

## The twofold interpenetrated three-connected three-dimensional (10,3)-net in 2-aminoethene-1,1,2-tricarbonitrile

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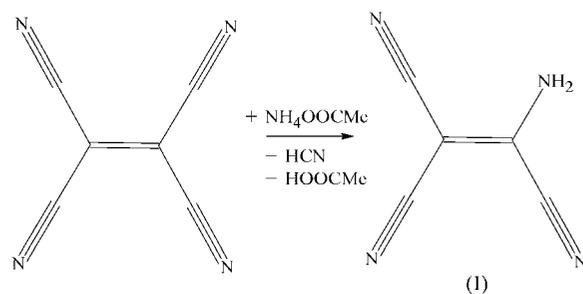
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In the crystal structure of the title compound,  $C_5H_2N_4$ , each molecule is linked by  $N-H \cdots N \equiv C$  hydrogen bonds to four other molecules, thus forming a network that can be described as a twofold interpenetrated three-connected three-dimensional (10,3)-net. The interpenetrated nets are related by (010) translation. If only intermolecular hydrogen bonds are taken into account, these nets can be considered as independent. However, the interactions between the cyano groups from different nets indicate mutual assistance of the two nets during their formation.

### Comment

Enaminonitriles are used as precursors in the synthesis of a wide variety of heterocyclic systems, such as pharmaceuticals, fungicides and solvatochromic dyes (Erian, 1993), as well as of various coordination compounds (Sidorov *et al.*, 1999). Therefore, investigations of the preparation and properties of the simplest enaminonitriles used for further chemical transformations form a major part of modern chemistry. We present here a novel and very efficient approach (94% yield) to the synthesis of 2-aminoethene-1,1,2-tricarbonitrile, (I). The crystallographic study of (I) extends our systematic investigation of the structural chemistry of enaminonitriles (Nasakin *et al.*, 1991; Tafeenko *et al.*, 1994*a,b,c,d*; Bogdan *et al.*, 1996*a,b*) and molecules containing the dicyanoethylene fragment (Nasakin *et al.*, 1992; Tafeenko *et al.*, 2003, 2005; Tafeenko, Nikolaev *et al.*, 2004; Tafeenko, Peschar *et al.*, 2004). Fig. 1 shows the molecular structure of (I) with the atom-labeling scheme, while the molecular dimensions are listed in Table 1. Particularly notable are the very short distance to the amine group (C2–N4), the lengthening of the adjacent C1=C2 double bond and the inequality of the C–C bonds that link

the cyano groups to the ethylene moiety. This results from a strong  $\pi$  conjugation of the amine group with the two cyano groups attached to atom C1, whereas the  $C3 \equiv N1$  cyano group does not take part in such conjugation. [In terms of energy,  $\pi$ - $\pi$  C2–C3 bonding is not advantageous, as it would result in either unpaired electrons or a large (+2) positive charge on atom N4 of the molecule.] Additional evidence of this conjugation is the planarity of the amine group [the sum of the angles around atom N4 is  $360(2)^\circ$ ]. Previous studies of enaminonitriles showed that the triple-bond distance in the cyano group is not sensitive to the action of different substituents, and this insensitivity is also seen in (I) (Table 1). Meanwhile, if we knew which of the cyano groups acquired additional negative charge we could understand the preferences in hydrogen bonding between the amine and cyano groups in the solid state. Atomic Mulliken charges were calculated with *GAUSSIAN98* (Frisch *et al.*, 1998) at the B3LYP/6-311G\*\* level (see Table 3). To elucidate how the amine group affects the charge distribution, the calculation was also carried out for 1,2,2-tricyanoethylene, (II). The data indicate that in (I) the negative charges on atoms N2 and N3 increase, while that on atom N1 decreases. The different charges correspond to the fact that only atoms N2 and N3 participate in hydrogen bonds (Table 2 and Fig. 2).



Previously, we concluded that the prevailing type of crystal packing of enaminonitriles includes formation of hydrogen-bonded centrosymmetric dimers (27 structures out of a total of 38), whereas hydrogen-bonded chains and other types of aggregation (which usually occur if a molecule of enaminonitrile contains other functional groups, such as hydroxy or ketone groups, or if a crystal contains solvent molecules, which

