

RefinementRefinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.038$ $wR(F^2) = 0.092$ $S = 0.901$

1571 reflections

162 parameters

All H-atom parameters
refined $w = 1/[\sigma^2(F_o^2) + (0.0615P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.21 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.22 \text{ e } \text{\AA}^{-3}$

Extinction correction: none

Scattering factors from

*International Tables for
Crystallography* (Vol. C)Table 1. *Hydrogen-bonding geometry* (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...O2 ⁱ	0.91 (2)	1.86 (2)	2.775 (2)	175 (2)
C62—H62A...O4 ⁱⁱ	1.01 (2)	2.51 (2)	3.518 (2)	178 (2)
C42—H42A...O2 ⁱⁱⁱ	1.01 (2)	2.45 (2)	3.380 (3)	152 (1)

Symmetry codes: (i) $-x, 1 - y, 2 - z$; (ii) $1 - x, 1 - y, 1 - z$;
(iii) $-1 - x, -y, 1 - z$.The refined N—H distance is 0.91 (2) \AA and the refined C—H distances are in the range 0.95 (2)–1.03 (2) \AA .Data collection: *COLLECT* (Nonius, 1998). Cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997). Data reduction: *DENZO-SMN*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b). Molecular graphics: *ORTEPIII* (Johnson & Burnett, 1997). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1365). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 2111–2114**Two Schiff base derivatives of 4-amino-3-propyl-1,2,4-triazole-5-thione**ROBERT M. McCARRICK,^a PHILIP J. SQUATTRITO,^{a*}
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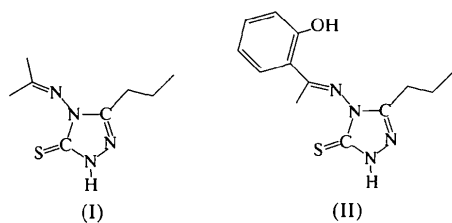
(Received 18 June 1999; accepted 6 September 1999)

Abstract

The Schiff base compounds 4-isopropylideneamino-3-propyl-4,5-dihydro-1*H*-1,2,4-triazole-5-thione, C₈H₁₄N₄S, (I), and 4-[1-(2-hydroxyphenyl)ethylideneamino]-3-propyl-4,5-dihydro-1*H*-1,2,4-triazole-5-thione, C₁₃H₁₆N₄OS, (II), contain essentially planar triazole rings in which the corresponding bond distances and angles are equivalent within experimental error. Both compounds show the same *anti* conformation of the propyl groups, however, they differ in the positioning of the functional groups on N atom. The isopropylidene group in (I) and the 1-(2-hydroxyphenyl)ethylideneamino group in (II) are rotated approximately 77° in opposite directions about the N—N bond relative to the triazole ring. In the case of (II), the adopted conformation permits an intramolecular hydrogen bond between the hydroxyl-H atom and the amine-N atom. Both compounds form hydrogen-bonded dimers through N—H...S interactions involving the thione-S atom and the adjacent protonated N atom on the ring. The structural features of these compounds are compared with those of similar amine- and thione-substituted triazoles and their Schiff base derivatives.

Comment

As part of a continuing study of Schiff bases of amine- and thione-substituted triazoles (Sen *et al.*, 1998) and their metal complexes (Sen *et al.*, 1996, 1997; Clark *et al.*, 1999), we have structurally characterized the compounds 4-isopropylideneamino-3-propyl-1,2,4-triazole-5-thione, (I), and 4-[1-(2-hydroxyphenyl)ethylideneamino]-3-propyl-1,2,4-triazole-5-thione, (II). As



