

5,5'-(*p*-Phenylene)di-1*H*-tetrazole

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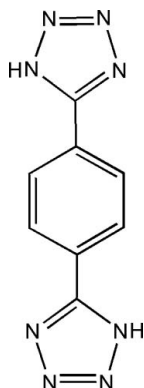
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.036; wR factor = 0.106; data-to-parameter ratio = 13.5.

Crystals of the title organic compound, $\text{C}_8\text{H}_6\text{N}_8$, were generated *in situ* through the [2 + 3]-cycloaddition reaction involving the precursor 1,4-dicyanobenzene and azide in water with Zn^{2+} as Lewis acid. The asymmetric unit consists of one half-molecule, and a twofold axis of symmetry passes through the centre of the benzene ring. There is an intermolecular $\text{N}-\text{H}\cdots\text{N}$ hydrogen bond. The molecules are assembled into a three-dimensional supramolecular framework by π - π stacking interactions, with a perpendicular distance of 3.256 Å [centroid-centroid = 3.9731 (8) Å] between two tetrazole ring planes, and 3.382 Å between the benzene ring and tetrazole ring planes [centroid-centroid = 3.5010 (9) Å].

Related literature

For related literature, see: Demko & Sharpless (2001, 2002); Furmeier & Metzger (2003); Huang *et al.* (2005); Wang *et al.* (2005); Xiong *et al.* (2002); Ye *et al.* (2005).



Experimental

Crystal data

$\text{C}_8\text{H}_6\text{N}_8$	$V = 434.28$ (7) Å ³
$M_r = 214.21$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 4.5396$ (4) Å	$\mu = 0.12$ mm ⁻¹
$b = 9.8219$ (10) Å	$T = 293$ (2) K
$c = 9.7525$ (10) Å	$0.70 \times 0.12 \times 0.10$ mm
$\beta = 92.910$ (5)°	

Data collection

Siemens SMART CCD diffractometer	3228 measured reflections
Absorption correction: multi-scan (SADABS; Siemens, 1996)	985 independent reflections
$T_{\min} = 0.701$, $T_{\max} = 1.000$	830 reflections with $I > 2\sigma(I)$
(expected range = 0.693–0.988)	$R_{\text{int}} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$	73 parameters
$wR(F^2) = 0.106$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{\max} = 0.26$ e Å ⁻³
985 reflections	$\Delta\rho_{\min} = -0.23$ e Å ⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N3}-\text{H3A}\cdots\text{N4}^i$	0.86	1.94	2.7805 (15)	167

Symmetry code: (i) $x, -y + \frac{3}{2}, z + \frac{1}{2}$.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Sheldrick, 2000); 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: AT2504).

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supporting information

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5,5'-(*p*-Phenylene)di-1*H*-tetrazole**Xiang He, Bao-Li An and Ming-Xing Li****S1. Comment**

Owing to the efforts of Sharpless and Demko in the past years, the preparation of 5-substituted tetrazolate ligands has now become a safe and convenient procedure (Demko *et al.*, 2001). Recently, Metzger and Furmeier reported that 5-substituted tetrazolates can also be synthesized from nitriles in toluene (Furmeier *et al.*, 2003), and Xiong *et al.* reported several coordination polymers obtained from the reaction of the tetrazoles generated *in situ* with a variety of 5-substituted groups under hydrothermal conditions (Xiong *et al.*, 2002). However, the coordination polymers containing the ligands synthesized *in situ* from the precursor ligands containing two-cyano groups have rarely been reported (Huang *et al.*, 2005; Wang *et al.*, 2005). Herein we report the title compound (I).

