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3-Phenyl-6-(2-pyridyl)-1,2,4,5-tetrazine

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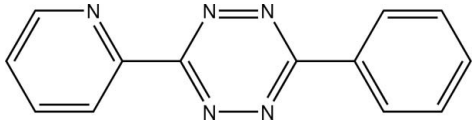
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; disorder in main residue; R factor = 0.041; wR factor = 0.112; data-to-parameter ratio = 10.7.

The title compound, $C_{13}H_9N_5$, is the first asymmetric diaryl-1,2,4,5-tetrazine to be crystallographically characterized. We have been interested in this motif for incorporation into supramolecular assemblies based on coordination chemistry. The solid state structure shows a centrosymmetric molecule, forcing a positional disorder of the terminal phenyl and pyridyl rings. The molecule is completely planar, unusual for aromatic rings with N atoms in adjacent *ortho* positions. The stacking observed is very common in diaryltetrazines and is dominated by π stacking [centroid-to-centroid distance between the tetrazine ring and the aromatic ring of an adjacent molecule is 3.6 Å, perpendicular (centroid-to-plane) distance of about 3.3 Å].

Related literature

For a review of the potential applications of this type of molecule, see: Cooke & Hanan (2007). Many symmetric tetrazine molecules have been studied for their reactivity in reverse electron-demand [2 + 2] cycloaddition reactions, unusually well resolved EPR spectra and X-ray crystallography (Neunhoffer, 1984). Pertinent articles for this molecule include work by Dinolfo *et al.* (2004), Ahmed & Kitaigorodsky (1972) and Klein *et al.* (1998).



Experimental

Crystal data

$C_{13}H_9N_5$
M_r = 235.25
Monoclinic, $P2_1/n$
a = 5.3129 (3) Å
b = 5.2867 (3) Å
c = 18.9052 (12) Å
β = 91.940 (4)°
V = 530.70 (5) Å^3
Z = 2
Cu $K\alpha$ radiation
μ = 0.77 mm^{-1}
T = 100 (2) K
0.24 × 0.10 × 0.03 mm

Data collection

Bruker APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick,1996)
T_{min} = 0.784, T_{max} = 0.98
8349 measured reflections
879 independent reflections
842 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.112
S = 1.17
879 reflections
82 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

Data collection: *APEX2* (Bruker, 2006); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *UdMX* (local program).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HJ2003).

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supplementary materials

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Comment

The most striking feature of the title compound is the near planarity of the molecule, with torsion angles deviating only by half a degree (see table 1 for details). While common for diaryltetrazine, like diphenyltetrazine (Ahmed & Kitaigorodsky, 1972), bis(2-pyridyl)tetrazine (Klein *et al.*., 1998) showed a 20 ° torsion angle between aromatic rings in order to accommodate the two nitrogen atoms directly in front of each other.

The molecule has three distinct interactions. First there are π stacking interactions present above and below the plane of the molecule, with both terminal rings interacting with the central tetrazine ring above or below the plane, while the tetrazine ring has interaction with two terminal aromatic rings. More precisely, the tetrazine ring has centroid-to-centroid distance of 3.6 Å and perpendicular (centroid-to-plane) distance of about 3.3 Å with the terminal ring of adjacent molecule (x, y, z and x, $y + 1$, z).

In the direction of the long axis of the molecule, the terminal rings form head-to-tail interaction with each other, having the closest intermolecular C···C (x,y,z and $0.5 - x$, $1/2 + y$, $1.5 - z$) distance of 3.6 Å and with a 75 ° angle formed by the planes of these two rings.

Finally, perpendicular to the plane and the long axis of the molecule, there is weak van der Waals interactions between adjacent molecules (x, y, z and $x + 1$, $y + 1$, z) with the shortest distance being 5.3 Å. The planes of adjacent molecules are almost at the same height, with only a 0.5 Å separation between them.

Experimental

The title compound was obtained following an adapted published procedure (Dinolfo *et al.*, 2004): Benzonitrile (3 eq., 27 mmoles, 2.7 ml), 2-cyanopyridine (1 eq., 8.95 mmoles, 932 mg) and hydrazine monohydrate (10 eq., 89.5 mmoles, 4.3 ml) were placed in a 25 ml round-bottom flask. One drop of concentrated HCl and water (~ 0.8 ml each) were added and the solution was refluxed for 2 h. To the cooled reaction mixture 25 ml of water was added and the resulting pink solid was filtered and immediately dissolved in a minimal amount of acetic acid (15–20 ml). To this stirred solution, 1 ml of 30% $NaNO_2$ (aq) was added drop-wise and stirred for 1 h. This mixture was diluted in 50 ml of water and extracted with dichloromethane (3 portions of 22 ml). The isolated organic fractions were washed successively with aqueous saturated $NaHCO_3$ and brine and finally dried over Na_2SO_4, filtered and evaporated under reduced pressure to afford a crude pink product. The product was purified by silica gel chromatography using DCM: 4% MeOH as eluent. The first pink band is the symmetric phenyl tetrazine (160 mg, 7%) and the second band is the title compound (133 mg, 6%). The last band is bis(2-pyridyl)-1,2,4,5-tetrazine (620 mg, 31%). Pink plates of title compound were obtained by slow diffusion of diethyl ether into concentrated dichloromethane solution of the compound.

