(CH_3)N - 5 - S - C_2N_3H$

The molecular structure of 4 is shown in Fig. 7, while a packing diagram and unit cell outline appears in Fig. 8. This molecule carries an ethyl group on the triazole ring as does 2, but differs from the other molecules in having the 2-acetylpyridylene group on the amine in place of the furfuralidene group. This molecule shows some significant structural differences from the other members of the series, most notably a longer N1-N4 bond, nearly equal C2-N1-N4 and C1-N1-N4 bond angles, and a smaller N1-N4-C3 bond angle. Presumably these differences arise from the presence of the methyl group on C3 instead of a hydrogen atom. The torsion angle C1-N1-N4-N3 is 82.3° and the dihedral angle between the rings is 107.4° indicating that in order to avoid steric interactions between the methyl group of the 2-acetylpyridylene and either the S atom or the ethyl group of the triazole, the two parts of the molecule are



Fig. 6. ORTEP packing diagram of **3** showing the outline of the unit cell. The view is approximately onto the [101] plane. The S, O and N atoms are shown with octant shading.

approximately perpendicular to one another. The nonplanarity of the molecule and the presence of the pyridine ring affect the crystal packing as well. As in 1-3 there are rows of molecules, in this case



Fig. 7. ORTEP diagram of the molecular structure of **4** showing the atom labelling scheme.



Fig. 8. ORTEP packing diagram of 4 showing the outline of the unit cell. View is approximately along the c axis. The S and N atoms are shown with octant shading.

running parallel to the *a* axis, with adjacent rows inverted. In **4** the rows are interleaved so as to afford a face-to-face contact between the pyridine rings about the center of inversion. This type of interaction is not observed in the furfuralidene derivatives. The triazole moieties are arranged so that the N2–H1…S hydrogen bonds are preserved (1.10; 2.20 Å; 166°).

#### 4. Discussion

Previously we [6], [15] and others [7] have found that 4-amine-3-methyl-4,5-dihydro-1H-1,2,4-triazole-5-thione forms bidentate complexes with the divalent first row transition metals Mn-Zn, coordinating to the metal ion via the thione and amine substituents on the triazole ring. It is of interest to examine the coordination chemistry of larger triazole derivatives, such as the four molecules in this study, that have organic functional groups on the amine N atom. Initial efforts to obtain crystals of the metal complexes suitable for structural studies have not been successful. One reason may be that in each case the conformation adopted by the free ligand in the solid state places the organic group attached to N4 on the same side of the N1-N4 bond as the S atom. Thus the C3 atom is blocking N4 from chelating a metal ion together with the S atom. If this is also the dominant conformation of these molecules in solution, it would help to explain the apparent tendency not to bind strongly to form metal chelates. This conformation presumably occurs, in part, to avoid non-bonded contacts between the H atoms on C3 (or C6 in 4) and those on the R group attached to C2. Other S-C-N-N-R' compounds have been observed to bind to metal ions in either a monodentate fashion through S [16] or in the desired chelating S, N arrangement [17], [18]. In the former case, the R' group is positioned as in 1-4, while in the latter cases, 2-acetylpyridine [17] and 2-formylpyridine [18] thiosemicarbazones, the pyridine N atom also coordinates to the metal making the ligand tridentate. These molecules adopt conformations as free ligands which have the coordinating amine N atom and thione S atom trans to one another across the C-N bond. Whether a similar coordination mode is possible for 4 remains to be determined. The ability of the molecules in this study to adopt conformations more favorable to metal chelation depends in part on the ease of rotation about the N1-N4 bond. This bond is longer (1.385(3)-1.420(4) Å) than the correspoding bond in the heterocyclic thiosemicarbazones (1.375(2) and 1.370(2) Å) [18]. Alternatively, replacing the R group with H, or choosing R and R' groups capable of forming intramolecular hydrogen bonds might result in greater stability for the conformation which places the lone pair of the amine N atom adjacent to the S atom, thus leading to greater likelihood of chelation. Experiments to test these ideas using reaction conditions, such as acidic media [19], which have been successful in related systems, are underway.

#### 5. Supplementary material

Hydrogen atom positions and complete tables of bond distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Additional crystallographic data can be obtained from the authors (P.J.S.).

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