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1-Acetyl-4-(*p*-chlorobenzylideneamino)-3-methyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.041
wR factor = 0.121
Data-to-parameter ratio = 14.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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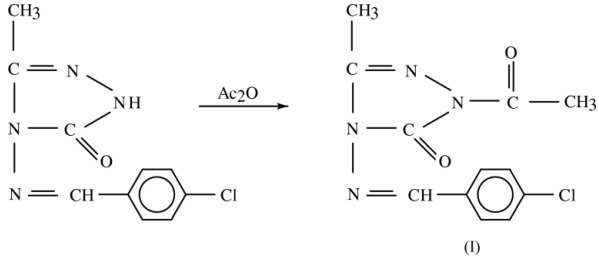
The molecules of the title compound, $C_{12}H_{11}ClN_4O_2$, are arranged as layers, stacking approximately along the *b* axis through C—H···O intermolecular hydrogen bonds. Some of these hydrogen-bond interactions which link two centrosymetrically related molecules generate π–π-stacking interactions between triazole rings.

Comment

The 1,2,4-triazole ring systems are typically planar 6π-electron partially aromatic systems, possessing an extensive chemistry (Temple, 1981; Benson, 1967). 1,2,4-Triazole and its derivatives are starting materials for the synthesis of many heterocycles (Desenko, 1995). In addition to its extensive chemical significance, the 1,2,4-triazole nucleus is also found to be associated with diverse pharmacological properties, such as analgesic, anti-asthmatic, diuretic, anti-inflammatory, fungicidal, bactericidal and pesticidal activities (Mohamed *et al.*, 1993; Sharma & Bahel, 1982; Heubach *et al.*, 1980; Bennur *et al.*, 1976; Webb & Parsons, 1977). Knowledge of the molecular structure of these compounds is important for understanding their reactivity under condensation reaction conditions. Therefore, the crystal structure analysis of the title compound, (I), has been carried out.



(I)

The structure of (I) (Fig. 1) consists of one 1,2,4-triazole ring (ring *A*: N2/C8/N3/N4/C11) with an acetyl group substituted at N3, and a methyl group and O atom substituted at C11 and C8, respectively. It also has a benzene ring (ring *B*: C1–C6). N=C bond lengths [N4=C11 = 1.278 (3) Å and N1=C7 = 1.269 (3) Å] agree with literature values (Puviarasan *et al.*, 1999; Liu *et al.*, 1999). The triazole ring is planar and the maximum deviation is −0.0026 (3) Å for atom C11. Atom O1 is also located in the plane. The bond lengths and angles in the acetyl group are comparable with reported values (Singh & Izydore, 1996). The dihedral angle between rings *A* and *B* is 7.29 (1)°, indicating that the whole molecule is nearly planar.

Atom H12*B* of the methyl group (C12) forms an intermolecular hydrogen bond with the acetyl group O atom (O2) of a symetry-related molecule [C12···O2^{ii} = 3.41 Å; symmetry

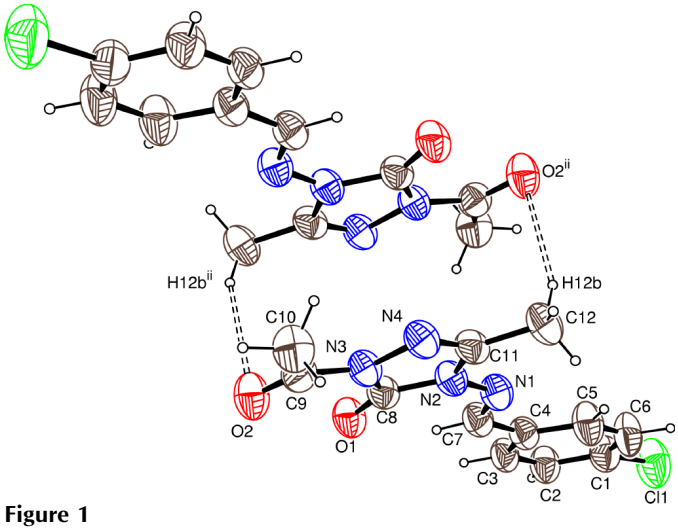


Figure 1
A view of (I) and its centrosymetrically related molecule, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

