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5-*p*-Tolyl-1*H*-tetrazole

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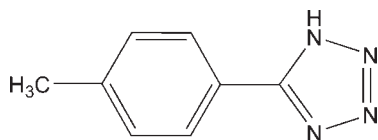
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.048; wR factor = 0.115; data-to-parameter ratio = 14.3.

The title compound, $\text{C}_8\text{H}_8\text{N}_4$, possesses crystallographic mirror symmetry, with four C atoms lying on the reflecting plane, which bisects the phenyl and tetrazole rings. It is composed of a planar r.m.s. deviation (0.0012 Å) tetrazole ring which is nearly coplanar with the benzene ring, the dihedral angle being $2.67(9)^\circ$. In the crystal, symmetry-related molecules are linked by intermolecular $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds. The molecules stack along [100] with a $\pi\cdots\pi$ interaction involving the phenyl and tetrazole rings of adjacent molecules [centroid-centroid distance = 3.5639 (15) Å]. The H atom of the $\text{N}-\text{H}$ group is disordered over two sites of equal occupancy. The methyl H atoms were modelled as disordered over two sets of sites of equal occupancy rotated by 60° with respect to each other.

Related literature

For related manganese(II) complexes, see: Hu *et al.* (2007); Lü (2008). For applications of tetrazoles in coordination chemistry, medicinal chemistry and materials science, see: Xiong *et al.* (2002); Xue *et al.* (2002); Wang *et al.* (2005); Dunica *et al.* (1991); Wittenberger *et al.* (1993).



Experimental

Crystal data

 $\text{C}_8\text{H}_8\text{N}_4$ $M_r = 160.18$ Orthorhombic, *Pbcm* $a = 4.5370(15)$ Å $b = 17.729(5)$ Å $c = 9.778(2)$ Å $V = 786.5(4)$ Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 0.09$ mm⁻¹ $T = 293$ K $0.20 \times 0.20 \times 0.20$ mm

Data collection

Rigaku, SCXmini diffractometer

Absorption correction: multi-scan

CrystalClear (Rigaku, 2005) $T_{\min} = 0.981$, $T_{\max} = 0.983$

7310 measured reflections

946 independent reflections

792 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.040$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.048$ $wR(F^2) = 0.115$ $S = 1.12$

946 reflections

66 parameters

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\max} = 0.17$ e Å⁻³ $\Delta\rho_{\min} = -0.16$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{N1}^i$	0.87 (3)	1.94 (3)	2.806 (2)	171 (3)

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

Data collection: *CrystalClear* (Rigaku 2005); 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: *PRPKAPPA* (Ferguson, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2134).

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supplementary materials

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5-*p*-Tolyl-1*H*-tetrazole

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Comment

Tetrazole-related molecules have attracted considerable attention due to their biological activities. The synthesis of new members of this family of ligands is an important direction in the development of modern coordination chemistry (Hu *et al.*, 2007; Lü, 2008). Tetrazole compounds have a wide range of applications in coordination chemistry, medicinal chemistry and material science (Xiong, *et al.*, 2002; Xue, *et al.*, 2002; Wang, *et al.*, 2005; Dunica, *et al.*, 1991; Wittenberger, *et al.*, 1993).

The title compound is a tetrazole ligand with a toluene substituent in position 5 (Fig. 1). In the solid state structure the molecule possesses crystallographic mirror symmetry. The mirror bisects the tolyl group and the tetrazole ring with atoms C1, C4, C7 and C8 lying in the mirror. The bond lengths and angles have normal values. The interplanar angle between the phenyl ring [C1/C2/C3/C4/C2A/C3A] and the tetrazole ring [N1/N2/N1A/N2A/C7] mean-planes is 2.67 (9) °.

In the crystal symmetry related molecules are linked by intermolecular N—H...N hydrogen bonds (Table 1), forming chains propagating in the [010] direction (Fig. 2). There is a $\pi\cdots\pi$ interaction involving the tetrazole and phenyl rings of adjacent molecules with a centroid-to-centroid distance of 3.5639 (15) Å.

Experimental

4-methylbenzonitrile (1.17 g, 10 mmol) and ammonium chloride (0.53 g, 10 mmol) were dissolved in DMF (40 ml) in the presence of sodium azide (0.98 g, 0.5 mmol) and refluxed for 24 h. After the mixture was cooled to rt and filtered. Most of the solvent was then removed under vacuum. Pale yellow crystals of the title compound, suitable for X-ray diffraction analysis, were obtained from the remaining solution on slow evaporation of the solvent.