shown in Fig. 1, (I) exists as the thione (C=S) tautomer with the proton H1 bonded to the adjacent N atom. This arrangement together with the bond distances and angles within the ring are consistent with the reported structures of similarly substituted triazoles (Escobar-Valderrama *et al.*, 1989; Weng, 1992). The ring is reasonably planar with an average deviation of 0.009 (2) Å. The propyl group is nearly coplanar with the ring [torsion angle N4—C2—C3—C4 10.1 (3)°] and adopts the stable *anti*-conformation [torsion angle C2—C3—C4—C5 -179.2 (2)°]. By contrast, the isopropylidene group is rotated well out of the plane of the ring [torsion angle C1—N2—N1—C6 77.9 (2)°] and the amine N1 atom is displaced 0.245 (2) Å below the ring. These distortions may occur to avoid non-bonded interactions between the S atom and methyl-H atoms of C8. Perhaps unexpectedly, the S—C1—N2 angle is nearly 2° smaller than S—C1—N3 (Table 1). The molecules pack in the triclinic cell so as to form dimers through a pair of symmetry-related linear N3—H1...S hydrogen bonds [0.88 (2), 2.43 (2) Å, 174 (2)°], shown as narrow lines in Fig. 2. This feature appears to be common to Schiff bases of 4-amino-3-alkyl-1,2,4-triazole-5-thiones (Sen *et al.*, 1998).

Compound (II) (see Fig. 3) also contains a planar triazole ring [mean deviation from the plane 0.006 (2) Å] within which the bond distances and angles do not differ significantly from those in (I). The propyl group is positioned similarly with an *anti*-conformation [torsion

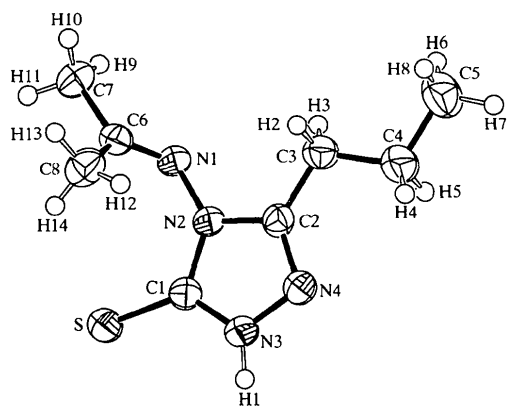


Fig. 1. An ORTEP diagram (Johnson, 1976) showing the molecular structure and atom-labeling scheme of (I). The displacement ellipsoids of the non-H atoms are shown at the 50% probability level.

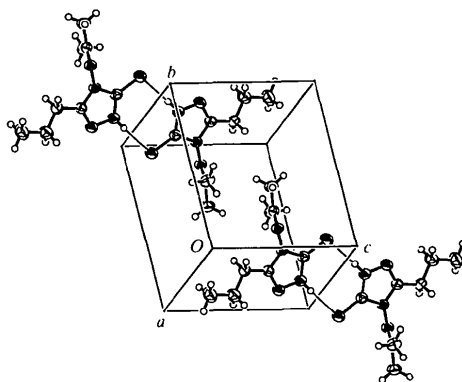


Fig. 2. An ORTEP diagram (Johnson, 1976) showing the crystal packing of (I). The S and N atoms are shown with octant shading. Intermolecular H...S hydrogen bonds are shown by narrow lines. The displacement ellipsoids of the non-H atoms are shown at the 50% probability level.

angle C2—C3—C4—C5 178.3 (3)°] and atoms C4 and C5 only *ca* 0.35 Å out of the plane of the ring [torsion angle N4—C2—C3—C4 19.6 (5)°]. The functional group on N1 is rotated in the opposite direction from that in (I) [*i.e.* away from the viewer in Fig. 3, torsion angle C1—N2—N1—C6 -76.7 (3)°]. The dihedral angle between the rings is 108°. The amine N1 atom is only *ca* 0.07 Å below the plane of the ring. The overall conformation of the 1-(2-hydroxyphenyl)ethylideneamino group is such as to permit an intramolecular hydrogen bond between the hydroxyl group and the amine-N atom [O—H9...N1 0.89 (3), 1.75 (3) Å, 150 (3)°]. As in (I), the S—C1—N2 angle is