The title compound is composed of 5,5'-(1,4-phenylene)bis(1*H*-tetrazole). As shown in Fig. 1, the asymmetric unit consists of one-half molecule, a twofold axis of symmetry passes through the centre of phenylene. There is a hydrogen bond; N3...N4 ($x, -y + 3/2, z + 1/2$) of 2.7805 (15) Å. The hydrogen bond and aromatic π - π -stacking interactions assemble the organic molecules into a three-dimensional supramolecular framework (Fig.2). Within the framework, the tetrazolyl ring (N1—N4/C9) at (x, y, z) is parallel to the tetrazolyl ring at ($-x, 1 - y, 1 - z$) and the perpendicular distance between the two ring planes is 3.256 Å, with the distance between ring centroids is 3.9731 (8) Å. The phenylene ring (C6—C8/C6ⁱ—C8ⁱ) [(i) $-x - 1, -y + 2, -z + 1$] is almost parallel to the tetrazolyl ring at ($-x, -y, 1 - z$) with a dihedral angle of 2.69°, and the perpendicular distance of phenylene ring on tetrazolyl ring planes is 3.382 Å, with the distance between ring centroids is 3.5010 (9) Å. The supramolecular structure is stabilized by aromatic π - π -stacking interactions.

S2. Experimental

A mixture of ZnCl₂ (1.5 mmol), 1,4-dicyanobenzene (1 mmol) and azide (3 mmol) in 15 ml H₂O was heated at 160°C for three days in a sealed 25 ml Teflon-Lined stainless steel vessel under autogenous pressure. After the reaction mixture was slowly cooled down to room temperature, colorless prismlike crystals were produced, which were collected by filtration and washed with distilled water and dried in air.

S3. Refinement

H atoms were placed in idealized positions, with C—H distances of 0.93 Å, N—H distances of 0.86 Å, and allowed to ride on their respective parent C atoms with the constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

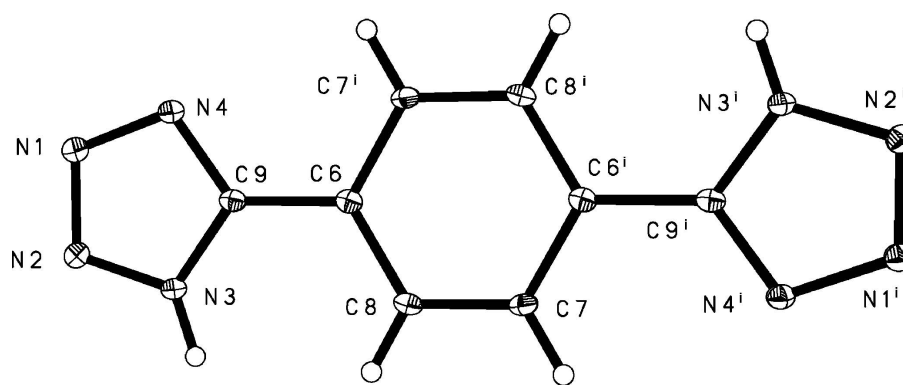


Figure 1

A perspective view of the locally expanded unit for (I). Displacement ellipsoids are drawn at the 30% probability level [symmetry codes: (i) $-x-1, -y+2, -z+1$].