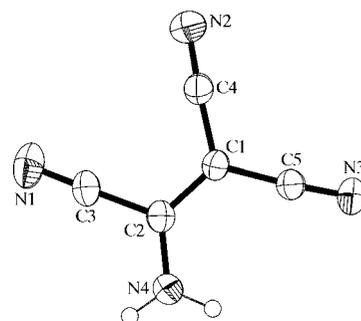


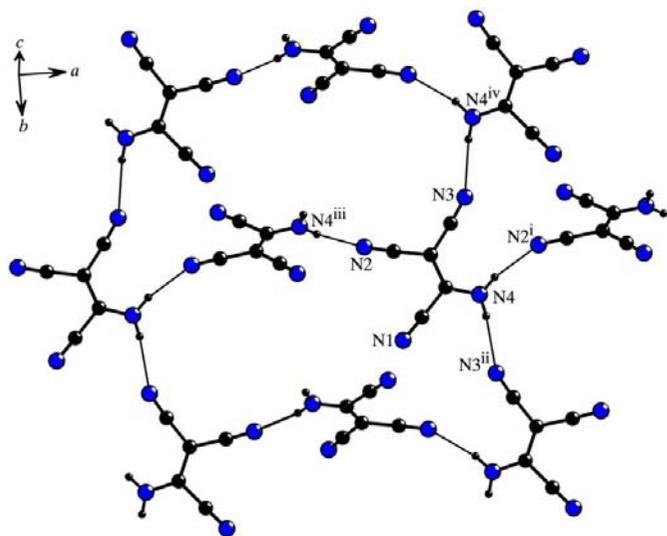
Figure 1

The atom-labeling scheme for (I). Displacement ellipsoids are drawn at the 50% probability level.

can lock the H atoms of the amine group) are relatively rare (Tafeenko *et al.*, 1991). On the basis of this observation and quantum chemical calculations, we suggested that the high probability of dimer formation is provided not only by hydrogen bonding between amine and cyano groups, but also by dipole–dipole interactions between the cyano groups; all dimer-containing structures exhibit short distances (2.9–3.3 Å) between N and C atoms of the cyano groups that form. Clearly, cyano–cyano interactions very often play a decisive role in the form of molecular aggregation in these solids (*e.g.* see Tafeenko *et al.*, 2005).

Preferential dimer formation was confirmed by data from the Cambridge Structural Database (CSD; Version 5.22; Allen, 2002). Under consideration were only the structures of organic compounds that had no disorder and refined to  $R < 0.075$ . Data visualization was performed with *MERCURY* (Version 1.2; Bruno *et al.*, 2002). Among 105 retrieved structures, 65 (62%) contained dimers, 17 (16%) contained chains and 23 (22%) adopted other types of aggregation. All dimeric structures had centrosymmetric space groups, *viz.*  $P\bar{1}$  (34 structures),  $P2_1/n,c$  (24) and  $C2/c$  (seven). Among the crystals that contained chains, eight structures (50%) had non-centrosymmetric space groups, *viz.*  $P2_12_12_1$  (four structures),  $Pna2_1$  (two), and  $P2_1$  and  $Pca2_1$  (one each).

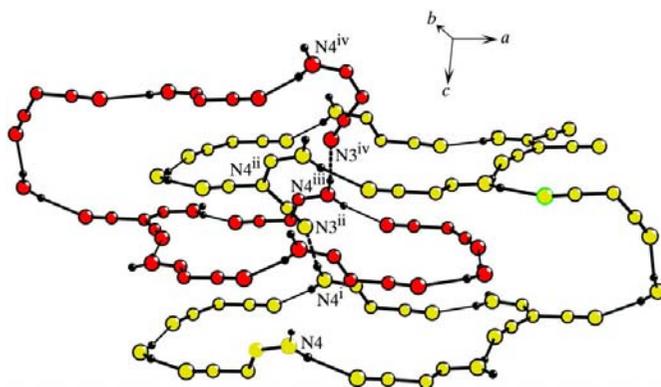
There are several approaches to the analysis of hydrogen-bonding patterns, but each of them provides an incomplete description of the picture observed in (I). According to Kuleshova & Zorky (1980), this pattern could be described as  $F_4^4(6)$ , thereby expressing that the six-molecule building blocks form a hydrogen-bonded framework in which every



