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5,5′-(*p*-Phenylene)di-1*H*-tetrazole

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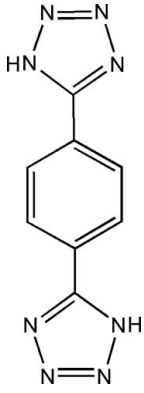
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.036; wR factor = 0.106; data-to-parameter ratio = 13.5.

Crystals of the title organic compound, $C_8H_6N_8$, 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 N—H···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

$C_8H_6N_8$
M_r = 214.21
Monoclinic, $P2_1/c$
a = 4.5396 (4) Å
b = 9.8219 (10) Å
c = 9.7525 (10) Å
β = 92.910 (5)°
V = 434.28 (7) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 293 (2) K
0.70 × 0.12 × 0.10 mm

Data collection

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

Refinement

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

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···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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supplementary materials

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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 co-ordination 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/C6^{i}—C8^{i}) [(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.

Experimental

A mixture of $ZnCl_2$ (1.5 mmol), 1,4-dicyanobenzene (1 mmol) and azide (3 mmol) in 15 ml H_2O was heated at 160oC 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.

Refinement

H atoms were placed in idealized positions, with 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 $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

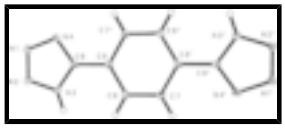

Fig. 1. A perspective view of the locally expanded unit for (I). Displacement ellipsoids are drawn at the 30% probability level [symmetry codes: (i) -x-1,-y+2,-z+1].

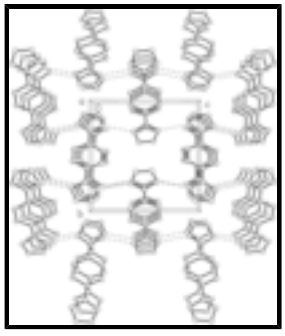

Fig. 2. Crystal packing diagram of compound (I).

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

Crystal data

$C_8H_6N_8$	$F(000) = 220$
$M_r = 214.21$	$D_x = 1.638$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 1058 reflections
$a = 4.5396$ (4) Å	$\theta = 4.2–27.5°$
$b = 9.8219$ (10) Å	$\mu = 0.12$ mm^{-1}
$c = 9.7525$ (10) Å	$T = 293$ K
$\beta = 92.910$ (5)°	Prism, colourless
$V = 434.28$ (7) Å^3	0.70 × 0.12 × 0.10 mm
$Z = 2$	

Data collection

Siemens SMART CCD diffractometer	985 independent reflections
Radiation source: fine-focus sealed tube	830 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.037$
Detector resolution: ω pixels mm^{-1}	$\theta_{max} = 27.5°$, $\theta_{min} = 4.2°$
dtprofit.ref scans	$h = -5\rightarrow5$
Absorption correction: multi-scan (*SADABS*; Siemens, 1996)	$k = -12\rightarrow10$
$T_{min} = 0.701$, $T_{max} = 1.000$	$l = -12\rightarrow12$
3228 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.036$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.106$	H-atom parameters constrained
$S = 1.07$	$w = 1/[\sigma^2(F_o^2) + (0.0565P)^2 + 0.0841P]$

	where $P = (F_o^2 + 2F_c^2)/3$
985 reflections	$(\Delta/\sigma)_{max} < 0.001$
73 parameters	$\Delta\rho_{max} = 0.26$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.23$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{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 (Å^2)

	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 codes: (i) −*x*−1, −*y*+2, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3A···N4^{ii}	0.86	1.94	2.7805 (15)	167

Symmetry codes: (ii) *x*, −*y*+3/2, *z*+1/2.