Refinement

All the H atoms could be located in the difference electron-density maps. Due to the mirror symmetry the NH H-atom, which is disorderd over N-atoms N1 and N1ⁱ [symmetry code (i) = x, y, -z+1/2], was freely refined with an occupancy of 0.5; distance N-H = 0.87 (3) Å. The C-bound H-atoms were included in idealized positions and treated as riding atoms: C-H = 0.93 - 0.96 Å, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent C-atom})$. The H-atoms on methyl C8 were modelled as disordered with two triplets of the H atoms with equal occupation (0.5:0.5) rotated by 60° to each other.

Figures

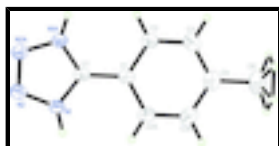


Fig. 1. The molecular structure of the title compound, with the displacement ellipsoids drawn at the 30% probability level. [Symmetry code: (A)= x, y, -z + 1/2].

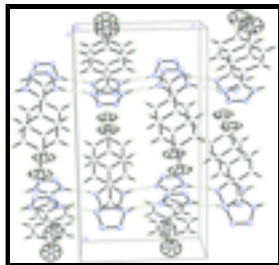


Fig. 2. Crystal packing diagram of the title compound, viewed along the a axis (hydrogen bonds are shown as dashed lines, see Table 1 for details).

5-*p*-tolyl-1*H*-tetrazole

Crystal data

$C_8H_8N_4$	$F_{000} = 336$
$M_r = 160.18$	$D_x = 1.353 \text{ Mg m}^{-3}$
Orthorhombic, $Pbcm$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: $-P\ 2c\ 2b$	Cell parameters from 1044 reflections
$a = 4.5370 (15) \text{ \AA}$	$\theta = 3.0\text{--}27.4^\circ$
$b = 17.729 (5) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$c = 9.778 (2) \text{ \AA}$	$T = 293 \text{ K}$
$V = 786.5 (4) \text{ \AA}^3$	Block, pale yellow
$Z = 4$	$0.20 \times 0.20 \times 0.20 \text{ mm}$

Data collection

Rigaku, SCXmini diffractometer	946 independent reflections
Radiation source: fine-focus sealed tube	792 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.040$
Detector resolution: $13.6612 \text{ pixels mm}^{-1}$	$\theta_{\text{max}} = 27.5^\circ$
$T = 293 \text{ K}$	$\theta_{\text{min}} = 3.1^\circ$
CCD_Profile_fitting scans	$h = -5 \rightarrow 5$
Absorption correction: multi-scan CrystalClear (Rigaku, 2005)	$k = -23 \rightarrow 22$
$T_{\text{min}} = 0.981$, $T_{\text{max}} = 0.983$	$l = -12 \rightarrow 12$
7310 measured reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.048$	$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 0.1774P]$
$wR(F^2) = 0.115$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.12$	$(\Delta/\sigma)_{\text{max}} < 0.001$
	$\Delta\rho_{\text{max}} = 0.17 \text{ e \AA}^{-3}$

946 reflections $\Delta\rho_{\min} = -0.16 \text{ e } \text{\AA}^{-3}$
 66 parameters Extinction correction: SHELXL,
 $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Primary atom site location: structure-invariant direct methods Extinction coefficient: 0.023 (5)
 Secondary atom site location: difference Fourier map

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.2469 (4)	0.17076 (11)	0.2500	0.0386 (5)	
C2	0.3511 (3)	0.14064 (8)	0.12792 (15)	0.0478 (4)	
H2	0.2895	0.1610	0.0451	0.057*	
C3	0.5451 (4)	0.08076 (9)	0.12874 (17)	0.0543 (5)	
H3	0.6133	0.0616	0.0461	0.065*	
C4	0.6408 (5)	0.04856 (12)	0.2500	0.0521 (6)	
C7	0.0344 (4)	0.23258 (11)	0.2500	0.0363 (5)	
C8	0.8408 (6)	-0.01930 (14)	0.2500	0.0746 (8)	
H8A	0.8837	-0.0336	0.3426	0.112*	0.50
H8B	1.0209	-0.0071	0.2035	0.112*	0.50
H8C	0.7450	-0.0604	0.2039	0.112*	0.50
N1	-0.0825 (3)	0.26572 (7)	0.35937 (12)	0.0435 (4)	
N2	-0.2736 (3)	0.31947 (7)	0.31588 (13)	0.0489 (4)	
H1	-0.064 (6)	0.2534 (19)	0.446 (3)	0.045 (8)*	0.50

