Crystal structure of 2-azido-1H-imidazole-4,5-dicarbonitrile

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In the title compound, C_5HN_7, the nitrile and azido substituents are close to being coplanar with the central ring. Molecules in the crystal are linked *via* an N—H···N hydrogen bond to a nitrile acceptor, forming a chain extending along the *c*-axis direction.

1. Related literature

For background to imidazole applications, see: Windaus & Vogt (1907); Katritzky *et al.* (2006); Epishina *et al.* (1967); Srinivas *et al.* (2014). For preparations, see: Sheppard & Webster (1973); Lu & Just (2001); Parrish *et al.* (2015).
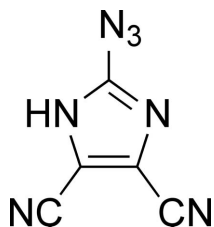
2. Experimental

2.1. Crystal data

C_5HN_7
$M_r = 159.13$
Monoclinic, $P2_1/n$
$a = 7.3217$ (6) Å
$b = 12.8128$ (11) Å
$c = 7.5202$ (6) Å
$\beta = 102.215$ (2)°

$V = 689.51$ (10) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.11$ mm^{-1}
$T = 100$ K
$0.36 \times 0.24 \times 0.10$ mm

2.2. Data collection

Bruker D8 Quest with CMOS diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{min} = 0.960$, $T_{max} = 0.989$

13020 measured reflections
2943 independent reflections
2535 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.117$
$S = 1.56$
2943 reflections

112 parameters
All H-atom parameters refined
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N4[i]	0.89 (2)	2.00 (2)	2.8572 (9)	160.9 (14)

Symmetry code: (i) $x, y, z - 1$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *CHEMDRAW Ultra* (Cambridge Soft, 2014).

Acknowledgements

Supporting information for this paper is available from the IUCr electronic archives (Reference: ZS2337).

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supporting information

Crystal structure of 2-azido-1*H*-imidazole-4,5-dicarbonitrile

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S1. Comment

Imidazoles have a storied history in the pharmaceutical (Windaus *et al.*, 1907), ionic liquid (Katritzky *et al.*, 2006), and energetic materials communities (Epishina *et al.* 1967). Recently, the title compound, C_5HN_7, appeared in a study of imidazoles as potential gas generators (Srinivas *et al.*, 2014). Given this background, we synthesized the title compound to examine the crystal structure, reported herein.

The entire molecule is essentially planar, with the maximum deviation indicated by the torsion angle in the ring atoms of 0.65 (7)° (C2—C1—N1—C3) and among the substituent groups, 176.76 (6)° (C3—N5—N6—N7) (Fig. 1). An intermolecular N1—H···N4 hydrogen bond involving a cyano N-atom acceptor (Table 1) generates a one-dimensional chain structure, extending along *c* (Fig. 2).

S2. Experimental

To a stirred room temperature solution of sodium azide (4.40 g, 67.7 mmol) in water (100 ml) was added 2-diazo-4,5-di-cyanoimidazole (4.05 g, 28.1 mmol) in portions (Sheppard & Webster, 1973; Lu & Just, 2001; Parrish *et al.*, 2015). Vigorous effervescence of liberated nitrogen gas occurred with each addition. The reaction was allowed to stir for a further 90 min after gas evolution ceased and was then extracted with ethyl acetate (4 *x* 20 ml). The organic layer was dried over magnesium sulfate and the solvent was removed by rotary evaporation to afford a light yellow solid. Crystals of the title compound suitable for X-ray diffraction were obtained by crystallization from ethyl acetate.

