Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

4,4′-(1,2,4,5-Tetrazine-3,6-diyl)dibenzonitrile

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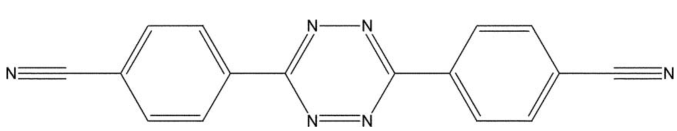
Received 16 February 2009; accepted 9 March 2009

Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.002 Å; R factor = 0.044; wR factor = 0.135; data-to-parameter ratio = 15.2.

Molecules of the title compound, $C_{16}H_8N_6$, lie on crystallographic inversion centres. A dihedral angle of 16.1 (1)° is formed between the central tetrazine ring and the plane of each cyanophenyl group. The molecules form stacks along [100] with a perpendicular interplanar separation of 3.25 (1) Å. C—H···N interactions are formed between molecules in neighbouring stacks.

Related literature

For synthesis details, see: Spychała *et al.* (1994, 2000). For related structures and discussion, see: Higashi & Osaki (1981); Infantes *et al.* (2003).



Experimental

Crystal data

$C_{16}H_8N_6$
M_r = 284.28
Monoclinic, $P2_1/c$
a = 4.8447 (5) Å
b = 12.1054 (12) Å
c = 11.6927 (11) Å
β = 94.363 (8)°
V = 683.75 (12) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 291 K
0.45 × 0.2 × 0.1 mm

Data collection

Kuma KM-4-CCD diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2007)
T_{min} = 0.925, T_{max} = 0.991
5912 measured reflections
1768 independent reflections
1094 reflections with $I > 2\sigma(I)$
R_{int} = 0.017

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.135
S = 1.06
1768 reflections
116 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···N10^{i}	0.989 (17)	2.539 (17)	3.370 (2)	141.6 (13)
C8—H8···N2^{ii}	0.956 (17)	2.850 (17)	3.6106 (19)	137.2 (12)
C9—H9···N10^{iii}	0.993 (17)	2.754 (17)	3.431 (2)	125.8 (12)

Symmetry codes: (i) $-x+2, -y+1, -z$; (ii) $x+1, -y+\frac{1}{2}, z+\frac{1}{2}$; (iii) $-x+2, y-\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

This work was supported by funds from Adam Mickiewicz University, Faculty of Chemistry.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BI2354).

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supporting information

Acta Cryst. (2009). E**65**, o824 [doi:10.1107/S1600536809008599]

4,4′-(1,2,4,5-Tetrazine-3,6-diyl)dibenzonitrile

Grzegorz Dutkiewicz, Teresa Borowiak and Jarosław Spychała

S1. Comment

Infantes *et al.* (2003) have found that the supramolecular structures of some substituted phenyl derivatives of 1,2,4,5-tetrazine are comparable to those of their carboxylic acid analogues. Being inspired by that, we have compared the supramolecular structures of the title compound 3,6-bis(4-cyanophenyl)-1,2,4,5-tetrazine (hereafter I) and *p*-cyano-benzoic acid (Higashi & Osaki, 1981) (hereafter II).

In (I), the tetrazine molecule is located on a crystallographic inversion centre (Fig. 1). The phenyl rings are twisted with respect to the tetrazine ring by 16.1 (1)° in opposite directions. The cyano-groups are coplanar with their phenyl rings. Two C6—H6···N10(cyano) interactions related by a centre of inversion can be considered to link the molecules into 1-D chains (Fig. 2). The chains are "stepped" rather than flat (Fig. 3). Each molecule interacts with the neighbouring chain through C8—H8···N2(tetrazine) and C9—H9···N10(cyano) interactions (Fig. 2), and the molecules are stacked along [100] with a perpendicular interplanar spacing of 3.25 (1) Å. This structure contrasts with the layered structures of other phenyl-derivatives of 1,2,4,5 tetrazines described in the paper by Infantes *et al.* (2003).

In the crystal structure of (II), similar 1-D chains are formed through the well-known centrosymmetric carboxylic acid dimer on one side of the molecule and centrosymmetric C—H···N(cyano) interactions on the other side of the molecule. The latter interactions are closely comparable to those in (I), except that the chains in (II) lie in approximately flat layers parallel to the (201) planes. The distinction between the two structures arises because of differences between the lateral C—H···O interactions between chains in (II) and the C—H···N(tetrazine) and C—H···N(cyano) interactions in (I).