Fig. 1

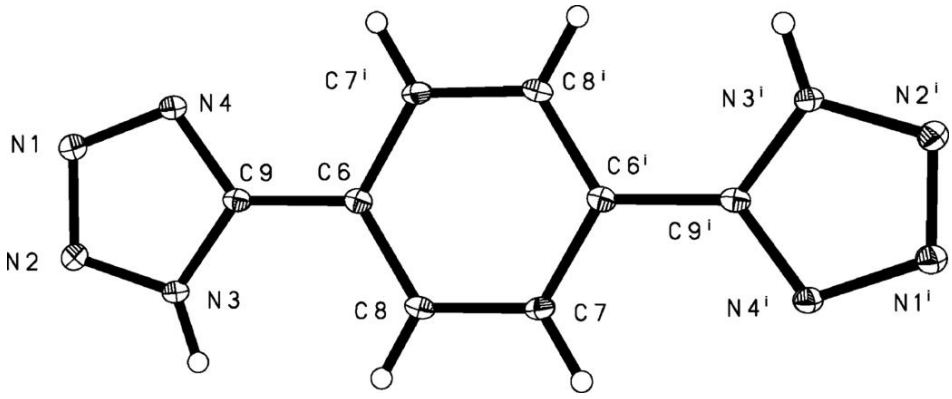
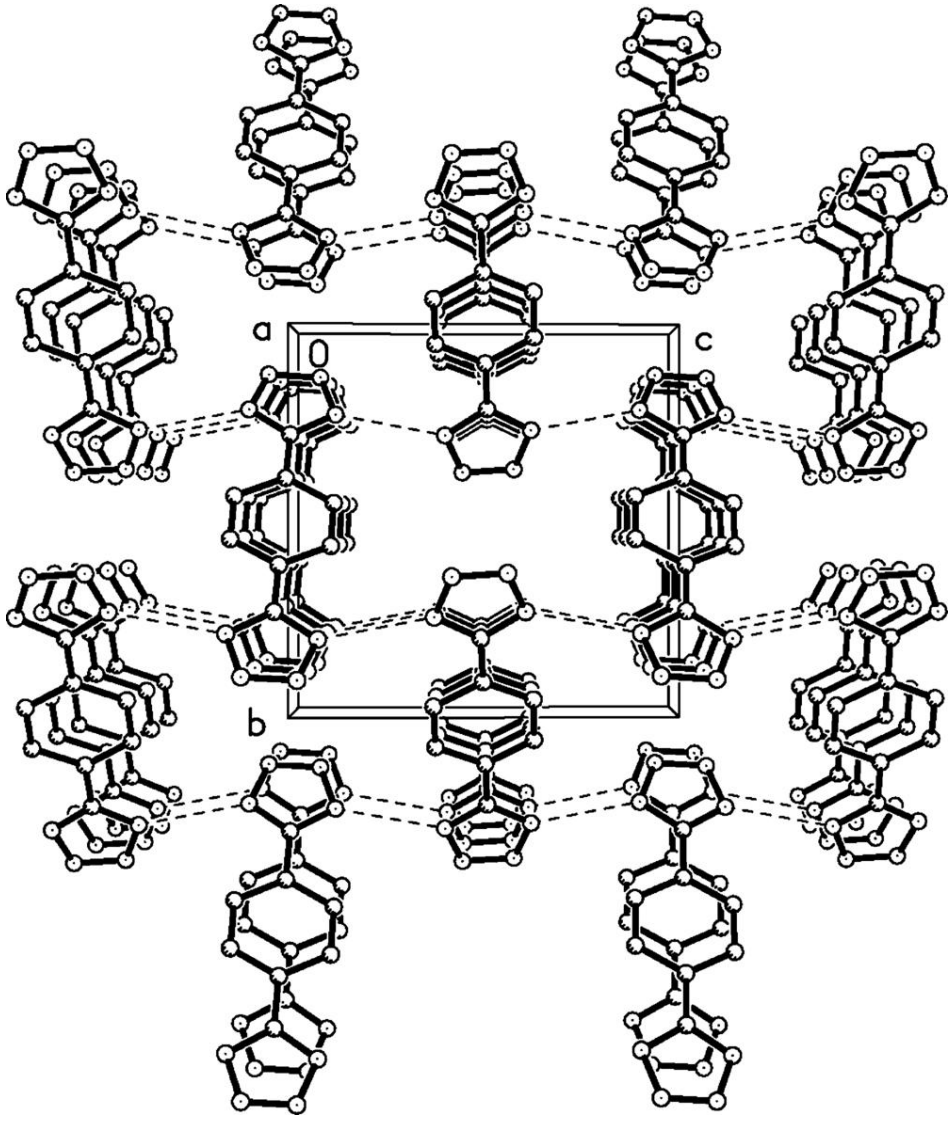
Fig. 2