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1-[3-(4-Chlorophenyl)-6-methyl-1,6-dihydro-1,2,4,5-tetrazin-1-yl]ethanone

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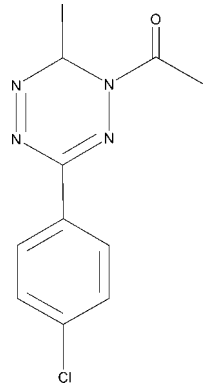
Key indicators: single-crystal X-ray study; T = 93 K; mean σ(C–C) = 0.003 Å; R factor = 0.049; wR factor = 0.152; data-to-parameter ratio = 17.3.

In the title compound, $C_{11}H_{11}ClN_4O$, the tetrazine ring adopts a non-symmetrical boat conformation. The crystal packing exhibits relatively short intermolecular C···N contacts of 3.118 (3) Å.

Related literature

For related structures, see: Hu *et al.* (2004, 2005); Jennison *et al.* (1986); Stam *et al.* (1982); Xu *et al.* (2010); Yang *et al.* (2010). For applications of 1,2,4,5-tetrazine derivatives, see: Sauer (1996).



Experimental

Crystal data

$C_{11}H_{11}ClN_4O$
M_r = 250.69
Orthorhombic, *Pbca*
a = 15.165 (3) Å
b = 8.0452 (15) Å
c = 19.349 (4) Å
V = 2360.7 (8) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.31 mm^{-1}
T = 93 K
0.47 × 0.40 × 0.37 mm

Data collection

Rigaku AFC10/Saturn724+ diffractometer
17617 measured reflections
2705 independent reflections
2599 reflections with $I > 2\sigma(I)$
R_{int} = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.152
S = 1.01
2705 reflections
156 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Data collection: *CrystalClear* (Rigaku/MSC, 2008); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2768).

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1-[3-(4-Chlorophenyl)-6-methyl-1,6-dihydro-1,2,4,5-tetrazin-1-yl]ethanone

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S1. Comment

1,2,4,5-Tetrazine derivatives have high potential for biological activity, possessing a wide spectrum of antiviral and antitumor properties. They have been widely used in pesticides and herbicides (Sauer,1996). Dihydro-1,2,4,5- tetrazine has four isomers, namely 1,2-, 1,4-, 1,6- and 3,6-dihydro-1,2,4,5- tetrazines. The 1,6-dihydro structures (Stam *et al.*, 1982; Jennison *et al.*, 1986) were found, by X-ray diffraction, to be homoaromatic. In continuation of our work on the structure-activity relationship of 1,6-dihydro-1,2,4,5-tetrazine derivatives (Hu *et al.*, 2004, 2005), we have obtained the title compound, (I) (Fig.1).

In the tetrazine ring of (I), atoms N1, N2, N3 and N4 are coplanar, while atoms C7 and C8 deviate from the plane by 0.254 (3) and 0.621 (3) Å, respectively. The N2/C7/N3 and N1/C8/N4 planes make dihedral angles of 7.61 (2)° and 44.04 (2)°, respectively, with the N1/N2/N3/N4 plane, the tetrazine ring adopts an unsymmetrical boat conformation. The benzene ring make dihedral angle of 18.5 (2)° with the N1/N2/N3/N4 plane. N1 is almost sp^2 hybridized due to the angles around it add up to 359.9 (2)°. Compairing with similar situations in 3-phenyl-6-ethyl- 1,6-dihydro-1,2,4,5-tetrazine (Stam *et al.*, 1982), *N*-(2-methylphenyl)-3-phenyl-6-methyl-1,6-dihydro-1,2,4,5-tetrazine (Xu *et al.*,2010), 1-acetyl-3,6-dimethyl-1,2,4,5-tetrazine (Jennison *et al.*,1986) and 1-[3-(4-Methoxyphenyl)-6-methyl-1,6-dihydro-1,2,4,5- tetrazin-1-yl]propanone (Yang *et al.*, 2010), one can state that the molecule in (I) is homoaromatic.

