

# (*E*)-*N,N'*-(1,2-Dicyanoethene-1,2-diyl)dipicolinamide

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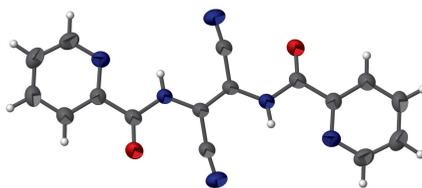
Keywords: crystal structure; picolinamide; dicyanoethene; hydrogen bonding.

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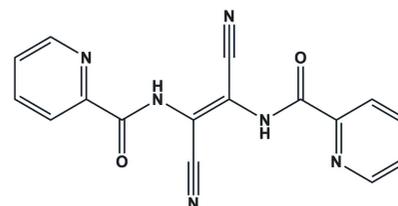
Structural data: full structural data are available from [iucrdata.iucr.org](http://iucrdata.iucr.org)

The whole molecule of the title dicyanoethene derivative, C<sub>16</sub>H<sub>10</sub>N<sub>6</sub>O<sub>2</sub>, is generated by inversion symmetry. The conformation about the central C=C bond, which is situated about the inversion center, is *E*. There are short intramolecular N—H···N contacts present and the molecule is slightly twisted, with the plane of the amide C(=O)N group being inclined to the pyridine ring by 10.6 (4)°, and by 20.2 (4)° to the plane of the dicyanoethene unit (N≡C—C=C—C≡N). In the crystal, molecules are linked by C—H···O and C—H···N hydrogen bonds, forming sheets parallel to (1 $\bar{2}$ 1), enclosing *R*<sub>2</sub><sup>2</sup>(10), *R*<sub>2</sub><sup>2</sup>(22) and *R*<sub>4</sub><sup>4</sup>(22) ring motifs.

## 3D view



## Chemical scheme



## Structure description

When synthesizing 2,3-bis(2-pyridyl)-5,6-dicyanopyrazine, whose structure and an alternative synthesis have been described (Du *et al.*, 2001), an orange–brown precipitate was formed. This precipitate was recrystallized from a mixture of solvents (see below) and found to be the title compound. From the filtrate, colourless crystals of 2,3-bis(2-pyridyl)-5,6-dicyanopyrazine were obtained.

The whole molecule of the title dicyanoethene derivative, Fig. 1, is generated by inversion symmetry. The conformation about the central C7=C7<sup>i</sup> bond [symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ ], situated about the inversion center, is *E*. There are short intramolecular N—H···N contacts present and the molecule is slightly twisted, with the plane of the amide C(=O)N group being inclined to the pyridine ring by 10.6 (4)°, and by 20.2 (4)° to the plane of the dicyanoethene unit (N≡C—C=C—C≡N).

In the crystal, molecules are linked by C—H···O and C—H···N hydrogen bonds, forming sheets parallel to (1 $\bar{2}$ 1), enclosing *R*<sub>2</sub><sup>2</sup>(10), *R*<sub>2</sub><sup>2</sup>(22) and *R*<sub>4</sub><sup>4</sup>(22) ring motifs (Table 1 and Fig. 2).

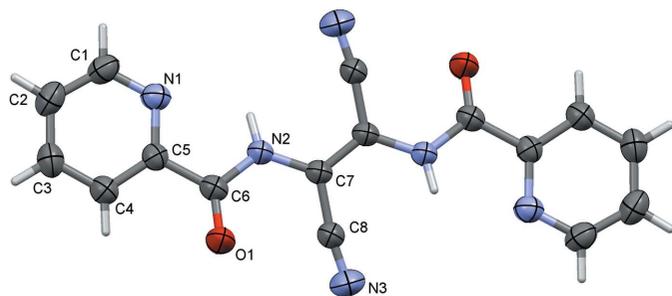
**Table 1**  
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H2N\cdots N1$	0.86 (3)	2.23 (3)	2.671 (3)	111 (3)
$C2-H2\cdots N3^i$	0.93	2.61	3.354 (4)	138
$C4-H4\cdots O1^{ii}$	0.93	2.51	3.274 (4)	140