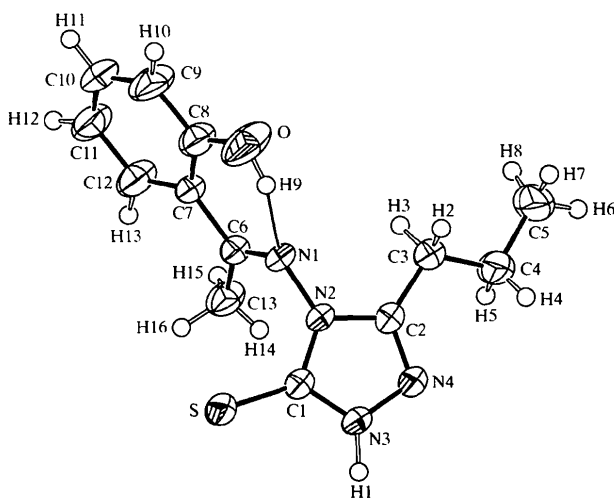


Fig. 3. An ORTEP diagram (Johnson, 1976) showing the molecular structure and atom-labeling scheme of (II). The displacement ellipsoids of the non-H atoms are shown at the 50% probability level. The intramolecular H9...N1 hydrogen bond is shown as a narrow line.

ca 2.5° smaller than S—C1—N3 despite the potential non-bonded interactions with the C13 methyl group. Small but significant differences occur in the N1—N2 and N1—C6 bond lengths between the two compounds. The N—N distance is shorter and the C—N distance is longer in (II). As the packing diagram (Fig. 4) reveals, the molecules are associated by the same type of hydrogen bonding as in (I): N3—H1···S 0.98 (2), 2.34 (2) Å, 175 (2)°.

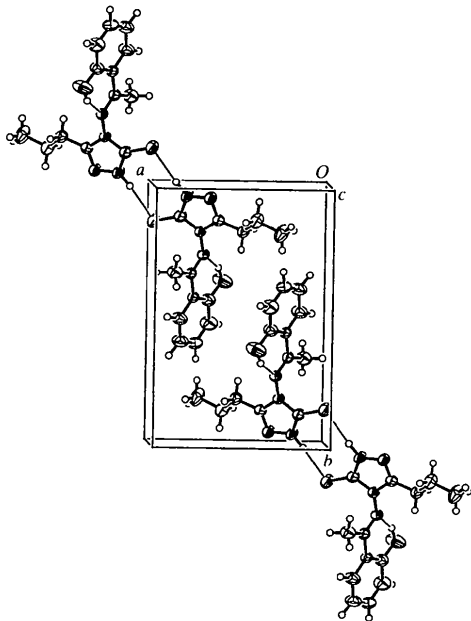


Fig. 4. An ORTEP diagram (Johnson, 1976) showing the crystal packing of (II). The S, O and N atoms are shown with octant shading. Intermolecular H···S hydrogen bonds are shown by narrow lines. The displacement ellipsoids of the non-H atoms are shown at the 50% probability level.

The similar compound 4-furfuralideneamino-3-propyl-1,2,4-triazole-5-thione (Sen *et al.*, 1998) differs from (I) and (II) in that the propyl group has a *gauche* conformation [C—C—C—C torsion angle $-71.9(4)^\circ$], though the middle C atom is only 6° out of the plane of the ring. The furfuralidene group is rotated only half as much about the N—N bond [torsion angle $-36.5(4)^\circ$] as the groups in (I) and (II). By contrast, 4-(2-acetylpyridylideneamino)-3-ethyl-1,2,4-triazole-5-thione (Sen *et al.*, 1998), which differs from (II) only in having ethyl in place of propyl and nitrogen in place of C—O—H in the 2-position of the ring, adopts a very different conformation. The 2-acetylpyridylidene group is rotated $82.3(5)^\circ$ about the N—N bond in the opposite direction from the 1-(2-hydroxyphenyl)ethylideneamino group in (II) and the phenyl-N atom is directed away from the

amine-N atom, unlike the hydroxyl group in (II). The dihedral angle between the rings, 107° , is nearly the same as that in (II). These studies show that although the triazole ring itself is rather invariant in its structure when substituted with various functional groups, the overall structure of the molecule can undergo large conformational changes with only small alterations in the identities of the functional groups. Moreover, in all of the Schiff base derivatives of 4-amino-3-alkyl-1,2,4-triazole-5-thiones examined so far, the solid state structure shows the amine functional group directed towards the S atom (*i.e.* the C—N—N—C torsion angle is less than 90°). This has implications for the potential of these molecules to form sulfur—nitrogen chelate complexes (Sen *et al.*, 1997), since the observed conformation of the free molecules would preclude such an interaction with a metal ion.