S2. Experimental

3-(4-Chlorophenyl)-6-methyl-1,6-dihydro-1,2,4,5-tetrazine (3.0 mmol), chloroform (10 ml) and pyridine(0.25 ml,3.1 mmol) were mixed. Acetyl chloride(3.0 mmol) in chloroform (10 ml) was added dropwise with stirring at room temperature. After the starting 1,6-dihydro-1,2,4,5-tetrazine was completely consumed (the reaction courses was monitored by TLC,dichloromethane system), evaporation of the chloroform, crude 1-acetyl-3-(4-chlorophenyl)-6-methyl-1,6-dihydro-1,2,4,5-tetrazine was obtained and purified by preparative thin-layer chromatography over silica gel GF254(2 mm) (dichloromethane: petroleum ether=1:1). The solution of the compound in anhydrous ethanol was concentrated gradually at room temperature to afford single crystals, which was suitable for X-ray diffraction. (*M*. P. 352–354 K).^{1}H NMR ($CDCl_3$) δ p.p.m.: 8.10 (d,2*H*, J = 8.0 Hz), 7.49 (d,2*H*, J = 8.0 Hz), 6.87 (q,1*H*, J = 6.7 Hz), 2.49(s,3*H*), 1.05(d,3*H*, J = 6.4 Hz).

S3. Refinement

Methyl H atoms were placed in calculated positions with C—H = 0.96 Å and torsion angles were refined to fit the electron density, U_{iso}(H) = 1.5U_{eq}(C). Other H atoms were placed in calculated positions with C—H = 0.93 and N—H = 0.86 Å, and refined in riding mode, with U_{iso}(H) = 1.2U_{eq}(C,*N*).

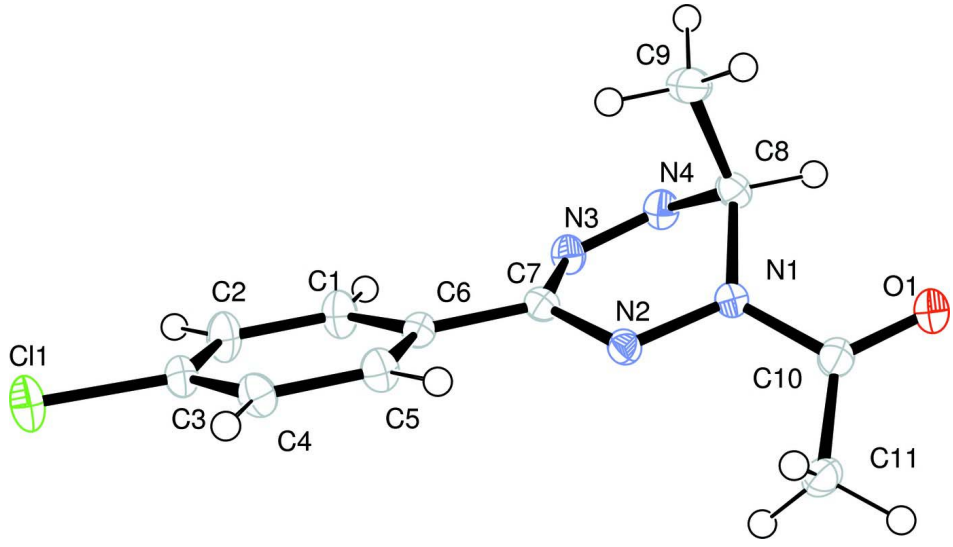

Figure 1

The structure of (I), shown with 30% probability displacement ellipsoids.

1-[3-(4-Chlorophenyl)-6-methyl-1,6-dihydro-1,2,4,5-tetrazin-1-yl]ethanone

Crystal data

$C_{11}H_{11}ClN_4O$
$M_r = 250.69$
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
$a = 15.165$ (3) Å
$b = 8.0452$ (15) Å
$c = 19.349$ (4) Å
$V = 2360.7$ (8) Å^3
$Z = 8$
$F(000) = 1040$
$D_x = 1.411$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6560 reflections
$\theta = 3.1$–$27.5°$
$\mu = 0.31$ mm^{-1}
$T = 93$ K
Block, orange
0.47 × 0.40 × 0.37 mm