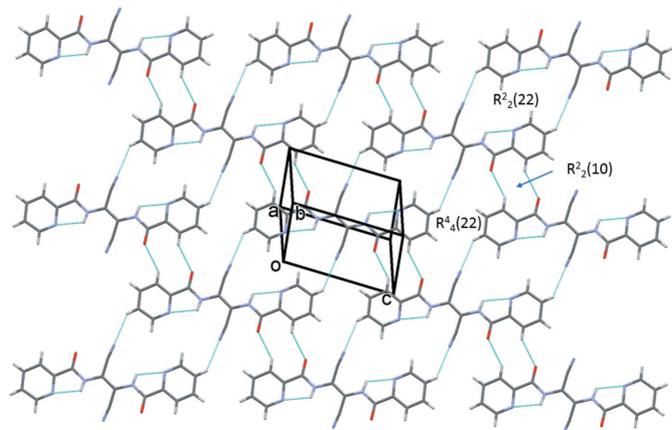
Symmetry codes: (i)  $x - 1, y - 1, z - 1$ ; (ii)  $-x + 2, -y + 1, -z$ .

### Synthesis and crystallization

In a round-bottomed flask outfitted with a reflux condenser, 9.3663 g (0.03 mol) of 2,2'-pyridyl were dissolved in 15 ml of dry *n*-butanol. A solution of 2.7026 g (0.025 mol) of diaminomaleonitrile in 15 ml of dry *n*-butanol was then added at 333 K with stirring. The mixture was refluxed for 3 h. After stopping the reaction, the mixture was filtered to remove the orange-brown precipitate that had formed. This orange-brown precipitate was recrystallized from a mixture of methanol/acetonitrile/acetylacetone (3/3/1), which resulted in the formation of yellow needle-like crystals of the title compound on slow evaporation of the solvents (yield 2.5 g, 32%; m.p. > 360 K). From the filtrate, colourless crystals of 2,3-bis(2-pyridyl)-5,6-dicyanopyrazine were obtained on slow evaporation of the solvent *n*-butanol.



**Figure 1**  
A view of the molecular structure of the title compound, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level. Unlabelled atoms are related to the labelled atoms by the inversion-symmetry operation  $-x + 1, -y + 1, -z + 1$ .



**Figure 2**  
A view along the normal to  $(\bar{1}1)$  of the crystal packing of the title compound. Hydrogen bonds are shown as dashed lines (see Table 1).

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{10}N_6O_2$
$M_r$	318.30
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	293
$a, b, c$ (Å)	5.1939 (11), 8.0697 (17), 9.1482 (15)
$\alpha, \beta, \gamma$ (°)	106.819 (19), 96.077 (18), 92.804 (18)
$V$ (Å <sup>3</sup> )	363.69 (13)
$Z$	1
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.10
Crystal size (mm)	0.72 × 0.30 × 0.30
Data collection	
Diffractometer	STOE-Siemens AED2, 4-circle
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	1281, 1281, 1196
$(\sin \theta/\lambda)_{\max}$ (Å <sup>-1</sup> )	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.073, 0.155, 1.40
No. of reflections	1281
No. of parameters	114
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.17, -0.17

Computer programs: STAD14 and X-RED (Stoe & Cie, 1997), SHELXS97 (Sheldrick, 2008), SHELXL2014/6 (Sheldrick, 2015), PLATON (Spek, 2009), Mercury (Macrae *et al.*, 2008) and publCIF (Westrip, 2010).

The mechanism for the synthesis of the title compound is unknown. However, Du *et al.* (2001) did note that 2,3-bis(2-pyridyl)-5,6-dicyanopyrazine is not stable when exposed to air for several months. Hence, we may postulate that the title compound may be formed by oxidation of 2,3-bis(2-pyridyl)-5,6-dicyanopyrazine.

### Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The NH H atom was located in a difference Fourier map and freely refined. Only one equivalent of data was measured, hence  $R_{\text{int}} = 0$ .

### Acknowledgements

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## full crystallographic data

*IUCrData* (2016). **1**, x161464 [doi:10.1107/S2414314616014644]

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**(*E*)-*N,N'*-(1,2-Dicyanoethene-1,2-diyl)dipicolinamide***Crystal data*

