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

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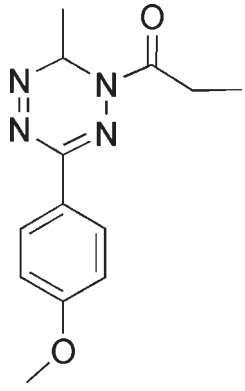
Key indicators: single-crystal X-ray study; T = 93 K; mean σ(C–C) = 0.002 Å; R factor = 0.036; wR factor = 0.081; data-to-parameter ratio = 16.7.

In the title compound, $C_{13}H_{16}N_4O_2$, the central tetrazine ring adopts an unsymmetrical boat conformation with the two C atoms as flagpoles. This compound can be considered as having homoaromaticity.

Related literature

For the biological activity of 1,2,4,5-tetrazine derivatives, see: Sauer (1996). For related structures, see: Jennison *et al.* (1986); Stam *et al.* (1982); Xu *et al.* (2010). For the structure–activity relationships of 1,6-dihydro-1,2,4,5-tetrazine derivatives, see: Hu *et al.* (2004, 2005).



Experimental

Crystal data

$C_{13}H_{16}N_4O_2$
M_r = 260.30
Triclinic, $P\overline{1}$
a = 8.345 (2) Å
b = 8.4898 (19) Å
c = 10.245 (3) Å
α = 113.232 (6)°
β = 99.820 (15)°
γ = 93.268 (11)°
V = 651.0 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 93 K
0.50 × 0.37 × 0.23 mm

Data collection

Rigaku AFC10/Saturn724+ diffractometer
6410 measured reflections
2920 independent reflections
2207 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.081
S = 1.00
2920 reflections
175 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 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: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI5067).

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Xu, F., Yang, Z. Z., Hu, W. X. & Xi, L. M. (2010). *Chin. J. Org. Chem.* **30**, 260–265.

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

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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 report here the crystal structure of the title compound (I) (Fig. 1).

In the tetrazine ring, atoms N1, N2, N3 and N4 are coplanar, while atoms C7 and C8 deviate from the plane by 0.239 (2) and 0.595 (2) Å, respectively. The N2/C7/N3 and N1/C8/N4 planes make dihedral angles of 21.0 (2)° and 42.2 (1)°, respectively, with the N1/N2/ N3/N4 plane, *i.e.* the tetrazine ring adopts an unsymmetrical boat conformation. The benzene ring make dihedral angle of 16.7 (1)° with the N1/N2/N3/N4 plane. Atom N1 is almost sp^2 hybridized due to the angles around it add up to 360.0 (2)°. In keeping 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) and 1-acetyl-3,6-dimethyl-1,2,4,5-tetrazine (Jennison *et al.*, 1986), it can be considered that the molecule is homoaromatic.

S2. Experimental

3-(4-Methoxyphenyl)-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. Propionyl 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-propionyl-3-(4-methoxyphenyl)-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. 340–342 K).^{1}H NMR ($CDCl_3$) δ p.p.m.: 8.10 (d,2*H*, J = 8.8 Hz), 7.03 (d,2*H*, J = 8.8 Hz), 6.84 (q,1*H*, J = 6.4 Hz), 3.89 (s,3*H*), 2.95–3.05(m,1*H*,CH_2), 2.72–2.85(m,1*H*,CH_2),1.20(t,3*H*, J = 7.6 Hz), 1.04 (d,3*H*, J = 6.4 Hz).

S3. Refinement

H atoms were placed in calculated positions with N—H = 0.86 Å, C-H = 0.93 (aromatic) and 0.96 Å (methyl), and refined in riding model, with U_{iso}(H) = 1.2U_{eq}(C,N) and 1.5U_{eq}(C_{methyl}).