**Figure 2**

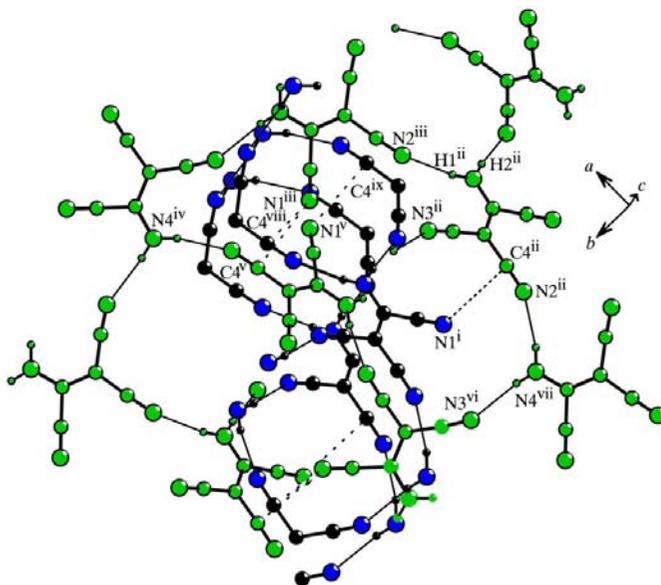
The arrangement of the  $R_6^c(32)$  building blocks in the crystal. Every molecule is connected to four others by  $N4-H1^i \cdots N2^i$ ,  $N4-H2^i \cdots N3^i$ ,  $N2 \cdots H1^{iii} - N4^{iii}$  and  $N3 \cdots H2^{iv} - N4^{iv}$  hydrogen bonds. Adjacent molecules in chains running along the  $a$  axis [*e.g.* the molecule at  $(x, y, z)$  and the related molecule with symmetry code (i)] make a dihedral angle of  $61^\circ$ , whereas molecules at  $(x, y, z)$  and related molecules with symmetry codes (ii) and (iv) are coplanar. [Symmetry codes: (i)  $\frac{1}{2} + x, -y, z$ ; (ii)  $\frac{3}{2} - x, 1 + y, -\frac{1}{2} + z$ ; (iii)  $\frac{1}{2} + x, -y, z$ ; (iv)  $\frac{3}{2} - x, -1 + y, \frac{1}{2} + z$ .]

molecule is connected to four others. The building block could be described as  $R_6^c(32)$  (Etter *et al.*, 1990; Bernstein *et al.*, 1995). According to Batten & Robson (1998), the network in



**Figure 3**

The mutual interpenetration of two nets (shown as dark and light shaded balls) occurs as a result of  $(N4-H2) \cdots N3$  hydrogen bonding. All atoms not involved in ring formation have been omitted for clarity. [Symmetry codes: (i)  $\frac{3}{2} - x, -1 + y, -\frac{1}{2} + z$ ; (ii)  $x, y, -1 + z$ ; (iii)  $x, -1 + y, -1 + z$ ; (iv)  $\frac{3}{2} - x, \frac{3}{2} - x, y, -\frac{3}{2} + z$ .]



**Figure 4**

An illustration of how molecules of the 'light' net form, on the one hand, their own helices and at the same time, owing to interaction between cyano groups, promote the formation of the 'dark' helices. As a first approximation, the structure could be represented as follows: atom  $N1^{ix}$  (dark) interacts with atom  $C4^x$  (light) in the molecule with symmetry code (x), which forms the six-molecule building block (see Fig. 2) through atoms  $N2^x$  and  $H1^x$ ; thereby the 'light' molecule net is assembled within the 'dark' net. Inside the 'dark' helix, 'light' atoms  $N1^{xiii}$  and  $N1^{xi}$  interact with 'dark' atoms  $C4^{xvii}$  and  $C4^{xvi}$ , respectively, as well as with  $C4^{xiii}$  from the 'light' net. Concurrently, the molecule at (x), through atoms  $N3^x$  and  $H2^x$ , forms two 'light' helices with opposite handedness in which 'dark' molecules are embedded. [Symmetry codes: (i)  $-\frac{1}{2} + x, -y, 1 + z$ ; (ii)  $-\frac{1}{2} + x, -1 - y, 1 + z$ ; (iii)  $x, -1 + y, 1 + z$ ; (iv)  $\frac{3}{2} - x, y, \frac{1}{2} + z$ ; (v)  $1 - x, -y, \frac{1}{2} + z$ ; (vi)  $\frac{1}{2} - x, y, \frac{1}{2} + z$ ; (vii)  $-1 + x, -1 + y, 1 + z$ ; (viii)  $x, y, 1 + z$ ; (ix)  $1 - x, -1 - y, \frac{1}{2} + z$ .]

(I) can be assigned as an interpenetrating three-connected three-dimensional (10,3)-net. The motif (Fig. 2) consists of ten nodes: five nodes are N4 atoms and five are C1 atoms. Each node is connected to two neighbors in a one-dimensional planar zigzag chain. The third connection at every node is to a node belonging to a zigzag chain running underneath at an interplanar angle of 61° to the original chain (Fig. 2). This structure conforms to the definition of a (10,3)-*b*-system. The second interpenetrating net originates from the first by a (010) translation. The interpenetration of the two nets is depicted in Fig. 3 (for clarity, only ring-forming atoms are shown). Alternatively, the network of (I) could be represented as parallel helices along the *c* axis with opposite handedness, which conform to the definition of a (10,3)-*a*-net. Fig. 4 shows how these helices penetrate each other as a result of interaction of the cyano groups not involved in hydrogen bonding (C3≡N1) with the cyano groups taking part in hydrogen bonding (C4≡N2). The N1...C4(*x*, 1 + *y*, *z*) and N1...C4(1 - *x*, 1 - *y*, -½ + *z*) distances are 3.257 (2) and 3.282 (2) Å, respectively. In other words, we can conclude that the two nets are independent if we take into account only hydrogen bonds, but each of these nets is also formed as a result of mutual assistance and co-polarization of cyano groups from different nets.