1H NMR (CDCl3, 400 MHz): 8.97 (d, 1H), 8.70 (d, 3H), 8.00 (ddd, 1H), 7.7–7.6 (m, 3H), 7.56 (ddd, 1H) p.p.m.. Elemental analysis: expected for C13H9N5; C = 66.37%, H = 3.86%, N = 29.77%; found: C = 66.12%, H = 3.18%, N = 30.12%.

Refinement

During refinement, it was found that the density at the position of atom C7 was too high for carbon and too low for nitrogen, but fitted perfectly for half an atom of each, thus giving the predicted compound. Those atoms (C7 and N3) had their occupancy fixed at 50% and their coordinates and thermal factors identical with EXYZ and EADP. Resolving at lower symmetry did not result in a preferential site for N or C, but the model had a lower structure factor when there was one of each, thus confirming that title compound is disordered in position over two sites. The fixation of the occupancy of the hydrogen of C7 at 50% also made the model more coherent with a better *R* value.

The H atoms were generated geometrically (C—H 0.95 Å) and were included in the refinement in the riding model approximation; their temperature factors were set to 1.2 times those of the equivalent isotropic temperature factors of the parent site.

Figures

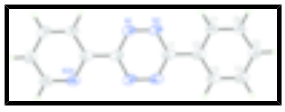

Fig. 1. *ORTEP* view of the title compound. Thermal ellipsoids are shown at 50% probability levels, H atoms are drawn as sphere of arbitary size, C7 and N3 atoms are 50% disordered on top of each other but are shown on different side of the asymetric unit to show the whole molecule.

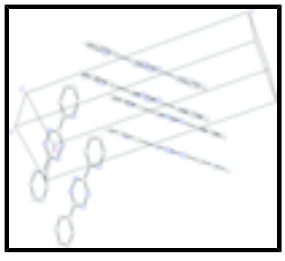

Fig. 2. Packing of the the title compound.

3-Phenyl-6-(2-pyridyl)-1,2,4,5-tetrazine

Crystal data

$C_{13}H_9N_5$	F_{000} = 244
M_r = 235.25	D_x = 1.472 Mg m^{-3}
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation λ = 1.54178 Å
Hall symbol: -P 2yn	Cell parameters from 5451 reflections
a = 5.3129 (3) Å	θ = 8.4–67.6º
b = 5.2867 (3) Å	μ = 0.77 mm^{-1}
c = 18.9052 (12) Å	T = 100 (2) K
β = 91.940 (4)º	Plate, pink
V = 530.70 (5) Å^3	0.24 × 0.10 × 0.03 mm
Z = 2	

Data collection

Bruker Microstar diffractometer	879 independent reflections
Radiation source: Rotating Anode	842 reflections with $I > 2\sigma(I)$
Monochromator: Helios optics	$R_{int} = 0.036$
$T = 100(2)$ K	$\theta_{max} = 67.9^{o}$
ω scans	$\theta_{min} = 8.7^{o}$
Absorption correction: multi-scan (SADABS; Sheldrick,1996)	$h = -6 \rightarrow 6$
$T_{min} = 0.784$, $T_{max} = 0.98$	$k = -6 \rightarrow 6$
8349 measured reflections	$l = -20 \rightarrow 21$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.041$	H-atom parameters constrained
$wR(F^2) = 0.112$	$w = 1/[\sigma^2(F_o^2) + (0.0547P)^2 + 0.1464P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.17$	$(\Delta/\sigma)_{max} < 0.001$
879 reflections	$\Delta\rho_{max} = 0.15$ e Å^{-3}
82 parameters	$\Delta\rho_{min} = -0.15$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Experimental. X-ray crystallographic data for the title compound were collected from a single-crystal sample, which was mounted on a loop fiber. Data were collected using a Bruker microstar diffractometer equiped with a Platinum 135 CCD Detector, a Montel 200 optics and a Kappa goniometer. The crystal-to-detector distance was 4.0 cm, and the data collection was carried out in 512 *x* 512 pixel mode. The initial unit-cell parameters were determined by a least-squares fit of the angular setting of strong reflections, collected by a 10.0 degree scan in 33 frames over three different parts of the reciprocal space (99 frames total). One complete sphere of data was collected.

