Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Wave-like structure in 3-(4,6-diamino-1,3,5-triazin-2-yl)-2-naphthonitrile

Jan Janczak

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, PO Box 1410, 50-950 Wrocław, Poland
Correspondence e-mail: j.janczak@int.pan.wroc.pl

Received 23 January 2008
Accepted 5 February 2008
Online 16 February 2008

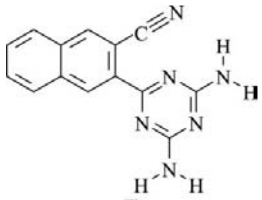
In the title compound, $C_{14}H_{10}N_6$, which crystallizes with $Z' = 2$ in the $C2/c$ space group, the molecules are linked by N—H···N hydrogen bonds into chains, which are arranged in a wave-like form stabilized by aromatic π–π stacking interactions. This work demonstrates the usefulness of aromatic triazine derivatives in crystal engineering.

Comment

A productive strategy in crystal engineering utilizes molecules which can form multiple interactions with their neighbours (Wuest, 2005). Hydrogen bonds are widely used as the principal interactions in this strategy since they are directional and relatively strong (Moulton & Zaworotko, 2001; Seiter, 2002). Many different self-complementary hydrogen-bonding groups can be used to control association in crystal engineering and to produce different arrangements, such as chains, sheets, ribbons, tapes, rosettes, *etc.*, having predictable structural features (Desiraju, 1990, 2002). Several studies have demonstrated the usefulness of melamine and its organic and inorganic complexes or salts in crystal engineering (Whitesides *et al.*, 1995; Janczak & Perpétuo, 2001, 2002, 2003, 2004, 2008; Perpétuo & Janczak, 2003, 2005, 2007), since their components contain complementary arrays of hydrogen-bonding sites. While π–π interactions are intermolecular forces whose nature is still a matter of discussion (Hunter & Sanders, 1990; Janiak, 2000; Cozzi *et al.*, 2003; Kobayashi & Saigo, 2005), in general, such an interaction can be said to consist of two aromatic rings arranged in a face-to-face orientation with a distance of 3.2–3.8 Å between the planes of the rings.

In an effort to engineer expanded versions of the structures formed during the transformation of the cyano group in dicyanobenzene isomers in the presence of cyanoguanidine (Janczak & Kubiak, 2005*a*,*b*), we have replaced the phenyl rings with naphthyl systems, using 2,3-dicyanonaphthalene, and we have investigated the role of π–π stacking interactions in the organization and stabilization of the resulting structures. We present here the crystal structure of one of these expanded systems, *viz.* the title compound, (I).

Compound (I) crystallizes with $Z' = 2$ and the two independent molecules, *M*1 and *M*2, are linked by N—H···N hydrogen bonds (Table 2) into a dimeric unit (Fig. 1). These units are linked by further N—H···N hydrogen bonds to form a zigzag chain (Fig. 3*a*). Although the bond lengths and angles in the two independent molecules are very similar, their conformations differ in the rotation angle of the triazine ring relative to the naphthalene system around the inter-ring bond: the dihedral angles between the triazine and naphthalene planes are 27.0 (2) and 10.7 (2)° in molecules *M*1 and *M*2, respectively. The rotation is caused by an interaction of the highly polar C≡N group with the triazine ring.


(I)

The gas-phase geometry obtained by *ab initio* molecular-orbital calculations (*GAUSSIAN98*; Frisch *et al.*, 1998) at the B3LYP/6-31+G* level confirms the nonplanar conformation of (I) (Fig. 2). The calculated dihedral angle between the planes of the triazine and naphthalene rings, *viz.* 14.7°, represents a global minimum on the potential energy surface (PES). During rotation of the triazine ring relative to naphthalene around the inter-ring bond from 0 to 360°, four equivalent minima and two pairs of maxima are found. The minima are observed at rotation angles of ±14.7 and 180±14.7° (*i.e.* 165.3 and 194.7°), while the maxima are observed at 0° (and 180°), with a barrier energy of ~5.85 kJ mol^{-1}, and at 90° (and 270°), with a barrier energy of ~14.35 kJ mol^{-1}.

