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C—H···O and C—H···π interactions in 1-acetyl-4-(*p*-chlorobenzylidene-amino)-3-ethyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one

Ufuk Çoruh,[a]* Bahittin Kahveci,[b] Selami Şaşmaz,[b] Erbil Ağar,[c] Youngme Kim[d] and Ahmet Erdönmez[e]

[a]Department of Computer Education and Instructional Science, Educational Faculty, Ondokuz Mayıs University, 55200-Atakum-Samsun, Turkey, [b]Department of Chemistry, Rize Art and Science Faculty, Karadeniz Teknik University, Rize, Turkey, [c]Department of Chemistry, Art and Science Faculty, Ondokuz Mayıs University, 55139-Samsun, Turkey, [d]Department of Chemistry, Ewha Womans University, Seoul 120-750, South Korea, and [e]Department of Physics, Art and Science Faculty, Ondokuz Mayıs University, 55139-Samsun, Turkey
Correspondence e-mail: ucoruh@hotmail.com

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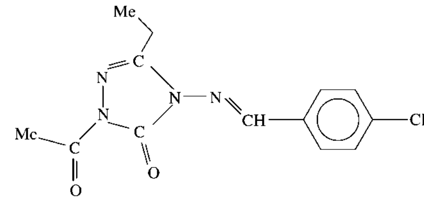
The title compound, $C_{13}H_{13}ClN_4O_2$, contains both a phenyl and a triazole ring, both of which are approximately coplanar with the entire molecule. The triazole ring has substituents at the 1-, 2- and 4-positions. Intramolecular C—H···O and C—H···N interactions, together with intermolecular C—H···O and C—H···π interactions, help to stabilize the structure.

Comment

1,2,4-Triazole ring systems are typical planar six-π-electron partially aromatic systems, and 1,2,4-triazole and its derivatives are used as starting materials for the synthesis of many heterocycles (Desenko, 1995). In addition to having extensive chemical significance (Benson, 1967; Temple, 1981), the 1,2,4-triazole nucleus is also associated with diverse pharmacological properties, such as analgesic, anti-asthmatic, diuretic, anti-inflammantory, fungicidal, bactericidal and pesticidal activities (Bennur *et al.*, 1976; Webb & Parsons, 1977; Heubach *et al.*, 1980; Mohamed *et al.*, 1993). Knowledge of the molecular structure of these compounds is important in order to understand their reactivity under condensation reaction conditions. Therefore, the crystal structure of the title compound, (I), has been investigated and is reported here.

Compound (I) (Fig. 1) consists of a triazole ring with an acetyl group substituted on the N atom in the 1-position, an ethyl group substituted on the C atom in the 3-position, an oxo O atom substituted on the C atom at the 5-position and a *p*-chlorobenzylidenamine group substituted at the 4-position. The N═C bond lengths [N1═C7 = 1.272 (3) Å and N3═C9 = 1.278 (3) Å; Table 1] agree with values reported in the literature [1.261 (4) Å in the 4-amino-3-methyl-1,2,4-triazole-5-thione derivative of *p*-nitrobenzaldehyde (Liu *et al.*, 1999) and 1.267 (2) Å in 4-(4-hydroxybenzylidenamino)-4*H*-1,2,4-triazole hemihydrate (Zhu *et al.*, 2000)].



(I)

The presence of an acetyl group on atom N4 causes a lengthening of the N—N bond length [N3—N4 = 1.394 (3) Å] with respect to the corresponding bonds in 5-(2-chlorophenyl)-4-phenyl-3,4-dihydro-2*H*-1,2,4-triazole-3-thione [N—N = 1.374 (2) Å; Puviarasan *et al.*, 1999] and in 4-methyl-1,2,4-triazole and 1-methyltetrazole [N—N = 1.344 (2) Å; Palmer & Parsons, 1996]. The Cl—C3 bond length [1.737 (3) Å] agrees with those found in 3,5-bis(2-pyridyl)-4-(*p*-chlorophenyl)-4*H*-1,2,4-triazole (Wang *et al.*, 1998) and 5-(2-chlorophenyl)-4-phenyl-3,4-dihydro-2*H*-1,2,4-triazole-3-thione (Puviarasan *et al.*, 1999). Atom N4, carrying the acetyl substituent, is trigonal, the sum of the three bond angles around it being 359.96°. Atom N2, carrying the *p*-chlorobenzylideneamine substituent, is also trigonal, the sum of the three bond angles around it being 360°.