S2. Experimental

The title compound was obtained from a multi-step procedure starting from 4-amidinobenzamide hydrochloride and anhydrous hydrazine. Dehydration of the biscarbamoyl intermediate compound to the appropriate biscyano red product was effected by means of phosphorus oxychloride in the same way as described for 2,4-bis(4- carbamoylphenyl)-1,3,5-triazine (Spychała *et al.*, 1994; Spychała (2000). M.p. 568–570 K (acetone); δ_H ($CDCl_3$, TMS) 7.94 (d, 4H, J = 8.8 Hz, CH), 8.82 (d, 4H, J = 8.8 Hz, CH); δ_C (DMSO-d$_6$) 114.7, 117.8, 128.2, 133.0, 135.6, 162.4; MS (EI) 284 (M^+, $C_{16}H_8N_6$; 13), 128 (100), 102 (9), 101 (33), 100 (7), 77 (9), 76 (12), 75 (16), 74 (4), 64 (11).

Single crystals were grown from hot acetone by slow cooling.

S3. Refinement

All H atoms were found from difference Fourier maps and refined freely with isotropic displacement parameters.

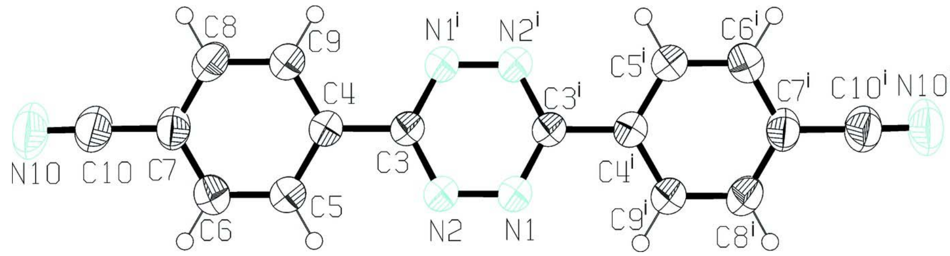

Figure 1

Molecular structure showing displacement ellipsoids at the 50% probability level for non-H atoms. Symmetry code: (i) -*x*, -*y*, -*z*.

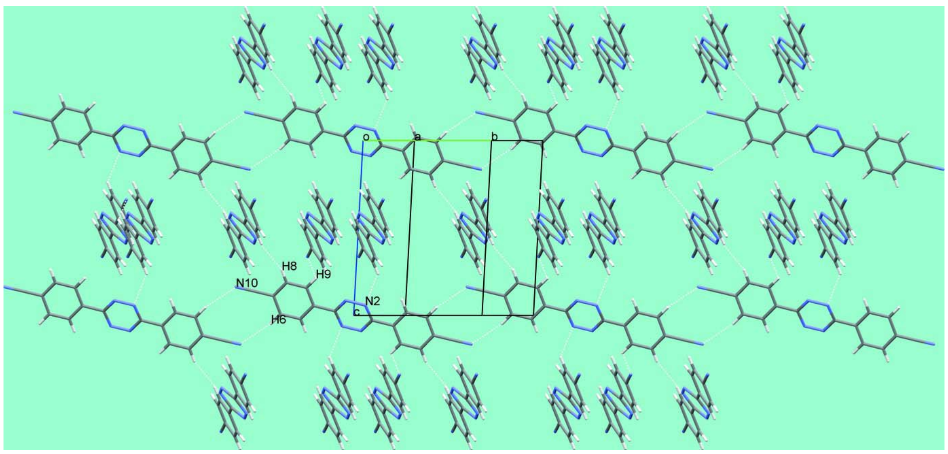

Figure 2

Chains of molecules (horizontal) linked by centrosymmetric pairs of C—H···N(cyano) interactions.