The difference between the barrier energies of the conformations at 0 and 90° (ΔE = 8.5 kJ mol^{-1}) can be attributed to the π-delocalization energy of the π electrons along the inter-ring bond. At a rotation angle of 90° (rings perpendicular), delocalization of the π electrons between the rings is impossible due to the symmetry of the orbitals. The lengthening of the inter-ring bond, from 1.488 Å for the most stable conformation to 1.511 Å for a rotation angle of 90°, supports this

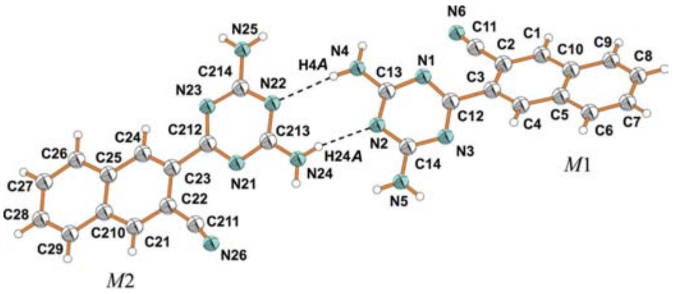


Figure 1
The independent components of compound (I), showing the atom-labelling scheme and the hydrogen bonds (dashed lines) within the selected asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

doi:10.1107/S0108270108003831

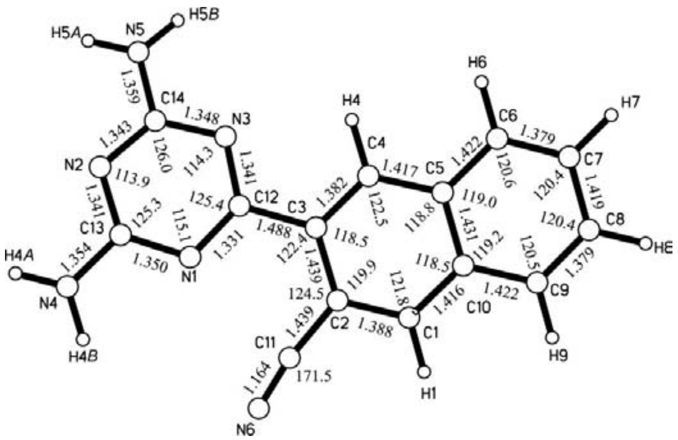


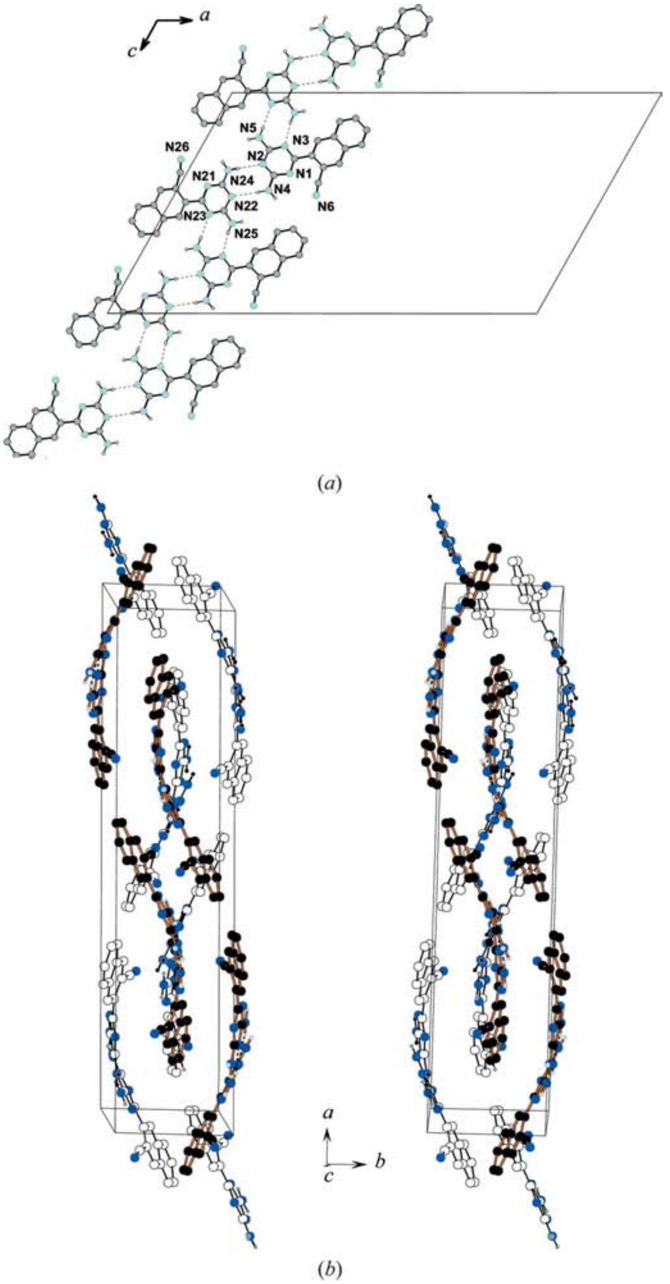
Figure 2
Results of the optimized molecular-orbital calculations (at the B3LYP/6-31+G* level) for (I) (Å, °).

fact. The estimated energy of molecule *M*1 in the conformation as present in the crystal structure is greater by ~6.75 kJ mol^{-1}, while for the second molecule it is greater only by ~1.85 kJ mol^{-1}. The differences between the energies of the molecules in the crystal structure and in the gas phase (obtained by molecular-orbital calculations) are compensated for by π–π interactions between the aromatic rings in the crystal structure.