Experimental

High quality crystals of (I) were obtained upon evaporation of a solution of 4-amino-3-propyl-1,2,4-triazole-5-thione (apt) in acetone. To prepare the compound in bulk, apt (3.12 g, 0.0195 mol) was dissolved in acetone (30 ml) and heated gently below boiling for 30 min. The Schiff base (I) was isolated at 77% yield and was characterized by melting range (451–455 K) and mass spectrometry [m/z (M^+) 198]. Compound (II) was prepared by refluxing an equimolar mixture of apt and 2-hydroxyacetophenone in ethanol for 4 h. The reaction mixture was then allowed to stand undisturbed for 2 d. Large colorless crystals of (II) were obtained in 75% yield (m.p. 358 K).

Compound (I)

Crystal data

$C_8H_{14}N_4S$
 $M_r = 198.29$
 Triclinic
 $P\bar{1}$
 $a = 8.425(3) \text{ \AA}$
 $b = 9.427(2) \text{ \AA}$
 $c = 8.087(2) \text{ \AA}$
 $\alpha = 103.64(2)^\circ$
 $\beta = 109.00(2)^\circ$
 $\gamma = 108.39(2)^\circ$
 $V = 533.6(3) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.234 \text{ Mg m}^{-3}$
 D_m not measured

Data collection

Rigaku AFC-6S diffractometer
 ω - 2θ scans
 Absorption correction: none
 2023 measured reflections
 1880 independent reflections
 1879 reflections with
 $I > 0$

Mo $K\alpha$ radiation
 $\lambda = 0.7107 \text{ \AA}$
 Cell parameters from 17 reflections
 $\theta = 16.4\text{--}20.8^\circ$
 $\mu = 0.255 \text{ mm}^{-1}$
 $T = 296 \text{ K}$
 Parallelepiped
 $0.25 \times 0.12 \times 0.10 \text{ mm}$
 Colorless

$R_{int} = 0.016$
 $\theta_{max} = 25^\circ$
 $h = 0 \rightarrow 10$
 $k = -11 \rightarrow 11$
 $l = -10 \rightarrow 10$
 3 standard reflections every 150 reflections
 intensity decay: 0.50%

Refinement

Refinement on F	$\Delta\rho_{\max} = 0.22 \text{ e } \text{\AA}^{-3}$
$R = 0.052$	$\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$
$wR = 0.037$	Extinction correction:
$S = 2.27$	Zachariasen (1968) type 2
1879 reflections	Gaussian isotropic
161 parameters	Extinction coefficient:
Only coordinates of H atoms	$50(4) \times 10^{-7}$
refined	Scattering factors from <i>International Tables for X-ray Crystallography</i> (Vol. IV)
$w = 4F_o^2/[\sigma^2(F_o^2)]$	
$(\Delta/\sigma)_{\max} = 0.014$	

Table 1. Selected geometric parameters (\AA , $^\circ$) for (I)

S—C1	1.686 (2)	N3—N4	1.384 (2)
N1—N2	1.423 (2)	N3—C1	1.332 (2)
N1—C6	1.280 (2)	N4—C2	1.304 (2)
N2—C1	1.372 (2)	C2—C3	1.489 (3)
N2—C2	1.377 (2)		
N2—N1—C6	114.3 (2)	N2—C1—N3	103.0 (2)
N1—N2—C1	125.3 (2)	N2—C2—N4	110.6 (2)
N1—N2—C2	124.2 (1)	N2—C2—C3	122.9 (2)
C1—N2—C2	108.7 (2)	N4—C2—C3	126.6 (2)
N4—N3—C1	114.0 (2)	N1—C6—C7	115.2 (2)
N3—N4—C2	103.7 (2)	N1—C6—C8	127.1 (2)
S—C1—N2	127.6 (1)	C7—C6—C8	117.7 (2)
S—C1—N3	129.4 (2)		