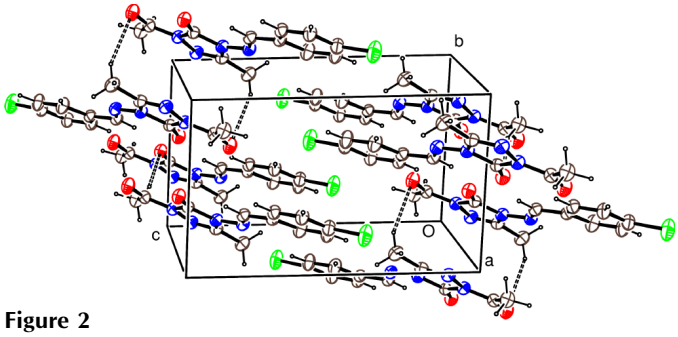


Figure 2
The hydrogen-bonding network observed in (I), viewed approximately along the [100] axis of the triclinic cell.

code: (ii) $1-x, -y, 2-z$]. Atom H10*C* of the acetyl group C10 is also involved in intermolecular hydrogen bonding with atom O1 [C10$\cdots$O1^{iii} = 3.500 (1) Å; symmetry code: (iii) $x-1, y, z$]. Furthermore, the sum of the van der Waals radii of H and O [1.20 + 1.52 = 2.72 Å; calculated using *PLATON* (Spek, 2000)] is somewhat longer than the distances found for C7—H7$\cdots$O1 [2.34 (1) Å] and C2—H2$\cdots$O2^{i} (2.52 Å) [symmetry code: (i) $2-x, 1-y, 2-z$], with C—H$\cdots$O angles of 123.7 (11) and 126°, respectively. Therefore, these contacts might be considered as weak interactions.

The crystal structure is stabilized not only by intermolecular hydrogen-bond interactions but also by π–π-stacking interactions occurring between the 1,2,4-triazole rings involved in hydrogen-bond interactions through an inversion center. The distance between the centroids of these rings is 3.4570 (8) Å.

Experimental

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

Crystal data

$C_{12}H_{11}ClN_4O_2$
M_r = 278.70
Triclinic, $P\overline{1}$
a = 6.910 (3) Å
b = 7.5682 (10) Å
c = 12.380 (3) Å
α = 93.13 (2)°
β = 98.20 (2)°
γ = 95.86 (2)°
V = 635.9 (3) Å^3
Z = 2
D_x = 1.456 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 8.2–13.4°
μ = 0.30 mm^{-1}
T = 293 (2) K
Plate, colorless
0.25 × 0.15 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 MACH3 diffractometer
ω–2θ scans
Absorption correction: none
2723 measured reflections
2503 independent reflections
1527 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
θ_{max} = 26.0°
$h = 0 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -15 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity decay: 0.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.121
S = 1.02
2503 reflections
174 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0593P)^2 + 0.0855P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl1—C1	1.730 (3)	C8—N3	1.387 (3)
C4—C7	1.447 (3)	N3—N4	1.399 (2)
C7—N1	1.271 (3)	N3—C9	1.403 (3)
N1—N2	1.378 (2)	N4—C11	1.279 (3)
N2—C11	1.381 (3)	C9—O2	1.197 (3)
N2—C8	1.387 (3)	C9—C10	1.479 (3)
C8—O1	1.209 (2)	C11—C12	1.481 (3)
O2—C9—N3	119.8 (2)	N4—C11—N2	112.30 (18)
O2—C9—C10	124.5 (2)	N4—C11—C12	125.2 (2)
N3—C9—C10	115.73 (19)	N2—C11—C12	122.5 (2)

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

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D\cdots A$	D—H$\cdots$$A$
C7—H7$\cdots$O1	0.93	2.28	2.938 (3)	127
C2—H2$\cdots$O2^{i}	0.93	2.52	3.162 (3)	126
C12—H12*B*$\cdots$O2^{ii}	0.96	2.52	3.414 (3)	154
C10—H10*C*$\cdots$O1^{iii}	0.96	2.61	3.499 (3)	154

Symmetry codes: (i) $2-x, 1-y, 2-z$; (ii) $1-x, -y, 2-z$; (iii) $x-1, y, z$.

The H atoms were positioned geometrically and refined using a riding model, fixing the aromatic C—H distance at 0.93 Å and the

methyl C—H distance at 0.96 Å, with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5_{eq}(C)$ for the methyl group.

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992); cell refinement: *CAD*-4-*PC Software*; data reduction: *XCAD*4 (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: *SHELXL*97.

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