Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

4,4′-Butane-1,4-diylbis[3-ethyl-1*H*-1,2,4-triazol-5(4*H*)-one] and 4-hydroxy-3-*n*-propyl-1*H*-1,2,4-triazol-5(4*H*)-one

Nazan Ocak İskeleli,[a]* Şamil Işık,[a] Kemal Sancak,[b] Selami Şaşmaz,[b] Yasemin Ünver[b] and Mustafa Er[b]

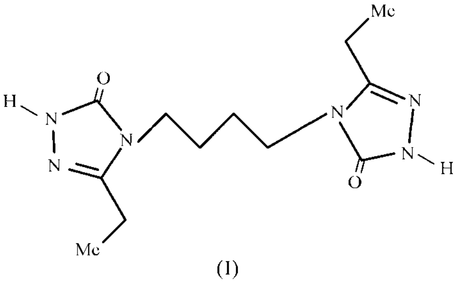
[a]Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayís University, TR-55139 Kurupelit–Samsun, Turkey, and [b]Karadeniz Teknik University, Rize Art and Science Faculty, Department of Chemistry, Rize, Turkey
Correspondence e-mail: nocak@omu.edu.tr

Received 10 February 2005
Accepted 16 March 2005
Online 13 May 2005

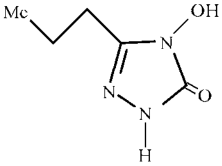
The title compounds, $C_{12}H_{20}N_6O_2$, (I), and $C_5H_9N_3O_2$, (II), display the characteristic features of 1,2,4-triazole derivatives. Compound (I) lies about an inversion centre which is at the mid-point of the central C—C bond. Compound (II) also contains a planar 1,2,4-triazole ring but differs from (I) in that it has a hydroxy group attached to the ring. Molecules of (I) are held together in the crystal structure by intermolecular N—H···O contacts and by weak π–π stacking interactions between the 1,2,4-triazole moieties. Compound (II) contains intermolecular O—H···O and N—H···O hydrogen bonds.

Comment

Recently, much attention has been focused on 1,2,4-triazole derivatives for their broad-spectrum fungicidal, insecticidal, herbicidal, anticonvulsant, antitumour and plant growth regulatory activities (Tsuda & Itoh, 2004; Chai *et al.*, 2003; Er-Rahimini & Mornet, 1992; Nakib *et al.*, 1994; Jenkins *et al.*, 1989). Disubstituted 1,2,4-triazole derivatives have also been reported to show antituberculotic activities (İkizler *et al.*, 1998). In a previous work, we reported that some 1,2,4-triazol-5-one compounds have antimicrobial effects (Demirbaş *et al.*, 2004). 3-Amino-1,2,4-triazole has been recognized as an inhibitor of chloroplast development, affecting both caretenoid and chlorophyll pigments (Wolf, 1960). The coordination chemistry of azoles acting as ligands for the production of organometallic compounds in the context of modelling biological systems has attracted much interest. In the 4-hydroxyazole tautomer (İkizler & Sancak, 1992), the presence of the O atom of the hydroxy group adjacent to the donor N atom of the heterocyclic ring enables the formation of a five-membered chelate ring with transition metal cations. Therefore, the formation of a chelate *via* an oxy/hydroxy tautomer is one of the major factors for the presence of intermolecular or intramolecular interactions (Kurtziel *et al.*, 2003). Spectroscopic and crystal structure data of some 1,2,4-triazoles have been reported previously (Çoruh *et al.*, 2003; Zhu *et al.*, 2000; Li *et al.*, 2004). In this paper, we present the synthesis and molecular and crystal structures of 4,4′-butane-1,4-diylbis[3-ethyl-1*H*-1,2,4-triazol-5(4*H*)-one], (I), and 4-hydroxy-3-*n*-propyl-1,2,4-triazol-5(4*H*)-one, (II).



(I)



(II)

Views of compounds (I) and (II), including the atom-numbering schemes, are shown in Figs. 1 and 2, and selected geometric parameters are shown in Tables 1 and 3. Compound (I) consists of two 1,2,4-triazole rings, with ethyl groups connected to the 3-positions of the rings, carbonyl O atoms in the 5-positions of the rings and a butane group connecting the two rings at the 4-positions. Compound (II) consists of a 1,2,4-triazole ring with an *n*-propyl group connected to the 3-position of the ring, a carbonyl O atom on the 5-position of the ring and a hydroxy group on the 4-position of the ring.