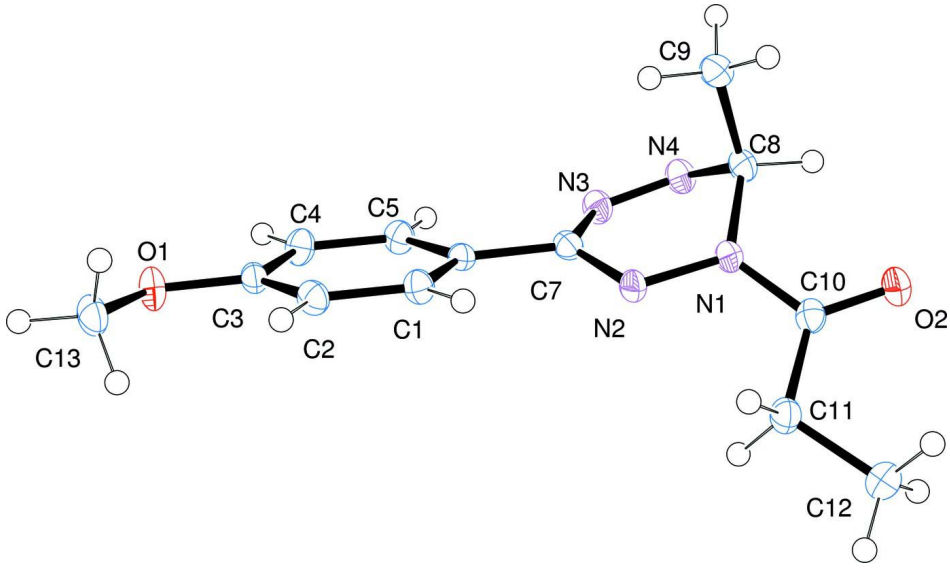

Figure 1

The molecular structure of the title compound, showing 50% probability displacement ellipsoids and the atomic numbering.

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

Crystal data

$C_{13}H_{16}N_4O_2$
$M_r = 260.30$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 8.345$ (2) Å
$b = 8.4898$ (19) Å
$c = 10.245$ (3) Å
$\alpha = 113.232$ (6)°
$\beta = 99.820$ (15)°
$\gamma = 93.268$ (11)°
$V = 651.0$ (3) Å^3
$Z = 2$
$F(000) = 276$
$D_x = 1.328$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1846 reflections
$\theta = 3.4$–27.5°
$\mu = 0.09$ mm^{-1}
$T = 93$ K
Prism, red
0.50 × 0.37 × 0.23 mm

Data collection

Rigaku AFC10/Saturn724+ diffractometer
Radiation source: Rotating Anode
Graphite monochromator
Detector resolution: 28.5714 pixels mm^{-1}
φ and ω scans
6410 measured reflections
2920 independent reflections
2207 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.4°$
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -13 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.081$
$S = 1.00$
2920 reflections
175 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
$w = 1/[\sigma^2(F_o^2) + (0.0282P)^2 + 0.16P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	1.03435 (11)	0.17376 (12)	0.48191 (9)	0.0240 (2)
O2	0.16763 (10)	0.73207 (11)	0.11227 (10)	0.0240 (2)
N1	0.33360 (12)	0.55086 (13)	0.15664 (11)	0.0189 (2)
N2	0.47200 (12)	0.53199 (13)	0.23910 (11)	0.0186 (2)
N3	0.47565 (13)	0.27926 (13)	0.02813 (11)	0.0209 (2)
N4	0.34190 (13)	0.29167 (14)	−0.04264 (11)	0.0224 (2)
C1	0.69924 (15)	0.41266 (16)	0.41273 (13)	0.0193 (3)
H1	0.6425	0.5041	0.4631	0.023*
C2	0.82340 (15)	0.36341 (16)	0.49081 (13)	0.0198 (3)
H2	0.8512	0.4207	0.5938	0.024*
C3	0.90723 (14)	0.22979 (16)	0.41785 (13)	0.0179 (3)
C4	0.86288 (15)	0.14452 (16)	0.26693 (13)	0.0213 (3)
H4	0.9183	0.0516	0.2169	0.026*
C5	0.73919 (15)	0.19411 (16)	0.18974 (13)	0.0198 (3)
H5	0.7102	0.1351	0.0869	0.024*
C6	0.65589 (14)	0.33049 (15)	0.26145 (13)	0.0166 (3)
C7	0.52322 (15)	0.38258 (16)	0.18025 (13)	0.0174 (3)
C8	0.23071 (15)	0.39564 (16)	0.04682 (13)	0.0197 (3)
H8	0.1475	0.4295	−0.0163	0.024*
C9	0.14232 (16)	0.29206 (17)	0.11103 (14)	0.0229 (3)
H9A	0.2213	0.2738	0.1846	0.027*
H9B	0.0908	0.1798	0.0339	0.027*
H9C	0.0577	0.3556	0.1561	0.027*
C10	0.29499 (15)	0.71638 (16)	0.18095 (13)	0.0188 (3)
C11	0.41530 (15)	0.86447 (16)	0.29536 (13)	0.0211 (3)
H11A	0.5256	0.8546	0.2720	0.025*
H11B	0.4215	0.8583	0.3906	0.025*
C12	0.36603 (17)	1.03756 (17)	0.30564 (15)	0.0267 (3)
H12A	0.3573	1.0429	0.2109	0.032*
H12B	0.4492	1.1311	0.3782	0.032*
H12C	0.2598	1.0506	0.3345	0.032*
C13	1.07827 (16)	0.24669 (18)	0.63702 (14)	0.0246 (3)