Considering both conformations of independent molecules *M*1 and *M*2 in the crystal structure of (I) (Fig. 1 and Table 1) and in the gas-phase conformation (Fig. 2) in more detail, besides the main difference mentioned above in the rotation angle of the rings, several other differences can also be found. For example, the C—C≡N angle in molecule *M*1 [173.9 (2)°] is closer to 180° than that in molecule *M*2 [167.7 (2)°]. These values correlate well with the rotation angles of the triazine ring in relation to the naphthalene system. The greater rotation angle around the inter-ring C—C bond lengthens the distance between the polar C≡N group and the triazine ring and results in a decrease in the repulsion between the substituents at positions 2 and 3 in the naphthalene system.

In the dimer unit formed by independent molecules *M*1 and *M*2 (Fig. 1), the two triazine rings are not coplanar; the dihedral angle between their planes is 22.6 (1)°. Dimers related by a *c*-glide plane interact *via* two pairs of N—H···N hydrogen bonds, forming infinite chains along the *c* axis (Fig. 3*a*). There is no hydrogen bonding between the chains, and the chains interact only *via* van der Waals forces and π–π stacking interactions. Although the triazine rings each contain one potential hydrogen-bonding site (atoms N1 and N21), these sites are inactive due to steric hindrance from the cyano groups.

The various chains along [001] form a wave-like architecture (Fig. 3*b*), with a distance of *ca* 3.45 Å between adjacent aromatic ring systems, consistent with the occurrence of π–π stacking interactions, since this distance is comparable with the sum of the van der Waals radii of two C atoms in an aromatic ring system (Pauling, 1967). The sheets of the wave-like structure lie parallel to the (010) plane (Fig. 3*b*).



(*a*)

(*b*)

Figure 3
(*a*) A view of the N—H···N hydrogen-bonded chains of (I), which exhibit $R_2^2(8)$ topology. (*b*) Stereoview of the wave-like structure in the crystal structure of (I). For the sake of clarity, H atoms bonded to C atoms have been omitted.

Our observations underscore the potential utility of (I) in crystal engineering. The amine groups can donate hydrogen bonds to the N atoms of neighbouring triazine rings, which act as acceptors, thus forming a characteristic dimeric motif. This dimeric motif, containing hydrogen-bonding active sites, can interact with neighbouring molecules *via* two pairs of N—H···N hydrogen bonds, favouring the formation of one-dimensional polymers. In the absence of hydrogen bonds between these one-dimensional polymers, π–π interactions between offset aromatic rings stabilize the overall structure.

Experimental

2,3-Dicyanonaphthalene (99% purity) and cyanoguanidine (99% purity) were purchased from Sigma–Aldrich. They were mixed together in a 1:1 molar ratio and the mixture was pressed into pellets. The pellets were inserted into an evacuated glass ampoule and annealed in the temperature gradient 523–503 K for 6 h. Crystals of 3-(4,6-diamino-1,3,5-triazin-2-yl)-2-naphthonitrile, (I), were formed in the low-temperature zone during migration from the high-temperature zone at which the compound was formed (Janczak & Kubiak, 2005*a*,*b*). Elemental analysis found: C 64.21, N 32.00, H 3.79%; calculated for $C_{14}H_{10}N_6$: C 64.11, N 32.05, H 3.84%.

Crystal data

$C_{14}H_{10}N_6$
$M_r = 262.28$
Monoclinic, $C2/c$
$a = 35.798\ (7)$ Å
$b = 7.3190\ (10)$ Å
$c = 21.459\ (4)$ Å
$\beta = 118.96\ (3)^\circ$
$V = 4919\ (2)$ Å^3
$Z = 16$
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 295\ (2)$ K
0.32 × 0.26 × 0.18 mm

Data collection

Kuma KM-4 diffractometer with a CCD area-detector
Absorption correction: analytical, face-indexed (*SHELXTL*; Sheldrick, 2008)
$T_{\min} = 0.974$, $T_{\max} = 0.981$
27666 measured reflections
5875 independent reflections
3357 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.071$
$S = 1.04$
5875 reflections
362 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}

The H atoms were treated as riding in geometrically idealized positions, with C—H = 0.93 Å and N—H = 0.86 Å, and with $U_{\rm iso}(\rm H) = 1.2U_{\rm eq}(\rm C,N)$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2006); software used to prepare material for publication: *SHELXL97*.