Compound (II)

Crystal data

C₁₃H₁₆N₄OS
 $M_r = 276.36$
 Triclinic
 $P\bar{1}$
 $a = 9.539(2) \text{ \AA}$
 $b = 14.177(2) \text{ \AA}$
 $c = 5.275(2) \text{ \AA}$
 $\alpha = 99.64(2)^\circ$
 $\beta = 95.69(3)^\circ$
 $\gamma = 90.03(1)^\circ$
 $V = 699.8(4) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.311 \text{ Mg m}^{-3}$
 D_m not measured

Data collection

Rigaku AFC-6S diffractometer
 ω - 2θ scans
 Absorption correction: none
 2627 measured reflections
 2466 independent reflections
 2465 reflections with $I > 0$

Refinement

Refinement on F^2
 $R(F) = 0.063$
 $wR(F^2) = 0.088$
 $S = 2.23$
 2465 reflections
 220 parameters
 Only coordinates of H atoms refined

Mo $K\alpha$ radiation
 $\lambda = 0.7107 \text{ \AA}$
 Cell parameters from 19 reflections
 $\theta = 15.6$ – 20.5°
 $\mu = 0.219 \text{ mm}^{-1}$
 $T = 296 \text{ K}$
 Block
 $0.35 \times 0.12 \times 0.04 \text{ mm}$
 Colorless

$R_{\text{int}} = 0.020$
 $\theta_{\text{max}} = 25.03^\circ$
 $h = 0 \rightarrow 11$
 $k = -17 \rightarrow 17$
 $l = -6 \rightarrow 6$
 3 standard reflections every 150 reflections intensity decay: 0.20%

$w = 4F_o^2/[\sigma^2(F_o^2)]$
 $(\Delta/\sigma)_{\max} = 0.0081$
 $\Delta\rho_{\max} = 0.26 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 2. Selected geometric parameters (\AA , $^\circ$) for (II)

S—C1	1.678 (2)	N2—C2	1.385 (3)
O—C8	1.361 (3)	N3—N4	1.381 (3)
N1—N2	1.412 (2)	N3—C1	1.339 (3)
N1—C6	1.303 (3)	N4—C2	1.304 (3)
N2—C1	1.372 (3)	C2—C3	1.490 (3)
N2—N1—C6	114.9 (2)	N2—C1—N3	102.6 (2)
N1—N2—C1	126.2 (2)	N2—C2—N4	109.8 (2)
N1—N2—C2	124.3 (2)	N2—C2—C3	123.0 (2)
C1—N2—C2	109.3 (2)	N4—C2—C3	127.2 (2)
N4—N3—C1	114.0 (2)	N1—C6—C7	115.7 (2)
N3—N4—C2	104.3 (2)	N1—C6—C13	124.6 (2)
S—C1—N2	127.4 (2)	C7—C6—C13	119.7 (2)
S—C1—N3	130.0 (2)		

The H atoms were located on difference electron-density maps and their positions refined with isotropic displacement parameters fixed at 1.2 times that of the attached atom at the time of their inclusion; C—H ranges: (I) 0.90 (3)–1.01 (2) \AA ; (II) 0.89 (2)–1.03 (3) \AA ; C—C ranges: (I) 1.488 (3)–1.509 (3) \AA ; (II) aliphatic 1.477 (3)–1.509 (4) \AA , aromatic 1.355 (4)–1.401 (4) \AA .

For both compounds, data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSCIAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1991); program(s) used to solve structures: *MITHRIL* (Gilmore, 1983); program(s) used to refine structures: *TEXSAN*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1094). Services for accessing these data are described at the back of the journal.

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