S3. Refinement

The hydrogen atom was located in a difference-Fourier and the positional parameters were fully refined, with U_{iso}(H) set invariant at 0.08.
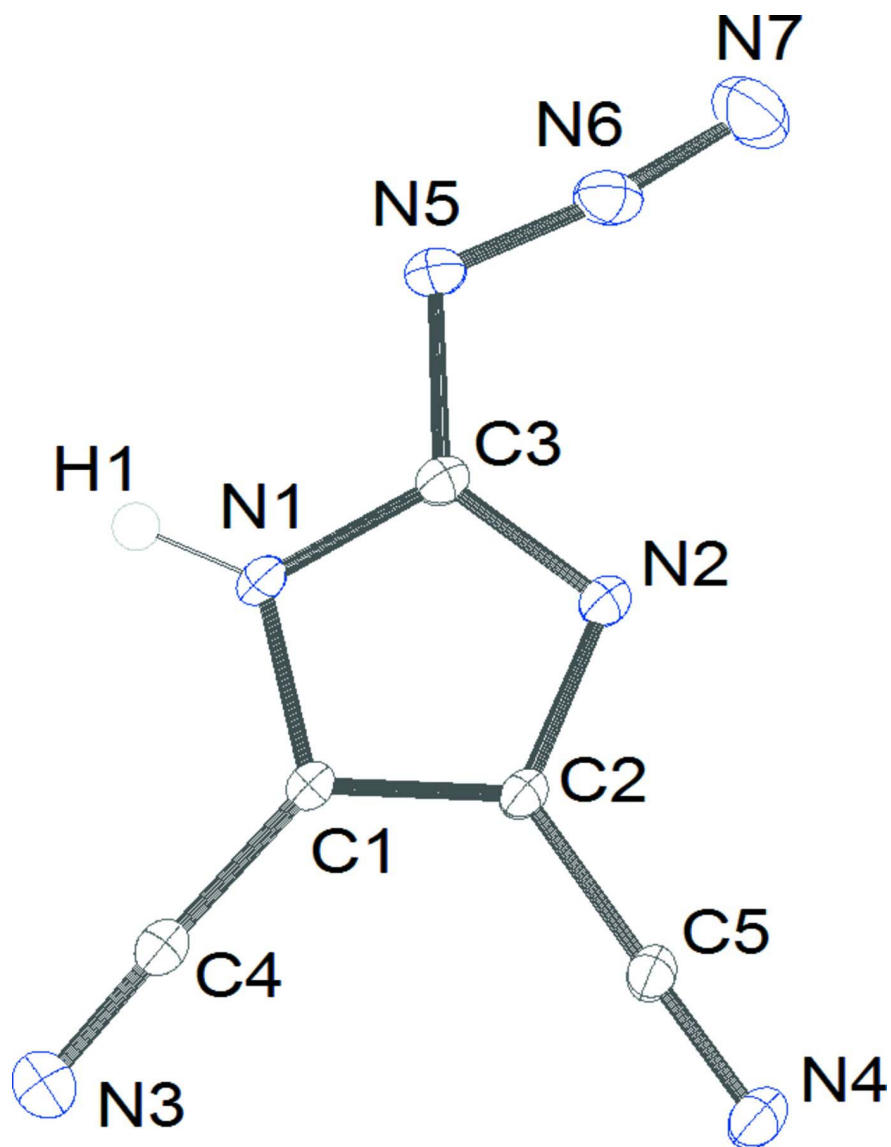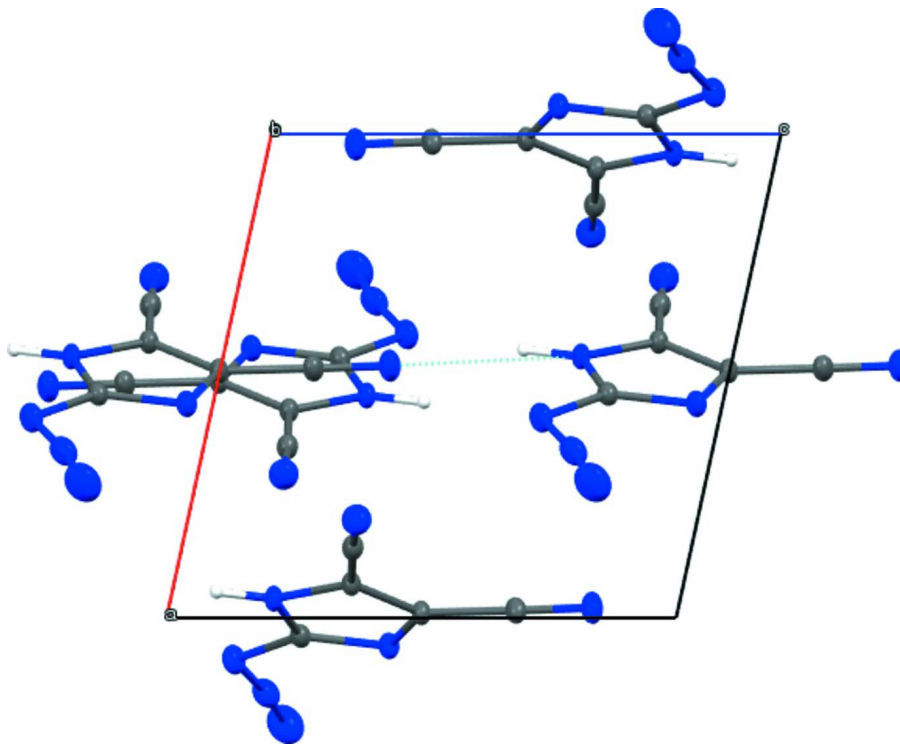
Figure 1