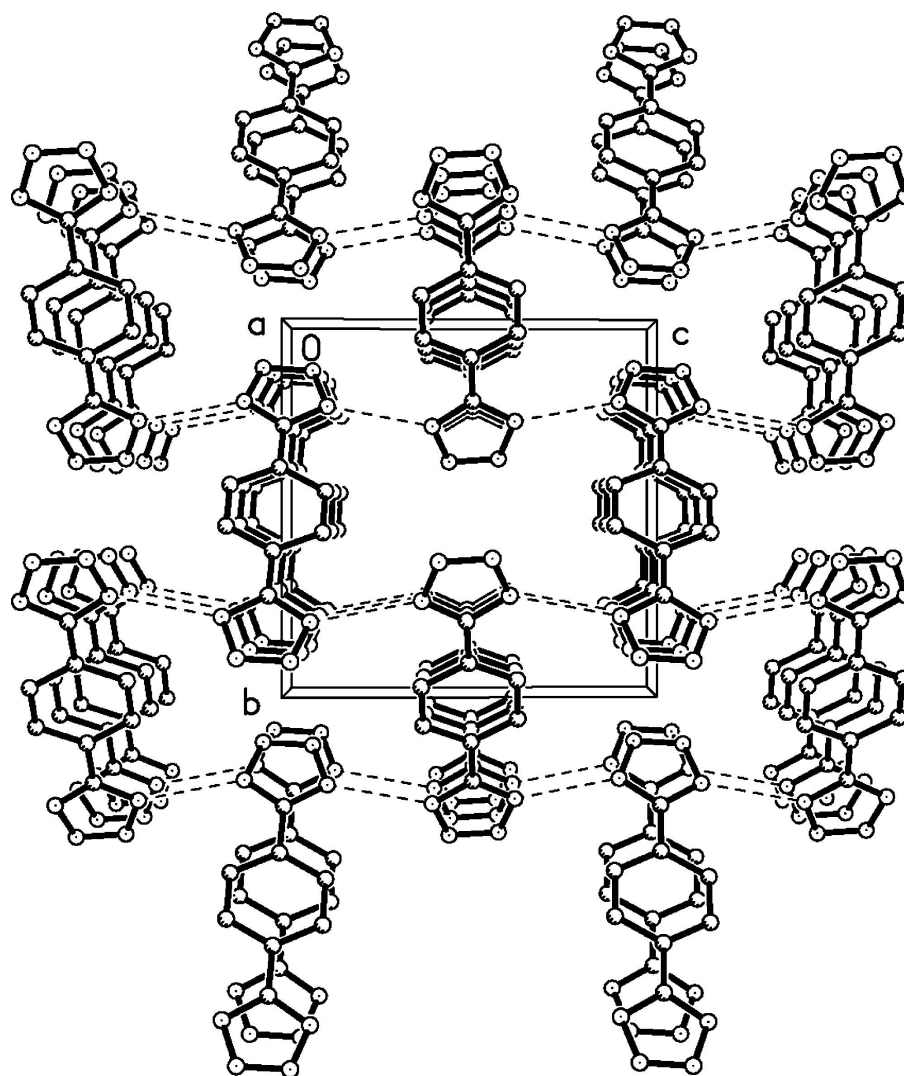


Figure 2

Crystal packing diagram of compound (I).

5,5'-(*p*-phenylene)di-1*H*-tetrazole*Crystal data*C₈H₆N₈ $M_r = 214.21$ Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

 $a = 4.5396$ (4) Å $b = 9.8219$ (10) Å $c = 9.7525$ (10) Å $\beta = 92.910$ (5)° $V = 434.28$ (7) Å³ $Z = 2$ $F(000) = 220$ $D_x = 1.638$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1058 reflections

 $\theta = 4.2$ – 27.5° $\mu = 0.12$ mm⁻¹ $T = 293$ K

Prism, colourless

 $0.70 \times 0.12 \times 0.10$ mm*Data collection*Siemens SMART CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: ω pixels mm⁻¹

dtprofit.ref scans

Absorption correction: multi-scan
(*SADABS*; Siemens, 1996) $T_{\min} = 0.701$, $T_{\max} = 1.000$

3228 measured reflections

985 independent reflections

830 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.037$ $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 4.2^\circ$ $h = -5 \rightarrow 5$ $k = -12 \rightarrow 10$ $l = -12 \rightarrow 12$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.036$ $wR(F^2) = 0.106$ $S = 1.07$

985 reflections

73 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0565P)^2 + 0.0841P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.26$ 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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.2260 (3)	0.63240 (12)	0.42296 (11)	0.0191 (3)