Data collection

Rigaku AFC10/Saturn724+ diffractometer
Radiation source: Rotating Anode
Graphite monochromator
Detector resolution: 28.5714 pixels mm^{-1}
phi and ω scans
17617 measured reflections
2705 independent reflections
2599 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.4°$
$h = -15 \rightarrow 19$
$k = -7 \rightarrow 10$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.152$
$S = 1.01$
2705 reflections
156 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 1.56P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.92289 (3)	0.63612 (7)	0.27240 (2)	0.02638 (19)
O1	0.28242 (9)	0.51349 (19)	0.42261 (8)	0.0260 (4)
N1	0.42522 (10)	0.5869 (2)	0.41004 (8)	0.0165 (3)
N2	0.50513 (10)	0.5506 (2)	0.38219 (8)	0.0167 (3)
N3	0.56159 (11)	0.7128 (2)	0.47435 (8)	0.0191 (4)
N4	0.48695 (11)	0.7527 (2)	0.49690 (9)	0.0203 (4)
C1	0.73156 (13)	0.6887 (3)	0.41229 (10)	0.0226 (4)
H1	0.7261	0.7262	0.4586	0.027*
C2	0.81377 (13)	0.6872 (3)	0.38052 (10)	0.0234 (4)
H2	0.8647	0.7229	0.4050	0.028*
C3	0.82041 (13)	0.6332 (2)	0.31290 (10)	0.0194 (4)
C4	0.74733 (13)	0.5800 (3)	0.27600 (9)	0.0202 (4)
H4	0.7531	0.5428	0.2296	0.024*
C5	0.66569 (13)	0.5822 (3)	0.30804 (10)	0.0200 (4)
H5	0.6149	0.5472	0.2832	0.024*
C6	0.65710 (12)	0.6353 (2)	0.37632 (10)	0.0168 (4)
C7	0.56927 (13)	0.6386 (2)	0.40816 (10)	0.0164 (4)
C8	0.41462 (13)	0.7456 (2)	0.44422 (10)	0.0184 (4)
H8	0.3564	0.7475	0.4685	0.022*
C9	0.42014 (14)	0.8936 (3)	0.39576 (12)	0.0251 (5)
H9A	0.4757	0.8890	0.3699	0.030*
H9B	0.4179	0.9966	0.4227	0.030*
H9C	0.3705	0.8906	0.3634	0.030*
C10	0.35516 (13)	0.4761 (2)	0.40099 (10)	0.0192 (4)
C11	0.37533 (13)	0.3182 (2)	0.36325 (11)	0.0217 (4)
H11A	0.3268	0.2393	0.3697	0.026*
H11B	0.4300	0.2700	0.3814	0.026*
H11C	0.3825	0.3418	0.3139	0.026*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0169 (3)	0.0416 (4)	0.0206 (3)	−0.00189 (19)	0.00381 (16)	−0.00357 (19)
O1	0.0156 (7)	0.0260 (8)	0.0363 (8)	−0.0012 (6)	0.0001 (6)	0.0006 (6)
N1	0.0153 (8)	0.0168 (8)	0.0175 (8)	0.0002 (6)	0.0009 (6)	0.0000 (6)
N2	0.0153 (8)	0.0174 (8)	0.0174 (8)	0.0010 (6)	0.0005 (6)	0.0019 (6)

N3	0.0181 (8)	0.0232 (9)	0.0158 (8)	−0.0004 (6)	0.0016 (6)	−0.0013 (6)
N4	0.0195 (8)	0.0231 (8)	0.0184 (8)	−0.0015 (7)	0.0008 (6)	−0.0024 (6)
C1	0.0195 (10)	0.0334 (11)	0.0148 (8)	−0.0025 (8)	0.0011 (7)	−0.0034 (8)
C2	0.0161 (9)	0.0357 (12)	0.0186 (9)	−0.0050 (8)	−0.0018 (7)	−0.0049 (8)
C3	0.0158 (9)	0.0237 (10)	0.0186 (9)	0.0000 (7)	0.0024 (7)	0.0008 (7)
C4	0.0200 (10)	0.0251 (10)	0.0153 (8)	0.0012 (8)	0.0005 (7)	−0.0035 (7)
C5	0.0178 (9)	0.0247 (10)	0.0175 (9)	−0.0008 (8)	−0.0015 (7)	−0.0027 (7)
C6	0.0163 (9)	0.0170 (9)	0.0172 (9)	−0.0010 (7)	0.0002 (7)	0.0005 (6)
C7	0.0170 (10)	0.0172 (9)	0.0150 (9)	0.0015 (7)	−0.0008 (6)	0.0004 (6)
C8	0.0178 (9)	0.0191 (9)	0.0184 (9)	0.0024 (7)	0.0010 (7)	−0.0025 (7)
C9	0.0264 (11)	0.0180 (10)	0.0309 (11)	0.0030 (8)	−0.0019 (8)	0.0014 (8)
C10	0.0174 (9)	0.0205 (10)	0.0198 (9)	−0.0011 (7)	−0.0027 (7)	0.0042 (7)
C11	0.0208 (10)	0.0182 (9)	0.0263 (10)	−0.0036 (8)	−0.0034 (7)	0.0007 (7)