In the crystal structure of (I), a strong intermolecular N1—H1···O1$(x - \frac{1}{2}, y, -z + \frac{1}{2})$ hydrogen-bonding interaction is formed (Table 2). Compound (I) also exhibits a weak π–π stacking interaction between the 1,2,4-triazole moieties, with a centroid–centroid distance of 3.917 (3) Å for $Cg\cdots$

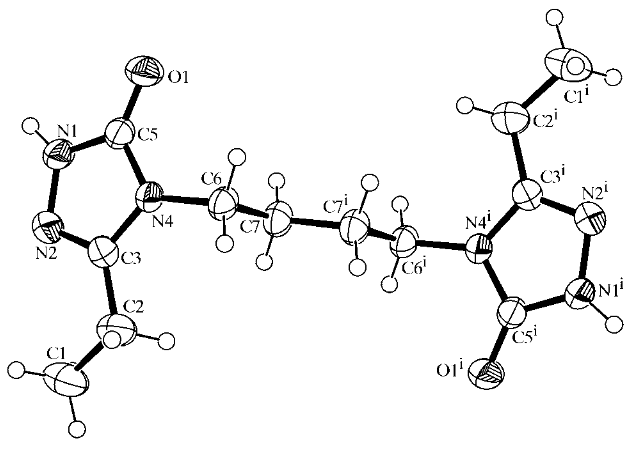


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii (symmetry code as in Table 1).

DOI: 10.1107/S0108270105008449

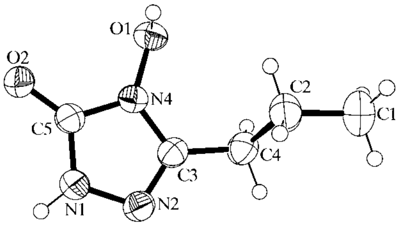


Figure 2
The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

$Cg(1-x, -y, -z)$. The crystal structure of (II) is formed by intermolecular hydrogen-bonding interactions, *viz.* O1—H1···O1$(-x, y, -z+\frac{3}{2})$ and N1—H2···O2$(-x, -y+1, -z+1)$ (Table 4). These bonds are consistent with those reported by Li *et al.* (2004).

Experimental

For the synthesis of (I), ethylpropionatethoxycarbonylhydrazone (0.02 mol) was treated with a solution of 1,4-diaminobutane (0.01 mol) in water (50 ml), and the mixture was refluxed for 6 h. After cooling, the precipitate which formed was recrystallized from ethanol–acetone (1:5) (yield 58%; m.p. 550–551 K). IR (cm^{-1}): 3155, 3053 (NH), 1675 (C═O), 1563 (C═N); ^{1}H NMR: δ 1.63 (*m*, 2CH$_2$), 1.85 (*s*, 2CH$_3$), 2.54 (*q*, 2CH$_2$), 3.70 (*t*, 2NCH$_2$), 11.35 (*s*, 2NH). ^{13}C NMR: δ 13.04 (2CH$_3$), 18.67 (2CH$_2$), 22.86 (2CH$_2$), 38.98 (2NCH$_2$), 149.51 (2 × C3-triazole), 152.47 (2 × C5-triazole). For the synthesis of (II), hydroxyamic acid *n*-propylethoxycarbonylhydrazide (0.01 mol) was dissolved in methanol (50 ml) and treated with 2 *N* NaOH (50 ml) with constant shaking. The mixture was refluxed for 2 h and cooled. After acidification with dilute HCl, the mixture was evaporated and the residue was dried. The solid residue was extracted with absolute ethanol. The extracts were collected and evaporated. Recrystallization of the crude product from acetone gave pure compound (II) (yield 72%; m.p. 406–407 K). IR (cm^{-1}): 3310 (OH), 3150 (NH), 1735 (C═O), 1652 (C═N); ^{1}H NMR: δ 0.85 (*t*, CH$_3$), 1.56 (sextet, CH$_2$), 2.42 (*t*, CH$_2$), 10.90 (*s*, OH); 11.35 (*s*, NH). ^{13}C NMR: δ 13.35 (CH$_3$), 18.71 (CH$_2$), 25.98 (CH$_2$), 145.65 (C3-triazole), 151.60 (C5-triazole).

Compound (I)

Crystal data

$C_{12}H_{20}N_6O_2$
$M_r = 280.34$
Orthorhombic, *Pbca*
$a = 8.326$ (5) Å
$b = 13.588$ (5) Å
$c = 12.401$ (5) Å
$V = 1403.0$ (11) Å^3
$Z = 4$
$D_x = 1.327$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 8578 reflections
$\theta = 1.5$–27.1°
$\mu = 0.10$ mm^{-1}
$T = 293$ (2) K
Plate, colourless
0.80 × 0.54 × 0.22 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
$T_{\min} = 0.951$, $T_{\max} = 0.992$
11 694 measured reflections
1379 independent reflections

832 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.073$
$\theta_{\max} = 26.0°$
$h = -10 \rightarrow 9$
$k = -16 \rightarrow 16$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.072$
$S = 0.80$
1379 reflections
92 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0366P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.16$ e Å^{-3}
$\Delta\rho_{\min} = -0.14$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0078 (9)

Table 1
Selected geometric parameters (Å, °) for (I).