N2	0.2387 (3)	0.62431 (12)	0.55599 (11)	0.0188 (3)
C9	−0.0803 (3)	0.78246 (13)	0.49215 (12)	0.0138 (3)
C6	−0.2968 (3)	0.89304 (13)	0.49702 (12)	0.0142 (3)
C7	−0.5995 (3)	1.04419 (14)	0.62493 (13)	0.0167 (3)
H7A	−0.6662	1.0738	0.7085	0.020*
C8	−0.3988 (3)	0.93858 (14)	0.62200 (13)	0.0167 (3)
H8A	−0.3312	0.8975	0.7036	0.020*
N4	0.0286 (3)	0.73052 (11)	0.37995 (11)	0.0166 (3)
N3	0.0463 (3)	0.71737 (11)	0.60025 (11)	0.0159 (3)
H3A	0.0108	0.7324	0.6847	0.019*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0222 (7)	0.0192 (6)	0.0159 (6)	0.0010 (5)	0.0004 (5)	−0.0008 (4)
N2	0.0221 (7)	0.0176 (6)	0.0167 (6)	0.0014 (5)	0.0015 (5)	−0.0015 (4)
C9	0.0145 (7)	0.0150 (7)	0.0118 (6)	−0.0047 (5)	−0.0007 (5)	0.0003 (4)
C6	0.0141 (6)	0.0150 (6)	0.0133 (6)	−0.0033 (5)	−0.0009 (5)	0.0007 (5)
C7	0.0199 (7)	0.0198 (7)	0.0105 (6)	−0.0001 (6)	0.0014 (5)	−0.0007 (5)
C8	0.0190 (7)	0.0197 (7)	0.0113 (6)	−0.0002 (5)	−0.0010 (5)	0.0027 (5)
N4	0.0190 (6)	0.0179 (6)	0.0129 (5)	0.0002 (5)	0.0000 (4)	−0.0006 (4)
N3	0.0194 (6)	0.0172 (6)	0.0112 (5)	0.0008 (5)	0.0012 (4)	−0.0002 (4)

Geometric parameters (Å, °)

N1—N2	1.2982 (16)	C6—C8	1.3991 (18)
N1—N4	1.3674 (16)	C7—C8	1.3819 (19)
N2—N3	1.3499 (16)	C7—C6 ⁱ	1.3997 (17)
C9—N4	1.3256 (17)	C7—H7A	0.9300
C9—N3	1.3376 (16)	C8—H8A	0.9300
C9—C6	1.4672 (18)	N3—H3A	0.8600
C6—C7 ⁱ	1.3997 (17)		
N2—N1—N4	110.17 (11)	C8—C7—H7A	119.8
N1—N2—N3	106.36 (10)	C6 ⁱ —C7—H7A	119.8
N4—C9—N3	107.65 (12)	C7—C8—C6	120.38 (12)
N4—C9—C6	126.17 (11)	C7—C8—H8A	119.8
N3—C9—C6	126.17 (12)	C6—C8—H8A	119.8
C7 ⁱ —C6—C8	119.18 (13)	C9—N4—N1	106.51 (10)
C7 ⁱ —C6—C9	119.70 (12)	C9—N3—N2	109.31 (11)
C8—C6—C9	121.11 (12)	C9—N3—H3A	125.3
C8—C7—C6 ⁱ	120.44 (12)	N2—N3—H3A	125.3
N4—N1—N2—N3	0.39 (14)	C9—C6—C8—C7	179.05 (12)
N4—C9—C6—C7 ⁱ	−1.7 (2)	N3—C9—N4—N1	−0.25 (15)
N3—C9—C6—C7 ⁱ	177.09 (13)	C6—C9—N4—N1	178.76 (12)
N4—C9—C6—C8	179.24 (13)	N2—N1—N4—C9	−0.09 (15)
N3—C9—C6—C8	−1.9 (2)	N4—C9—N3—N2	0.50 (15)

C6 ⁱ —C7—C8—C6	0.0 (2)	C6—C9—N3—N2	−178.51 (12)
C7 ⁱ —C6—C8—C7	0.0 (2)	N1—N2—N3—C9	−0.55 (15)

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

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N3—H3A $\cdots$ N4 ⁱⁱ	0.86	1.94	2.7805 (15)	167

Symmetry code: (ii) $x, -y+3/2, z+1/2$.