The molecular structure of the title compound with atom labeling. Ellipsoids are drawn at the 50% probability level, and the hydrogen atom is drawn as a sphere of arbitrary size.

Figure 2

A crystal packing diagram of the title compound viewed along the *b* axis. The N—H···N hydrogen bond is shown as a dashed line.

2-Azido-1*H*-imidazole-4,5-dicarbonitrile

Crystal data

C_5HN_7	$F(000) = 320$
$M_r = 159.13$	$D_x = 1.533$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 2943 reflections
$a = 7.3217$ (6) Å	$\theta = 3.2–35.1°$
$b = 12.8128$ (11) Å	$\mu = 0.11$ mm^{-1}
$c = 7.5202$ (6) Å	$T = 100$ K
$\beta = 102.215$ (2)°	Block, pale yellow
$V = 689.51$ (10) Å^3	$0.36 \times 0.24 \times 0.10$ mm
$Z = 4$	

Data collection

Bruker D8 Quest with CMOS diffractometer	13020 measured reflections
Radiation source: fine-focus sealed tube	2943 independent reflections
Bruker Triumph curved graphite monochromator	2535 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.024$
ω scans	$\theta_{max} = 35.1°$, $\theta_{min} = 3.2°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)	$h = -11 \rightarrow 11$
	$k = -20 \rightarrow 19$
$T_{min} = 0.960$, $T_{max} = 0.989$	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.036$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.117$	
$S = 1.56$	All H-atom parameters refined
2943 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2]$
112 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} = 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.51$ e Å⁻³
	$\Delta\rho_{min} = -0.25$ 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	0.95971 (8)	0.23656 (4)	0.20204 (8)	0.01244 (12)
H1	0.946 (2)	0.2147 (12)	0.087 (3)	0.080*
N3	0.79681 (9)	−0.00660 (5)	0.33122 (9)	0.01989 (14)
N4	0.97866 (9)	0.20303 (5)	0.83076 (8)	0.01915 (14)
N5	1.08587 (9)	0.39994 (5)	0.14988 (8)	0.01601 (13)
N6	1.15492 (9)	0.48197 (5)	0.22731 (9)	0.01800 (14)
N7	1.21954 (11)	0.55869 (5)	0.27860 (11)	0.02869 (17)
N2	1.05744 (8)	0.33629 (4)	0.44841 (8)	0.01346 (13)
C1	0.92901 (9)	0.17977 (5)	0.34810 (8)	0.01148 (13)
C2	0.98919 (9)	0.24295 (5)	0.49778 (8)	0.01203 (13)
C3	1.03672 (9)	0.32810 (5)	0.27026 (9)	0.01232 (13)
C4	0.85397 (9)	0.07743 (5)	0.33564 (9)	0.01397 (13)
C5	0.98406 (9)	0.22016 (5)	0.68201 (9)	0.01401 (14)