Geometric parameters (Å, º)

Cl1—C3	1.741 (2)	C4—C5	1.385 (3)
O1—C10	1.218 (2)	C4—H4	0.9500
N1—N2	1.358 (2)	C5—C6	1.395 (3)
N1—C10	1.398 (3)	C5—H5	0.9500
N1—C8	1.447 (2)	C6—C7	1.468 (3)
N2—C7	1.304 (2)	C8—C9	1.518 (3)
N3—N4	1.255 (2)	C8—H8	1.0000
N3—C7	1.418 (2)	C9—H9A	0.9800
N4—C8	1.499 (2)	C9—H9B	0.9800
C1—C2	1.390 (3)	C9—H9C	0.9800
C1—C6	1.394 (3)	C10—C11	1.497 (3)
C1—H1	0.9500	C11—H11A	0.9800
C2—C3	1.382 (3)	C11—H11B	0.9800
C2—H2	0.9500	C11—H11C	0.9800
C3—C4	1.386 (3)		
N2—N1—C10	119.42 (16)	N2—C7—N3	121.02 (17)
N2—N1—C8	118.06 (15)	N2—C7—C6	120.36 (17)
C10—N1—C8	122.38 (16)	N3—C7—C6	117.48 (16)
C7—N2—N1	113.33 (16)	N1—C8—N4	105.26 (15)
N4—N3—C7	119.73 (16)	N1—C8—C9	113.80 (16)
N3—N4—C8	114.46 (16)	N4—C8—C9	110.49 (16)
C2—C1—C6	120.20 (17)	N1—C8—H8	109.1
C2—C1—H1	119.9	N4—C8—H8	109.1
C6—C1—H1	119.9	C9—C8—H8	109.1
C3—C2—C1	119.11 (18)	C8—C9—H9A	109.5
C3—C2—H2	120.4	C8—C9—H9B	109.5
C1—C2—H2	120.4	H9A—C9—H9B	109.5
C2—C3—C4	121.77 (18)	C8—C9—H9C	109.5
C2—C3—Cl1	119.14 (15)	H9A—C9—H9C	109.5
C4—C3—Cl1	119.08 (15)	H9B—C9—H9C	109.5
C5—C4—C3	118.70 (17)	O1—C10—N1	119.20 (18)

C5—C4—H4	120.7	O1—C10—C11	124.23 (18)
C3—C4—H4	120.7	N1—C10—C11	116.56 (17)
C4—C5—C6	120.77 (18)	C10—C11—H11A	109.5
C4—C5—H5	119.6	C10—C11—H11B	109.5
C6—C5—H5	119.6	H11A—C11—H11B	109.5
C1—C6—C5	119.45 (17)	C10—C11—H11C	109.5
C1—C6—C7	121.32 (17)	H11A—C11—H11C	109.5
C5—C6—C7	119.21 (17)	H11B—C11—H11C	109.5
C10—N1—N2—C7	−163.54 (16)	N4—N3—C7—C6	163.93 (18)
C8—N1—N2—C7	20.6 (2)	C1—C6—C7—N2	−162.04 (18)
C7—N3—N4—C8	−11.1 (3)	C5—C6—C7—N2	19.9 (3)
C6—C1—C2—C3	0.4 (3)	C1—C6—C7—N3	5.9 (3)
C1—C2—C3—C4	−0.2 (3)	C5—C6—C7—N3	−172.22 (17)
C1—C2—C3—Cl1	178.44 (17)	N2—N1—C8—N4	−54.1 (2)
C2—C3—C4—C5	0.3 (3)	C10—N1—C8—N4	130.11 (17)
Cl1—C3—C4—C5	−178.33 (16)	N2—N1—C8—C9	67.0 (2)
C3—C4—C5—C6	−0.6 (3)	C10—N1—C8—C9	−108.8 (2)
C2—C1—C6—C5	−0.7 (3)	N3—N4—C8—N1	47.4 (2)
C2—C1—C6—C7	−178.79 (19)	N3—N4—C8—C9	−75.8 (2)
C4—C5—C6—C1	0.8 (3)	N2—N1—C10—O1	−175.83 (17)
C4—C5—C6—C7	178.96 (19)	C8—N1—C10—O1	−0.1 (3)
N1—N2—C7—N3	22.6 (2)	N2—N1—C10—C11	2.9 (2)
N1—N2—C7—C6	−169.92 (16)	C8—N1—C10—C11	178.63 (17)
N4—N3—C7—N2	−28.2 (3)		