H13A	1.1083	0.3722	0.6737	0.030*
H13B	1.1719	0.1957	0.6680	0.030*
H13C	0.9848	0.2222	0.6757	0.030*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0227 (5)	0.0325 (5)	0.0196 (5)	0.0115 (4)	0.0026 (4)	0.0134 (4)
O2	0.0192 (5)	0.0280 (5)	0.0261 (5)	0.0064 (4)	0.0008 (4)	0.0134 (4)
N1	0.0169 (5)	0.0206 (5)	0.0185 (5)	0.0019 (4)	−0.0015 (4)	0.0094 (4)
N2	0.0166 (5)	0.0217 (5)	0.0192 (5)	0.0028 (4)	0.0004 (4)	0.0114 (4)
N3	0.0206 (6)	0.0244 (6)	0.0174 (5)	0.0031 (4)	0.0013 (4)	0.0094 (5)
N4	0.0210 (6)	0.0256 (6)	0.0195 (5)	0.0030 (5)	0.0004 (5)	0.0096 (5)
C1	0.0184 (6)	0.0202 (6)	0.0187 (6)	0.0047 (5)	0.0037 (5)	0.0073 (5)
C2	0.0205 (6)	0.0224 (6)	0.0151 (6)	0.0019 (5)	0.0014 (5)	0.0073 (5)
C3	0.0147 (6)	0.0219 (6)	0.0200 (6)	0.0027 (5)	0.0020 (5)	0.0123 (5)
C4	0.0239 (7)	0.0220 (6)	0.0199 (6)	0.0088 (5)	0.0065 (5)	0.0091 (5)
C5	0.0227 (7)	0.0210 (6)	0.0144 (6)	0.0033 (5)	0.0022 (5)	0.0066 (5)
C6	0.0147 (6)	0.0182 (6)	0.0181 (6)	0.0001 (5)	0.0017 (5)	0.0096 (5)
C7	0.0157 (6)	0.0207 (6)	0.0169 (6)	0.0007 (5)	0.0026 (5)	0.0094 (5)
C8	0.0173 (6)	0.0218 (6)	0.0180 (6)	0.0017 (5)	−0.0015 (5)	0.0083 (5)
C9	0.0200 (6)	0.0238 (7)	0.0237 (7)	0.0003 (5)	0.0008 (5)	0.0103 (5)
C10	0.0188 (6)	0.0232 (6)	0.0184 (6)	0.0053 (5)	0.0057 (5)	0.0118 (5)
C11	0.0212 (7)	0.0218 (7)	0.0209 (7)	0.0048 (5)	0.0024 (5)	0.0101 (5)
C12	0.0261 (7)	0.0213 (7)	0.0332 (8)	0.0049 (5)	0.0047 (6)	0.0120 (6)
C13	0.0222 (7)	0.0329 (7)	0.0200 (7)	0.0043 (6)	−0.0006 (5)	0.0141 (6)

Geometric parameters (Å, º)

O1—C3	1.3596 (14)	C5—C6	1.3995 (17)
O1—C13	1.4291 (15)	C5—H5	0.95
O2—C10	1.2155 (14)	C6—C7	1.4647 (16)
N1—N2	1.3669 (14)	C8—C9	1.5160 (17)
N1—C10	1.3941 (16)	C8—H8	1.00
N1—C8	1.4531 (15)	C9—H9A	0.98
N2—C7	1.3044 (16)	C9—H9B	0.98
N3—N4	1.2571 (14)	C9—H9C	0.98
N3—C7	1.4236 (16)	C10—C11	1.5015 (17)
N4—C8	1.4917 (16)	C11—C12	1.5169 (17)
C1—C2	1.3852 (17)	C11—H11A	0.99
C1—C6	1.3952 (17)	C11—H11B	0.99
C1—H1	0.95	C12—H12A	0.98
C2—C3	1.3911 (17)	C12—H12B	0.98
C2—H2	0.95	C12—H12C	0.98
C3—C4	1.3939 (17)	C13—H13A	0.98
C4—C5	1.3791 (17)	C13—H13B	0.98
C4—H4	0.95	C13—H13C	0.98

