organic compounds

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

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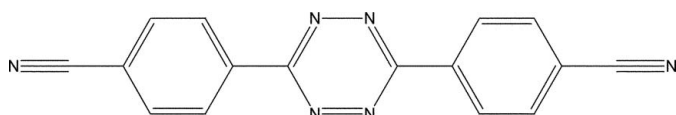
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Molecules of the title compound, $C_{16}H_8N_6$, lie on crystallographic inversion centres. A dihedral angle of 16.1 (1)° is formed between the central tetrazine ring and the plane of each cyanophenyl group. The molecules form stacks along [100] with 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

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

Data collection

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

Refinement

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
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*.

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supplementary materials

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

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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*-cyanobenzoic 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).

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$_8$N$_6$; 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.

Refinement

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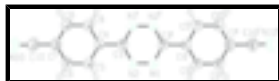
supplementary materials

Figures

Fig. 1. Molecular structure showing displacement ellipsoids at the 50% probability level for non-H atoms. Symmetry code: (i) -*x*, -*y*, -*z*.
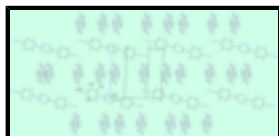

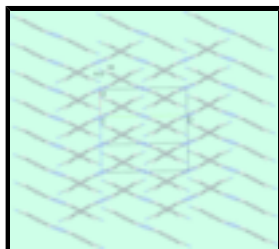Fig. 2. Chains of molecules (horizontal) linked by centrosymmetric pairs of C—H···N(cyano) interactions.

Fig. 3. Stacks of molecules (vertical) showing the "stepped" arrangement within the 1-D chains.

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

Crystal data

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

Data collection

Kuma KM-4-CCD diffractometer	1768 independent reflections
Radiation source: fine-focus sealed tube	1094 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.017$
Detector resolution: 8.1929 pixels mm^{-1}	$\theta_{max} = 29.7º$
$T = 291$ K	$\theta_{min} = 3.4º$
ω scans	$h = -6 \rightarrow 6$
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2007)	$k = -16 \rightarrow 15$
$T_{min} = 0.925$, $T_{max} = 0.991$	$l = -15 \rightarrow 14$
5912 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.044$	All H-atom parameters refined
$wR(F^2) = 0.135$	$w = 1/[\sigma^2(F_o^2) + (0.0683P)^2 + 0.0311P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
1768 reflections	$\Delta\rho_{max} = 0.16$ e Å^{-3}
116 parameters	$\Delta\rho_{min} = -0.13$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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, °)

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 codes: (i) −*x*, −*y*, −*z*.

Hydrogen-bond geometry (Å, °)

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.

Fig. 1

Fig. 2

Fig. 3