### Experimental

Tetracyanoethylene (0.64 g, 5 mmol) was added to a mixture of ammonium acetate (0.97 g, 12.5 mmol) and dioxane (5 ml). After 20 min of stirring, surplus ammonium acetate was filtered off. The solution was evaporated *in vacuo*, and the solid residue was triturated with hexane and filtered to yield (I) (0.55 g, 4.7 mmol, 94%). Recrystallization from acetonitrile afforded yellow crystals of (I) suitable for X-ray analysis.

#### Crystal data

C <sub>5</sub> H <sub>2</sub> N <sub>4</sub>	Mo Kα radiation
<i>M<sub>r</sub></i> = 118.11	Cell parameters from 25 reflections
Orthorhombic, <i>Pca</i> 2 <sub>1</sub>	<i>θ</i> = 15–19°
<i>a</i> = 13.3146 (8) Å	<i>μ</i> = 0.10 mm <sup>-1</sup>
<i>b</i> = 5.7488 (4) Å	<i>T</i> = 295 (2) K
<i>c</i> = 7.1774 (6) Å	Prism, yellow
<i>V</i> = 549.38 (7) Å <sup>3</sup>	0.20 × 0.15 × 0.10 mm
<i>Z</i> = 4	
<i>D<sub>x</sub></i> = 1.428 Mg m <sup>-3</sup>	

#### Data collection

Enraf–Nonius CAD-4 diffractometer	<i>h</i> = 0 → 18
Non-profiled <i>ω</i> scans	<i>k</i> = 0 → 8
860 measured reflections	<i>l</i> = 0 → 10
860 independent reflections	2 standard reflections
814 reflections with <i>I</i> > 2σ( <i>I</i> )	frequency: 120 min
<i>θ</i> <sub>max</sub> = 30.0°	intensity decay: none

#### Refinement

Refinement on <i>F</i> <sup>2</sup>	$w = 1/[\sigma^2(F_o^2) + (0.0487P)^2 + 0.0401P]$
$R[F^2 > 2\sigma(F^2)] = 0.032$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.085$	( $\Delta/\sigma$ ) <sub>max</sub> < 0.001
<i>S</i> = 1.07	$\Delta\rho_{max} = 0.12 \text{ e } \text{Å}^{-3}$
860 reflections	$\Delta\rho_{min} = -0.18 \text{ e } \text{Å}^{-3}$
91 parameters	Extinction correction: <i>SHELXL97</i>
All H-atom parameters refined	Extinction coefficient: 0.0083 (17)

**Table 1**  
Selected geometric parameters (Å, °).

N4–C2	1.326 (2)	C2–C1	1.366 (2)
N1–C3	1.131 (3)	C2–C3	1.462 (2)
N2–C4	1.136 (2)	C1–C4	1.421 (2)
N3–C5	1.138 (2)	C1–C5	1.430 (2)
C2–N4–H1	118.5 (14)	C2–C1–C4	120.34 (15)
C2–N4–H2	120.0 (19)	C2–C1–C5	122.94 (14)
H1–N4–H2	121 (2)	C4–C1–C5	116.72 (15)
N4–C2–C1	127.07 (15)	N1–C3–C2	178.7 (2)
N4–C2–C3	116.27 (15)	N2–C4–C1	177.2 (2)
C1–C2–C3	116.65 (14)	N3–C5–C1	176.56 (19)

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

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N4–H1...N2 <sup>i</sup>	0.87 (2)	2.10 (2)	2.955 (2)	166 (2)
N4–H2...N3 <sup>ii</sup>	0.85 (3)	2.22 (3)	3.061 (2)	171 (3)

Symmetry codes: (i)  $x + \frac{1}{2}, -y, z$ ; (ii)  $-x + \frac{3}{2}, y + 1, z - \frac{1}{2}$ .

**Table 3**  
Atomic Mulliken charges in (I) and (II).

Atom	(I)	(II)
C1	0.004	0.069
C2	0.354	0.054
C3	0.048	0.056
N1	-0.162	-0.177
C4	0.026	0.067
N2	-0.196	-0.167
C5	0.071	0.093
N3	-0.201	-0.177

The positions of the H atoms were determined from a Fourier difference map, and their coordinates and isotropic displacement parameters were refined freely. Owing to the absence of any significant anomalous scatterers, the direction of the polar axis was assigned arbitrarily.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2000) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1210). Services for accessing these data are described at the back of the journal.

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