C3—O1—C13	118.23 (10)	N1—C8—H8	108.9
N2—N1—C10	119.47 (10)	N4—C8—H8	108.9
N2—N1—C8	118.20 (10)	C9—C8—H8	108.9
C10—N1—C8	122.32 (10)	C8—C9—H9A	109.5
C7—N2—N1	113.70 (10)	C8—C9—H9B	109.5
N4—N3—C7	120.02 (11)	H9A—C9—H9B	109.5
N3—N4—C8	115.25 (10)	C8—C9—H9C	109.5
C2—C1—C6	121.25 (12)	H9A—C9—H9C	109.5
C2—C1—H1	119.4	H9B—C9—H9C	109.5
C6—C1—H1	119.4	O2—C10—N1	119.15 (11)
C1—C2—C3	119.76 (11)	O2—C10—C11	124.57 (12)
C1—C2—H2	120.1	N1—C10—C11	116.27 (10)
C3—C2—H2	120.1	C10—C11—C12	111.53 (11)
O1—C3—C2	125.16 (11)	C10—C11—H11A	109.3
O1—C3—C4	115.33 (11)	C12—C11—H11A	109.3
C2—C3—C4	119.50 (11)	C10—C11—H11B	109.3
C5—C4—C3	120.48 (12)	C12—C11—H11B	109.3
C5—C4—H4	119.8	H11A—C11—H11B	108.0
C3—C4—H4	119.8	C11—C12—H12A	109.5
C4—C5—C6	120.64 (11)	C11—C12—H12B	109.5
C4—C5—H5	119.7	H12A—C12—H12B	109.5
C6—C5—H5	119.7	C11—C12—H12C	109.5
C1—C6—C5	118.35 (11)	H12A—C12—H12C	109.5
C1—C6—C7	120.72 (11)	H12B—C12—H12C	109.5
C5—C6—C7	120.91 (11)	O1—C13—H13A	109.5
N2—C7—N3	121.12 (11)	O1—C13—H13B	109.5
N2—C7—C6	121.13 (11)	H13A—C13—H13B	109.5
N3—C7—C6	116.68 (11)	O1—C13—H13C	109.5
N1—C8—N4	106.07 (9)	H13A—C13—H13C	109.5
N1—C8—C9	112.98 (10)	H13B—C13—H13C	109.5
N4—C8—C9	110.99 (10)		

C10—N1—N2—C7	−159.83 (10)	N4—N3—C7—C6	164.47 (10)
C8—N1—N2—C7	20.73 (14)	C1—C6—C7—N2	18.43 (17)
C7—N3—N4—C8	−9.80 (16)	C5—C6—C7—N2	−163.36 (11)
C6—C1—C2—C3	0.09 (18)	C1—C6—C7—N3	−173.30 (11)
C13—O1—C3—C2	5.43 (17)	C5—C6—C7—N3	4.91 (16)
C13—O1—C3—C4	−175.44 (11)	N2—N1—C8—N4	−52.33 (13)
C1—C2—C3—O1	177.78 (11)	C10—N1—C8—N4	128.25 (11)
C1—C2—C3—C4	−1.32 (18)	N2—N1—C8—C9	69.47 (13)
O1—C3—C4—C5	−177.85 (11)	C10—N1—C8—C9	−109.95 (13)
C2—C3—C4—C5	1.33 (18)	N3—N4—C8—N1	45.04 (13)
C3—C4—C5—C6	−0.12 (18)	N3—N4—C8—C9	−78.02 (13)
C2—C1—C6—C5	1.10 (17)	N2—N1—C10—O2	−176.38 (11)
C2—C1—C6—C7	179.36 (11)	C8—N1—C10—O2	3.04 (17)
C4—C5—C6—C1	−1.09 (17)	N2—N1—C10—C11	2.16 (16)
C4—C5—C6—C7	−179.34 (11)	C8—N1—C10—C11	−178.43 (10)
N1—N2—C7—N3	20.73 (16)	O2—C10—C11—C12	−5.10 (17)

N1—N2—C7—C6	−171.53 (10)	N1—C10—C11—C12	176.46 (11)
N4—N3—C7—N2	−27.26 (17)		