Table 1
Selected geometric parameters (Å, °).

N6—C11	1.136 (3)	N26—C211	1.141 (2)
C2—C3	1.425 (3)	C22—C211	1.444 (2)
C2—C11	1.443 (3)	C23—C212	1.488 (2)
C3—C12	1.488 (2)		
C12—N1—C13	114.13 (15)	C212—N21—C213	115.00 (15)
C14—N2—C13	114.67 (15)	C214—N22—C213	114.09 (15)
C12—N3—C14	113.74 (15)	C212—N23—C214	113.13 (14)
N6—C11—C2	173.9 (2)	N26—C211—C22	167.7 (2)
N1—C12—N3	126.72 (16)	N21—C212—N23	126.70 (16)
N2—C13—N1	125.04 (16)	N22—C213—N21	124.95 (15)
N2—C14—N3	125.60 (16)	N22—C214—N23	126.13 (16)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4*A*···N22	0.86	2.32	3.171 (2)	172
N5—H5*B*···N23$^{\rm i}$	0.86	2.30	3.132 (2)	163
N24—H24*A*···N2	0.86	2.16	2.984 (2)	161
N24—H24*B*···N26$^{\rm ii}$	0.86	2.30	3.078 (3)	150
N25—H25*B*···N3$^{\rm iii}$	0.86	2.28	3.096 (2)	158

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

This work was supported financially by the Ministry of Science and Information Society Technologies (project No. 3T09A12128).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3192). Services for accessing these data are described at the back of the journal.

References

Brandenburg, K. & Putz, H. (2006). *DIAMOND*. Release 3.0. Crystal Impact GbR, Bonn, Germany.
Cozzi, F., Annunziata, R., Benagalia, M., Cinquini, M., Raimoudi, L., Baldridge, K. K. & Siegel, J. S. (2003). *Org. Biomol. Chem.* **1**, 157–162.
Desiraju, G. R. (1990). *Crystal Engineering. The Design of Organic Solids*. Amsterdam: Elsevier Science Publishers.
Desiraju, G. R. (2002). *Acc. Chem. Res.* **35**, 565–573.
Frisch, J. M. *et al.* (1998). *GAUSSIAN98*. Revision A3. Gaussian Inc., Pittsburgh, Pennsylvania, USA.
Hunter, C. A. & Sanders, J. K. M. (1990). *J. Am. Chem. Soc.* **112**, 5525–5534.
Janczak, J. & Kubiak, R. (2005*a*). *J. Mol. Struct.* **749**, 60–69.
Janczak, J. & Kubiak, R. (2005*b*). *J. Mol. Struct.* **751**, 74–84.
Janczak, J. & Perpétuo, G. J. (2001). *Acta Cryst.* C**57**, 1431–1433.
Janczak, J. & Perpétuo, G. J. (2002). *Acta Cryst.* C**58**, o455–o459.
Janczak, J. & Perpétuo, G. J. (2003). *Acta Cryst.* C**59**, o349–o352.
Janczak, J. & Perpétuo, G. J. (2004). *Acta Cryst.* C**60**, o211–o214.
Janczak, J. & Perpétuo, G. J. (2008). *Acta Cryst.* C**64**, o91–o94.
Janiak, C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3885–3896.
Kobayashi, Y. & Saigo, K. (2005). *J. Am. Chem. Soc.* **127**, 15054–15060.
Moulton, B. & Zaworotko, M. (2001). *Chem. Rev.* **101**, 1629–1658.
Oxford Diffraction (2006). *CrysAlis CCD* and *CrysAlis RED*. Versions 171.31.8. Oxford Diffraction Poland, Wrocław, Poland.
Pauling, L. (1967). *The Chemical Bond: A Brief Introduction to Modern Structural Chemistry*, ch. 3. Ithaca: Cornell University Press.
Perpétuo, G. J. & Janczak, J. (2003). *Pol. J. Chem.* **77**, 1323–1337.
Perpétuo, G. J. & Janczak, J. (2005). *Acta Cryst.* E**61**, o287–o289.
Perpétuo, G. J. & Janczak, J. (2007). *Acta Cryst.* C**63**, o271–o273.
Seiter, T. (2002). *Angew. Chem. Int. Ed.* **41**, 48–76.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Whitesides, G. M., Simanek, E. E., Mathias, J. P., Seto, C. T., Chin, D. N., Mammen, M. & Gordon, D. M. (1995). *Acc. Chem. Res.* **28**, 37–44.
Wuest, D. (2005). *Chem. Commun.* pp. 5830–5837.