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0394 (10)	0.0431 (10)	0.0333 (10)	-0.0074 (9)	0.000	0.000
C2	0.0540 (9)	0.0525 (9)	0.0369 (8)	-0.0014 (7)	0.0021 (7)	-0.0017 (6)
C3	0.0544 (9)	0.0552 (9)	0.0532 (10)	-0.0016 (8)	0.0081 (7)	-0.0105 (8)
C4	0.0428 (12)	0.0430 (12)	0.0705 (16)	-0.0079 (10)	0.000	0.000
C7	0.0415 (10)	0.0411 (10)	0.0262 (8)	-0.0109 (8)	0.000	0.000
C8	0.0601 (15)	0.0542 (15)	0.109 (2)	0.0045 (13)	0.000	0.000
N1	0.0538 (7)	0.0477 (7)	0.0291 (6)	-0.0020 (6)	0.0017 (5)	-0.0010 (5)
N2	0.0607 (8)	0.0489 (7)	0.0371 (6)	0.0011 (6)	0.0030 (6)	-0.0019 (5)

supplementary materials

Geometric parameters (\AA , $^\circ$)

C1—C2	1.3905 (18)	C7—N1 ⁱ	1.3306 (17)
C1—C2 ⁱ	1.3905 (18)	C7—N1	1.3306 (17)
C1—C7	1.460 (3)	C8—H8A	0.9600
C2—C3	1.379 (2)	C8—H8B	0.9600
C2—H2	0.9300	C8—H8C	0.9600
C3—C4	1.386 (2)	N1—N2	1.3566 (17)
C3—H3	0.9300	N1—H1	0.87 (3)
C4—C3 ⁱ	1.386 (2)	N2—N2 ⁱ	1.288 (2)
C4—C8	1.507 (3)		
C2—C1—C2 ⁱ	118.28 (19)	N1 ⁱ —C7—C1	126.51 (9)
C2—C1—C7	120.86 (10)	N1—C7—C1	126.51 (9)
C2 ⁱ —C1—C7	120.86 (10)	C4—C8—H8A	109.5
C3—C2—C1	120.51 (15)	C4—C8—H8B	109.5
C3—C2—H2	119.7	H8A—C8—H8B	109.5
C1—C2—H2	119.7	C4—C8—H8C	109.5
C2—C3—C4	121.47 (16)	H8A—C8—H8C	109.5
C2—C3—H3	119.3	H8B—C8—H8C	109.5
C4—C3—H3	119.3	C7—N1—N2	108.24 (12)
C3 ⁱ —C4—C3	117.7 (2)	C7—N1—H1	129 (2)
C3 ⁱ —C4—C8	121.17 (11)	N2—N1—H1	123 (2)
C3—C4—C8	121.17 (11)	N2 ⁱ —N2—N1	108.27 (7)
N1 ⁱ —C7—N1	106.98 (17)		

Symmetry codes: (i) $x, y, -z+1/2$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 ⁱ —N1 ⁱⁱ	0.87 (3)	1.94 (3)	2.806 (2)	171 (3)

Symmetry codes: (ii) $x, -y+1/2, -z+1$.

Fig. 1

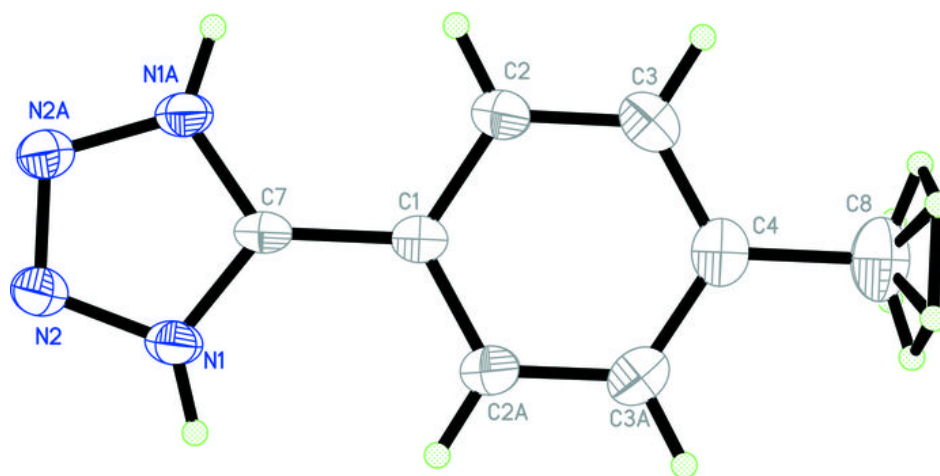


Fig. 2