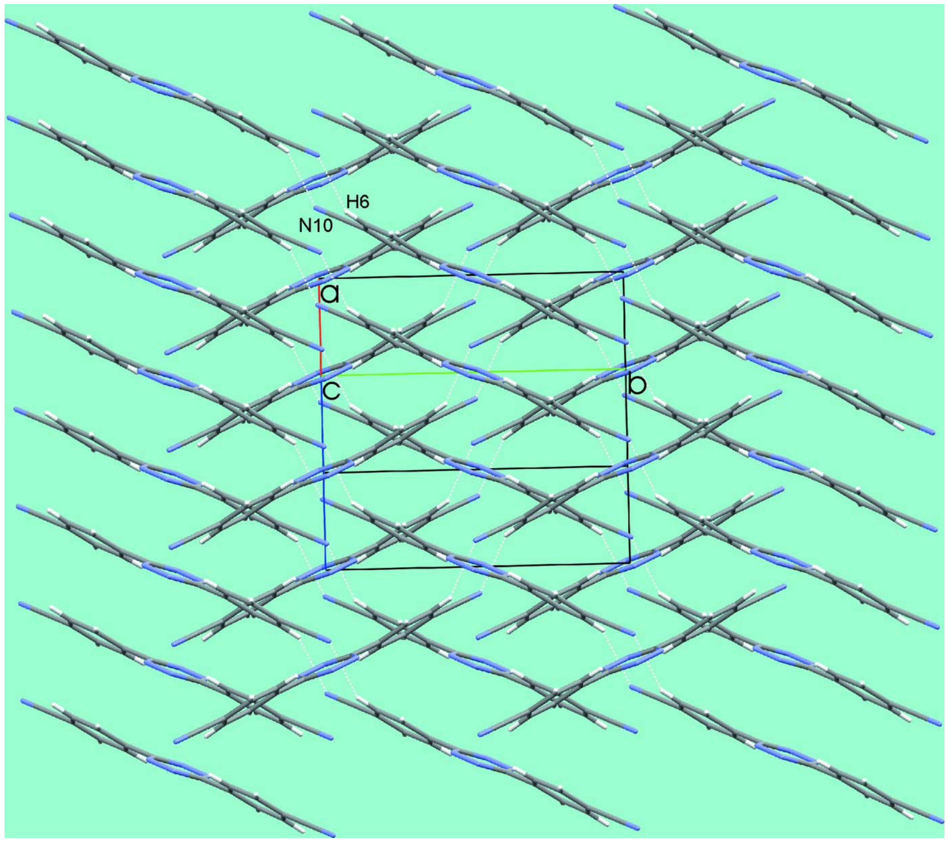

Figure 3

Stacks of molecules (vertical) showing the "stepped" arrangement within the 1-D chains.

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Crystal data

$C_{16}H_8N_6$
$M_r = 284.28$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 4.8447$ (5) Å
$b = 12.1054$ (12) Å
$c = 11.6927$ (11) Å
$\beta = 94.363$ (8)°
$V = 683.75$ (12) Å^3
$Z = 2$
$F(000) = 292$
$D_x = 1.381$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2059 reflections
$\theta = 2.4$–29.6°
$\mu = 0.09$ mm^{-1}
$T = 291$ K
Block, orange
0.45 × 0.2 × 0.1 mm

Data collection

Kuma KM-4-CCD
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.1929 pixels mm^{-1}
ω scans
Absorption correction: multi-scan
(*CrysAlis RED*; Oxford Diffraction, 2007)
$T_{min} = 0.925$, $T_{max} = 0.991$
5912 measured reflections
1768 independent reflections
1094 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 29.7°$, $\theta_{min} = 3.4°$
$h = -6 \rightarrow 6$
$k = -16 \rightarrow 15$
$l = -15 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.135$
$S = 1.06$
1768 reflections
116 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0683P)^2 + 0.0311P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.16$ e Å^{-3}
$\Delta\rho_{min} = -0.13$ 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	−0.2003 (2)	0.01444 (9)	−0.08623 (10)	0.0532 (4)
N2	−0.0256 (2)	0.09630 (9)	−0.05942 (10)	0.0528 (4)
C3	0.1693 (2)	0.07922 (10)	0.02639 (10)	0.0418 (3)
C4	0.3614 (2)	0.17078 (10)	0.05676 (11)	0.0434 (3)
C5	0.3849 (3)	0.25828 (12)	−0.01845 (13)	0.0546 (4)
C6	0.5664 (3)	0.34327 (13)	0.00878 (14)	0.0596 (4)
C7	0.7235 (3)	0.34205 (12)	0.11308 (13)	0.0542 (4)
C8	0.7010 (3)	0.25569 (14)	0.18883 (14)	0.0626 (5)
C9	0.5218 (3)	0.16937 (13)	0.16039 (13)	0.0564 (4)
C10	0.9104 (3)	0.43269 (15)	0.14189 (14)	0.0682 (5)
N10	1.0547 (4)	0.50498 (14)	0.16340 (14)	0.0986 (6)
H6	0.588 (3)	0.4047 (13)	−0.0455 (16)	0.080 (5)*
H5	0.271 (3)	0.2606 (13)	−0.0895 (14)	0.065 (4)*
H8	0.811 (3)	0.2535 (13)	0.2601 (15)	0.078 (5)*
H9	0.509 (3)	0.1054 (14)	0.2128 (14)	0.076 (5)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0548 (7)	0.0474 (7)	0.0549 (7)	−0.0081 (5)	−0.0131 (5)	0.0051 (5)
N2	0.0546 (7)	0.0469 (7)	0.0542 (7)	−0.0070 (5)	−0.0128 (5)	0.0056 (5)
C3	0.0429 (7)	0.0433 (7)	0.0388 (7)	−0.0019 (6)	0.0003 (5)	−0.0008 (5)
C4	0.0423 (7)	0.0441 (7)	0.0433 (7)	−0.0026 (6)	−0.0005 (5)	−0.0012 (6)
C5	0.0578 (8)	0.0545 (9)	0.0496 (8)	−0.0100 (7)	−0.0075 (6)	0.0061 (7)
C6	0.0670 (10)	0.0537 (9)	0.0572 (9)	−0.0152 (8)	−0.0005 (7)	0.0056 (7)