In (I), the 1,2,4-triazole ring (*A*; C8/N2/C9/N3/N4) and the phenyl ring (*B*; C1–C6) are planar, with the maximum deviation from the least-squares planes being 0.003 (2) Å for atom C8 and 0.004 (3) Å for atom C3. The dihedral angle between the planes of rings *A* and *B* is 6.13°, indicating that the whole molecule is nearly planar, which agrees well with the value observed in 1-acetyl-4-(*p*-chlorobenzylideneamino)-3-methyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one (Çoruh *et al.*, 2003).

There are intramolecular and intermolecular C—H···O interactions and intramolecular C—H···N interactions in the structure of (I). Firstly, atom C7 interacts with atom O1. Secondly, atom C13 interacts with atom N3 of the 1,2,4-triazole ring. Atom O2 of the acetyl group forms an intermolecular bifurcated hydrogen bond with the H atoms of ring *B* (atoms H4 and H5) of a symmetry-related molecule

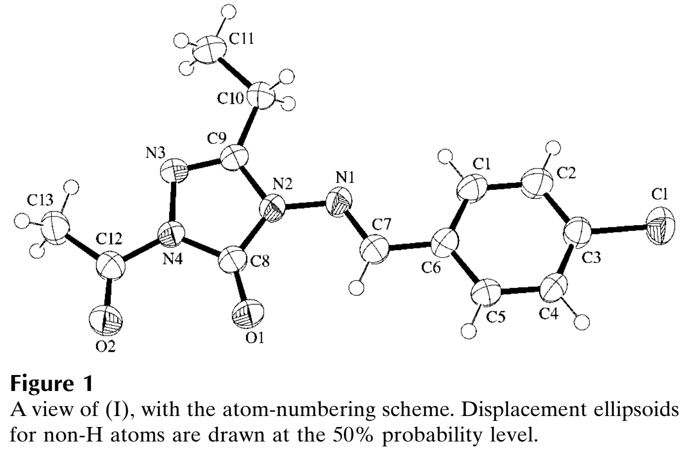


Figure 1
A view of (I), with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

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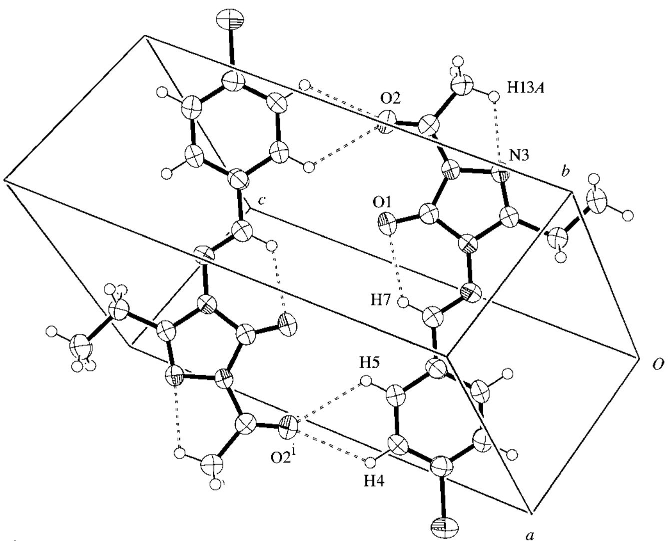

Figure 2
The hydrogen-bond network in (I); a view of the triclinic cell.

[C4···O2^{i} = 3.139 (3) Å and C5···O2^{i} = 3.152 (3) Å; symmetry code: (i) $1 - x$, $1 - y$, $1 - z$; Fig. 2 and Table 2].

The crystal structure also contains an intermolecular C—H···π contact involving the 1,2,4-triazole ring of a symmetry-related molecule at ($1 + x$, y, z) [C5···*Cg*1 = 3.694 (3) Å, H5···*Cg*1 = 3.34 Å and C5—H5···*Cg*1 = 105°; *Cg*1 is the centroid of ring *A* at ($1 + x$, y, z)] and two intermolecular C—H···π interactions in which atoms C10 and C13 interact with rings *B* of symmetry-related molecules at ($-1 + x$, y, z) and ($-1 + x$, $1 + y$, z) [C10···*Cg*2 = 3.633 (3) Å, H10*A*···*Cg*2 = 2.80 Å and C10—H10*A*···*Cg*2 = 145°; *Cg*2 is the centroid of ring *B* at ($-1 + x$, y, z); C13···*Cg*3 = 3.733 (3) Å, H13*B*···*Cg*3 = 3.17° and C13—H13*B*···*Cg*3 = 119°; *Cg*3 is the centroid of ring *B* at ($-1 + x$, $1 + y$, z)]. These interactions play a role in the structural packing of (I).