Due to geometrical constraints of the instrument and the use of copper radiation, we obtain consistently a data completeness lower than 100% in dependence of the crystal system and the orientation of the mounted crystal, even with appropriate data collection routines. Typical values for data completeness range from 83–92% for triclinic, 85–97% for monoclinic and 85–98% for all other crystal systems.

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 $F^2 > 2\text{sigma}(F^2)$ is used only for calculat-

ing *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}	Occ. (<1)
N1	−0.2061 (2)	−0.1514 (2)	0.99344 (7)	0.0346 (4)	
N2	−0.1772 (2)	0.0302 (2)	0.94668 (7)	0.0346 (4)	
N3	−0.1139 (2)	0.4124 (2)	0.84843 (8)	0.0355 (4)	0.50
C1	0.0294 (2)	0.1780 (3)	0.95437 (8)	0.0319 (4)	
C2	0.0639 (2)	0.3820 (3)	0.90237 (8)	0.0318 (4)	
C3	0.2726 (2)	0.5426 (3)	0.90769 (8)	0.0351 (4)	
H3	0.3971	0.5185	0.9443	0.042*	
C4	0.2969 (3)	0.7360 (3)	0.85966 (9)	0.0368 (4)	
H4	0.4373	0.8471	0.8634	0.044*	
C5	0.1164 (3)	0.7682 (3)	0.80592 (9)	0.0360 (4)	
H5	0.1308	0.9011	0.7725	0.043*	
C6	−0.0864 (3)	0.6023 (3)	0.80185 (9)	0.0370 (4)	
H6	−0.2101	0.6236	0.7649	0.044*	
C7	−0.1139 (2)	0.4124 (2)	0.84843 (8)	0.0355 (4)	0.50
H7	−0.2540	0.3011	0.8441	0.043*	0.50

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0242 (6)	0.0391 (7)	0.0406 (8)	−0.0021 (5)	0.0014 (5)	−0.0054 (5)
N2	0.0236 (6)	0.0393 (7)	0.0411 (8)	−0.0036 (5)	0.0029 (5)	−0.0052 (5)
N3	0.0255 (6)	0.0338 (7)	0.0467 (9)	0.0002 (5)	−0.0060 (6)	−0.0032 (6)
C1	0.0204 (6)	0.0357 (8)	0.0397 (9)	0.0008 (5)	0.0025 (6)	−0.0113 (6)
C2	0.0217 (6)	0.0335 (7)	0.0403 (10)	0.0025 (5)	0.0027 (6)	−0.0096 (6)
C3	0.0223 (7)	0.0429 (8)	0.0402 (10)	−0.0016 (6)	−0.0008 (6)	−0.0072 (7)
C4	0.0239 (7)	0.0385 (8)	0.0483 (10)	−0.0029 (6)	0.0044 (7)	−0.0087 (7)
C5	0.0290 (7)	0.0334 (7)	0.0456 (10)	0.0030 (6)	0.0043 (6)	−0.0018 (6)
C6	0.0286 (7)	0.0375 (8)	0.0445 (10)	0.0016 (6)	−0.0067 (6)	0.0013 (6)
C7	0.0255 (6)	0.0338 (7)	0.0467 (9)	0.0002 (5)	−0.0060 (6)	−0.0032 (6)

Geometric parameters (Å, °)

N1—N2	1.3177 (18)	C3—C4	1.376 (2)
N1—C1^{i}	1.3462 (19)	C3—H3	0.9500
N2—C1	1.3514 (18)	C4—C5	1.384 (2)
N3—C6	1.347 (2)	C4—H4	0.9500
N3—C2	1.3758 (19)	C5—C6	1.389 (2)
C1—N1^{i}	1.3462 (19)	C5—H5	0.9500
C1—C2	1.475 (2)	C6—H6	0.9500
C2—C3	1.398 (2)		
N2—N1—C1^{i}	118.26 (12)	C2—C3—H3	120.1
N1—N2—C1	117.52 (12)	C3—C4—C5	119.83 (13)