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0156 (3)	0.0141 (3)	0.0079 (2)	0.00008 (18)	0.00303 (19)	0.00052 (17)
N3	0.0220 (3)	0.0172 (3)	0.0203 (3)	−0.0027 (2)	0.0043 (2)	−0.0015 (2)
N4	0.0240 (3)	0.0226 (3)	0.0118 (3)	−0.0040 (2)	0.0057 (2)	−0.0011 (2)
N5	0.0204 (3)	0.0149 (3)	0.0138 (3)	−0.00141 (19)	0.0059 (2)	0.00269 (19)
N6	0.0200 (3)	0.0162 (3)	0.0196 (3)	−0.0002 (2)	0.0082 (2)	0.0035 (2)
N7	0.0357 (4)	0.0186 (3)	0.0346 (4)	−0.0069 (3)	0.0137 (3)	−0.0007 (3)
N2	0.0162 (3)	0.0143 (3)	0.0104 (2)	−0.00187 (18)	0.00392 (19)	−0.00013 (18)
C1	0.0136 (3)	0.0123 (3)	0.0088 (3)	−0.0004 (2)	0.0029 (2)	0.00006 (19)

C2	0.0140 (3)	0.0136 (3)	0.0088 (3)	−0.0007 (2)	0.0033 (2)	−0.00039 (19)
C3	0.0132 (3)	0.0136 (3)	0.0107 (3)	0.0005 (2)	0.0036 (2)	0.0010 (2)
C4	0.0154 (3)	0.0159 (3)	0.0105 (3)	0.0004 (2)	0.0027 (2)	−0.0001 (2)
C5	0.0160 (3)	0.0154 (3)	0.0110 (3)	−0.0025 (2)	0.0038 (2)	−0.0021 (2)

Geometric parameters (Å, º)

N1—C3	1.3545 (8)	N6—N7	1.1232 (9)
N1—C1	1.3752 (8)	N2—C3	1.3202 (8)
N1—H1	0.893 (19)	N2—C2	1.3770 (9)
N3—C4	1.1530 (8)	C1—C2	1.3808 (9)
N4—C5	1.1489 (9)	C1—C4	1.4171 (9)
N5—N6	1.2549 (8)	C2—C5	1.4241 (9)
N5—C3	1.3907 (8)		
C3—N1—C1	106.32 (5)	N2—C2—C1	111.15 (6)
C3—N1—H1	126.2 (11)	N2—C2—C5	121.75 (6)
C1—N1—H1	127.1 (10)	C1—C2—C5	127.10 (6)
N6—N5—C3	112.74 (6)	N2—C3—N1	113.73 (6)
N7—N6—N5	172.47 (8)	N2—C3—N5	128.17 (6)
C3—N2—C2	103.55 (5)	N1—C3—N5	118.09 (6)
N1—C1—C2	105.25 (6)	N3—C4—C1	177.65 (7)
N1—C1—C4	124.29 (6)	N4—C5—C2	179.07 (8)
C2—C1—C4	130.45 (6)		
C3—N1—C1—C2	0.65 (7)	C2—N2—C3—N5	−178.86 (7)
C3—N1—C1—C4	−178.28 (6)	N6—N5—C3—N1	179.67 (6)
C1—N1—C3—N2	−0.56 (8)	N6—N5—C3—N2	−1.31 (11)
C1—N1—C3—N5	178.61 (6)	N1—C1—C2—N2	−0.56 (8)
C3—N2—C2—C1	0.24 (8)	N1—C1—C2—C5	178.90 (7)
C3—N2—C2—C5	−179.26 (6)	C4—C1—C2—N2	178.28 (7)
C2—N2—C3—N1	0.20 (8)	C4—C1—C2—C5	−2.26 (12)

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯N4[i]	0.89 (2)	2.00 (2)	2.8572 (9)	160.9 (14)

Symmetry code: (i) *x*, *y*, *z*−1.