Experimental

4-(*p*-Chlorobenzylideneamino)-3-methyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one (0.01 mol) was treated with acetic anhydride (10 ml) and the mixture was refluxed for 30 min. After addition of absolute ethanol (30 ml) to the solution, the mixture was refluxed for 1 h and the product was filtered off and dried *in vacuo*. Several recrystallizations of this product from ethanol gave pure (I) (yield 82%; m.p. 454–455 K). IR (KBr, cm^{-1}): ν(C=O) 1769 and 1697, ν(C=N) 1623 and 1593, ν(benzoid ring) 820; ^{1}H NMR (p.p.m. in DMSO-d_6): δ 2.40 (*s*, 3H), 2.50 (*s*, acetyl, 3H), 7.36 (*d*, 2H, ArH), 7.60 (*d*, 2H, ArH), 9.36 (*s*, CH); ^{13}C NMR (in DMSO-d_6): δ 166.24 (acetyl C=O), 155.79 (N=CH), 151.18 (triazole C=O), 148.14, 133.68, 132.95, 132.13 (2C), 131.80 (2C), 23.61, 12.18.

Crystal data

$C_{13}H_{13}ClN_4O_2$	$Z = 2$
$M_r = 292.72$	$D_x = 1.435$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 6.341$ (2) Å	Cell parameters from 2907 reflections
$b = 8.6092$ (10) Å	$\theta = 2.5$–$26.0°$
$c = 13.083$ (2) Å	$\mu = 0.29$ mm^{-1}
$\alpha = 76.011$ (10)°	$T = 293$ (2) K
$\beta = 84.03$ (2)°	Prism, colourless
$\gamma = 78.26$ (2)°	$0.35 \times 0.20 \times 0.10$ mm
$V = 677.4$ (3) Å^3	

Data collection

Enraf–Nonius CAD-4 MACH3 diffractometer	$h = 0 \rightarrow 7$
$2\theta-\omega$ scans	$k = -10 \rightarrow 10$
2907 measured reflections	$l = -16 \rightarrow 16$
2654 independent reflections	3 standard reflections
1818 reflections with $I > 2\sigma(I)$	frequency: 60 min
$R_{int} = 0.017$	intensity decay: negligible
$\theta_{max} = 26.0°$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0885P)^2 + 0.0264P]$
$R(F) = 0.049$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.144$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.04$	$\Delta\rho_{max} = 0.40$ e Å^{-3}
2654 reflections	$\Delta\rho_{min} = -0.33$ e Å^{-3}
181 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cl—C3	1.737 (3)	N2—C9	1.379 (3)
O1—C8	1.206 (3)	N3—N4	1.394 (3)
O2—C12	1.193 (3)	N3—C9	1.278 (3)
N1—N2	1.378 (3)	N4—C8	1.390 (3)
N1—C7	1.272 (3)	N4—C12	1.403 (3)
N2—C8	1.390 (3)		
N2—N1—C7	119.2 (2)	N1—C7—C6	118.5 (2)
N1—N2—C8	131.2 (2)	O1—C8—N2	129.0 (2)
N1—N2—C9	119.79 (19)	O1—C8—N4	129.6 (2)
C8—N2—C9	109.04 (19)	N2—C8—N4	101.44 (19)
N4—N3—C9	104.71 (19)	N2—C9—N3	112.1 (2)
N3—N4—C8	112.72 (18)	N2—C9—C10	122.8 (2)
N3—N4—C12	120.04 (19)	N3—C9—C10	125.1 (2)
C8—N4—C12	127.2 (2)	O2—C12—N4	121.0 (2)
Cl—C3—C2	119.3 (2)	O2—C12—C13	124.5 (2)
Cl—C3—C4	119.5 (2)	N4—C12—C13	114.5 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···O2^{i}	0.93	2.54	3.139 (3)	123
C5—H5···O2^{i}	0.93	2.55	3.152 (3)	123
C7—H7···O1	0.93	2.26	2.931 (3)	128
C13—H13*A*···N3	0.96	2.18	2.721 (3)	114

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

H atoms were treated as riding atoms using *SHELXL*97 (Sheldrick, 1997) defaults, with methyl C—H distances of 0.96 Å and other C—H distances of 0.93 Å.

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992); cell refinement: *CAD*-4-*PC Software*; data reduction: *XCAD*4/*PC* (Harms, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1165). Services for accessing these data are described at the back of the journal.

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