C6—N3—C2	118.99 (12)	C3—C4—H4	120.1
N1^{i}—C1—N2	124.22 (15)	C5—C4—H4	120.1
N1^{i}—C1—C2	117.74 (12)	C4—C5—C6	118.68 (15)
N2—C1—C2	118.04 (13)	C4—C5—H5	120.7
N3—C2—C3	120.37 (14)	C6—C5—H5	120.7
N3—C2—C1	118.80 (12)	N3—C6—C5	122.39 (13)
C3—C2—C1	120.83 (13)	N3—C6—H6	118.8
C4—C3—C2	119.73 (13)	C5—C6—H6	118.8
C4—C3—H3	120.1		
C1^{i}—N1—N2—C1	0.0 (2)	N2—C1—C2—C3	179.51 (12)
N1—N2—C1—N1^{i}	0.0 (2)	N3—C2—C3—C4	1.6 (2)
N1—N2—C1—C2	180.00 (11)	C1—C2—C3—C4	−178.19 (12)
C6—N3—C2—C3	−1.4 (2)	C2—C3—C4—C5	−0.8 (2)
C6—N3—C2—C1	178.37 (12)	C3—C4—C5—C6	−0.1 (2)
N1^{i}—C1—C2—N3	179.81 (12)	C2—N3—C6—C5	0.5 (2)
N2—C1—C2—N3	−0.2 (2)	C4—C5—C6—N3	0.3 (2)
N1^{i}—C1—C2—C3	−0.4 (2)		

Symmetry codes: (i) −*x*, −*y*, −*z*+2.

Fig. 1

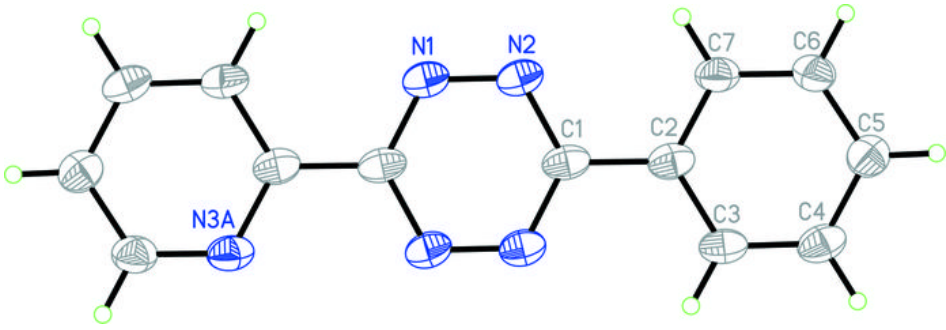
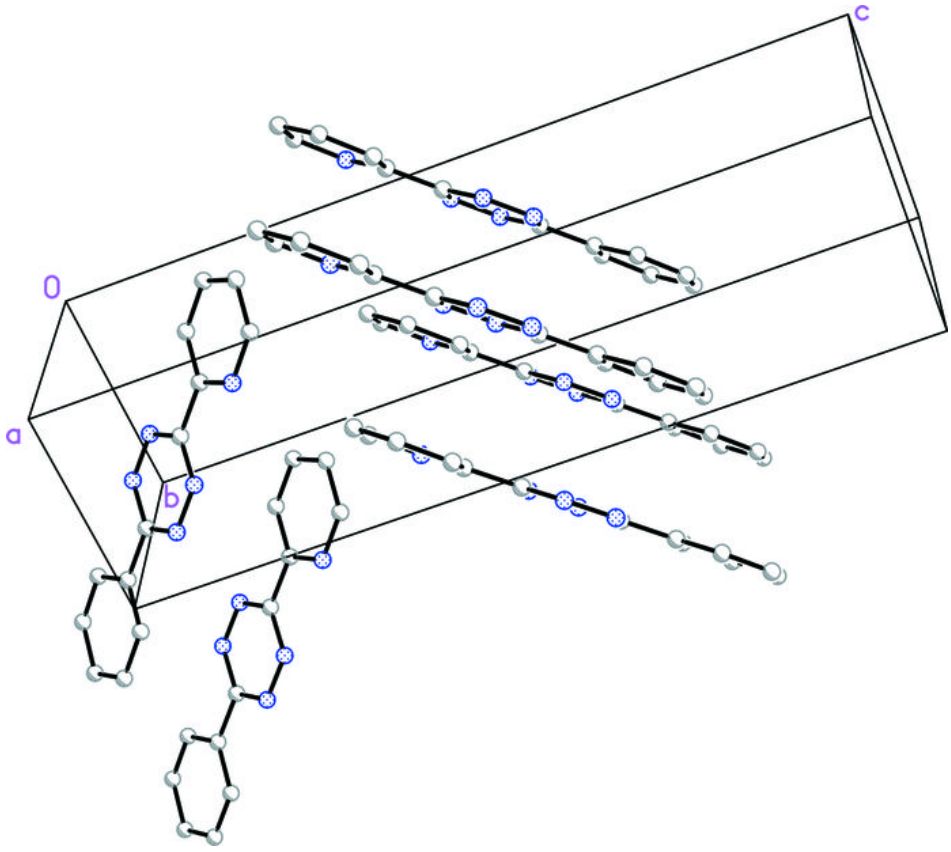
Fig. 2