C3—N2	1.2938 (19)	C5—N4	1.3710 (19)
C3—N4	1.3742 (18)	C7—C7$^{\rm i}$	1.514 (3)
C5—O1	1.2396 (18)	N1—N2	1.3846 (18)
C5—N1	1.341 (2)		
N4—C6—C7—C7$^{\rm i}$	−179.05 (16)		

Symmetry code: (i) $-x+1, -y+1, -z$.

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1$^{\rm ii}$	0.86	1.96	2.805 (2)	166

Symmetry code: (ii) $x-\frac{1}{2}, y, -z+\frac{1}{2}$.

Compound (II)

Crystal data

$C_5H_9N_3O_2$
$M_r = 143.15$
Monoclinic, $C2/c$
$a = 27.010$ (3) Å
$b = 4.2067$ (3) Å
$c = 12.1089$ (14) Å
$\beta = 91.715$ (9)°
$V = 1375.2$ (2) Å^3
$Z = 8$

$D_x = 1.383$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5155 reflections
$\theta = 1.5$–26.7°
$\mu = 0.11$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.50 × 0.35 × 0.22 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
$T_{\min} = 0.946$, $T_{\max} = 0.972$
5874 measured reflections
1347 independent reflections

1207 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\max} = 26.0°$
$h = -32 \rightarrow 32$
$k = -4 \rightarrow 5$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.098$
$S = 1.13$
1347 reflections
95 parameters
H atoms refined by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 0.2687P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.16$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}

Table 3
Selected interatomic distances (Å) for (II).

C3—N2	1.298 (2)	C5—N4	1.364 (2)
C3—N4	1.370 (2)	N1—N2	1.3873 (14)
C5—O2	1.250 (14)	N4—O1	1.3706 (12)
C5—N1	1.336 (2)		

Table 4
Hydrogen-bond geometry (Å, °) for (II).

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
$\mathrm{O1-H1}\cdots\mathrm{O1}^{\mathrm{iii}}$	0.97 (2)	1.64 (2)	2.6000 (12)	170 (2)
$\mathrm{N1-H2}\cdots\mathrm{O2}^{\mathrm{iv}}$	0.86	1.99	2.8292 (13)	166

Symmetry codes: (iii) $-x, y, -z+\frac{3}{2}$; (iv) $-x, -y+1, -z+1$.

The hydroxy H atom in (II) was found in a difference map and refined. All other H atoms were located geometrically and treated using a riding model, fixing the C—H distances at 0.97 ($\mathrm{CH_2}$ H atoms) and 0.96 Å ($\mathrm{CH_3}$ H atoms), the N—H distances at 0.86 Å and the O—H distances at 0.82 Å.

For both compounds, data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ1000). Services for accessing these data are described at the back of the journal.

References

Burnett, M. N. & Johnson, C. K. (1996). Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Chai, B., Qian, X., Cao, S., Liu, H. & Song, G. (2003). *Arkivoc*, Part ii, pp. 141–145. URL: http://www.arkat-usa.org/ark/journal/2003/I02_Huang/ZH-700D/ZH-700D.asp.

Çoruh, U., Ustabaş, R., Sancak, K., Şaşmaz, S., Ağar, E. & Kim, Y. M. (2003). *Acta Cryst.* E**59**, o1277–o1279.

Demirbaş, N., Karaoğlu, S. A., Demirbaş, A. & Sancak, K. (2004). *Eur. J. Med. Chem.* **39**, 793–804.

Er-Rahimini, A. & Mornet, R. (1992). *J. Heterocycl. Chem.* **29**, 1561–1566.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Íkizler, A. A., Demirbaş, A., Cohansson, C. B., Çelik, C., Serdar, M. & Yüksek, H. (1998). *Acta Pol. Pharm. Drug Res.* **55**, 117–123.

Íkizler, A. A. & Sancak, K. (1992). *Monatsh. Chem.* **123**, 257–263.

Jenkins, T. C., Stratford, I. J. & Stephens, M. A. (1989). *Anticancer Drug Des.* **4**, 145–160.

Kurtziel, K., Glowiak, T. & Jezierska, J. (2003). *Inorg. Chem. Commun.* **6**, 459–461.

Li, B., Zhu, X., Zhou, J., Peng, Y. & Zhang, Y. (2004). *Polyhedron*, **23**, 3133–3141.

Nakib, A. T., Meegen, J. M. & Burke, L. M. (1994). *J. Chem. Res.* (*S*), pp. 170–171.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Stoe & Cie (2002). *X-AREA* (Version 1.18) and *X-RED32* (Version 1.04). Stoe & Cie, Darmstadt, Germany.

Tsuda, M. & Itoh, H. K. S. (2004). *Pest Manag. Sci.* **60**, 881–886.

Wolf, F. T. (1960). *Nature* (*London*), **188**, 164–169.

Zhu, D., Zhu, X., Xu, L., Shao, S., Raj, S. S. S., Fun, H.-K. & You, X. (2000). *J. Chem. Crystallogr.* **30**, 429–432.