C7	0.0534 (8)	0.0538 (9)	0.0553 (9)	−0.0146 (7)	0.0033 (6)	−0.0068 (7)
C8	0.0640 (9)	0.0719 (10)	0.0494 (8)	−0.0190 (8)	−0.0114 (7)	0.0007 (8)
C9	0.0620 (9)	0.0566 (9)	0.0487 (8)	−0.0149 (7)	−0.0086 (7)	0.0060 (7)
C10	0.0749 (10)	0.0741 (11)	0.0554 (9)	−0.0259 (9)	0.0034 (8)	−0.0063 (8)
N10	0.1182 (13)	0.1029 (13)	0.0742 (11)	−0.0672 (11)	0.0037 (9)	−0.0105 (9)

Geometric parameters (Å, º)

N1—N2	1.3254 (14)	C6—C7	1.388 (2)
N1—C3^{i}	1.3347 (17)	C6—H6	0.989 (17)
N2—C3	1.3403 (17)	C7—C8	1.380 (2)
C3—N1^{i}	1.3347 (17)	C7—C10	1.446 (2)
C3—C4	1.4735 (17)	C8—C9	1.383 (2)
C4—C5	1.3869 (19)	C8—H8	0.955 (17)
C4—C9	1.3888 (18)	C9—H9	0.993 (17)
C5—C6	1.375 (2)	C10—N10	1.1360 (18)
C5—H5	0.962 (16)		
N2—N1—C3^{i}	117.81 (11)	C5—C6—H6	120.8 (10)
N1—N2—C3	117.55 (11)	C7—C6—H6	119.6 (10)
N1^{i}—C3—N2	124.64 (11)	C8—C7—C6	120.49 (13)
N1^{i}—C3—C4	117.94 (11)	C8—C7—C10	120.27 (13)
N2—C3—C4	117.42 (11)	C6—C7—C10	119.25 (14)
C5—C4—C9	119.68 (12)	C7—C8—C9	119.80 (14)
C5—C4—C3	120.17 (12)	C7—C8—H8	121.0 (10)
C9—C4—C3	120.15 (12)	C9—C8—H8	119.1 (10)
C6—C5—C4	120.43 (13)	C8—C9—C4	119.99 (14)
C6—C5—H5	119.6 (9)	C8—C9—H9	120.7 (10)
C4—C5—H5	120.0 (9)	C4—C9—H9	119.4 (10)
C5—C6—C7	119.60 (14)	N10—C10—C7	178.9 (2)
C3^{i}—N1—N2—C3	−0.3 (2)	C4—C5—C6—C7	−1.0 (2)
N1—N2—C3—N1^{i}	0.3 (2)	C5—C6—C7—C8	0.7 (2)
N1—N2—C3—C4	−179.39 (11)	C5—C6—C7—C10	−178.94 (15)
N1^{i}—C3—C4—C5	164.01 (13)	C6—C7—C8—C9	0.4 (3)
N2—C3—C4—C5	−16.25 (19)	C10—C7—C8—C9	−179.95 (15)
N1^{i}—C3—C4—C9	−15.40 (19)	C7—C8—C9—C4	−1.2 (3)
N2—C3—C4—C9	164.34 (13)	C5—C4—C9—C8	0.9 (2)
C9—C4—C5—C6	0.2 (2)	C3—C4—C9—C8	−179.71 (14)
C3—C4—C5—C6	−179.18 (13)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···N10^{ii}	0.989 (17)	2.539 (17)	3.370 (2)	141.6 (13)

C8—H8···N2^{iii}	0.956 (17)	2.850 (17)	3.6106 (19)	137.2 (12)
C9—H9···N10^{iv}	0.993 (17)	2.754 (17)	3.431 (2)	125.8 (12)

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