$C_{16}H_{10}N_6O_2$	$Z = 1$
$M_r = 318.30$	$F(000) = 164$
Triclinic, $P\bar{1}$	$D_x = 1.444 \text{ Mg m}^{-3}$
$a = 5.1939 (11) \text{ \AA}$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$b = 8.0697 (17) \text{ \AA}$	Cell parameters from 18 reflections
$c = 9.1482 (15) \text{ \AA}$	$\theta = 12.5\text{--}19.5^\circ$
$\alpha = 106.819 (19)^\circ$	$\mu = 0.10 \text{ mm}^{-1}$
$\beta = 96.077 (18)^\circ$	$T = 293 \text{ K}$
$\gamma = 92.804 (18)^\circ$	Needle, yellow
$V = 363.69 (13) \text{ \AA}^3$	$0.72 \times 0.30 \times 0.30 \text{ mm}$

*Data collection*

STOE–Siemens AED2, 4-circle diffractometer	$R_{\text{int}} = 0.0$
Radiation source: fine-focus sealed tube	$\theta_{\text{max}} = 25.0^\circ$ , $\theta_{\text{min}} = 2.7^\circ$
Plane graphite monochromator	$h = -6 \rightarrow 6$
$\omega/2\theta$ scans	$k = -9 \rightarrow 9$
1281 measured reflections	$l = 0 \rightarrow 10$
1281 independent reflections	3 standard reflections every 60 min
1196 reflections with $I > 2\sigma(I)$	intensity decay: 4%

*Refinement*

Refinement on $F^2$	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.1443P]$
$R[F^2 > 2\sigma(F^2)] = 0.073$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.155$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.40$	$\Delta\rho_{\text{max}} = 0.17 \text{ e \AA}^{-3}$
1281 reflections	$\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$
114 parameters	Extinction correction: SHELXL,
0 restraints	$Fc^* = kFc[1 + 0.001x Fc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Hydrogen site location: mixed	Extinction coefficient: 0.063 (14)

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.8969 (4)	0.4716 (3)	0.2158 (2)	0.0663 (7)
N1	0.3495 (4)	0.1893 (3)	0.0137 (3)	0.0459 (6)
N2	0.5113 (4)	0.4118 (3)	0.2910 (3)	0.0440 (6)
H2N	0.359 (7)	0.360 (4)	0.255 (4)	0.069 (10)*
N3	0.9259 (6)	0.7628 (4)	0.5384 (3)	0.0728 (9)
C1	0.2632 (5)	0.0829 (4)	-0.1254 (3)	0.0524 (8)
H1	0.1094	0.0137	-0.1371	0.063*
C2	0.3889 (6)	0.0691 (4)	-0.2533 (3)	0.0573 (8)
H2	0.3210	-0.0075	-0.3483	0.069*
C3	0.6154 (6)	0.1702 (4)	-0.2379 (3)	0.0573 (8)
H3	0.7030	0.1644	-0.3226	0.069*
C4	0.7115 (6)	0.2807 (4)	-0.0949 (3)	0.0492 (7)
H4	0.8652	0.3506	-0.0807	0.059*
C5	0.5737 (5)	0.2848 (3)	0.0266 (3)	0.0405 (6)
C6	0.6791 (5)	0.3986 (4)	0.1837 (3)	0.0441 (7)
C7	0.5678 (5)	0.5119 (3)	0.4442 (3)	0.0396 (6)
C8	0.7738 (5)	0.6490 (4)	0.4874 (3)	0.0473 (7)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0450 (12)	0.0910 (17)	0.0489 (13)	-0.0214 (11)	0.0134 (9)	0.0003 (11)
N1	0.0381 (12)	0.0477 (13)	0.0495 (14)	-0.0021 (10)	0.0072 (10)	0.0110 (11)
N2	0.0359 (12)	0.0535 (14)	0.0370 (13)	-0.0098 (10)	0.0077 (10)	0.0059 (10)
N3	0.0664 (18)	0.0739 (19)	0.0645 (18)	-0.0321 (16)	0.0050 (14)	0.0064 (15)
C1	0.0429 (16)	0.0514 (17)	0.0549 (19)	-0.0035 (13)	-0.0033 (13)	0.0077 (14)
C2	0.0615 (19)	0.0557 (18)	0.0441 (17)	0.0014 (15)	-0.0043 (14)	0.0027 (14)
C3	0.0638 (19)	0.067 (2)	0.0387 (16)	0.0033 (16)	0.0120 (14)	0.0109 (14)
C4	0.0456 (16)	0.0547 (17)	0.0454 (17)	-0.0026 (13)	0.0110 (12)	0.0110 (13)
C5	0.0391 (14)	0.0423 (14)	0.0387 (15)	0.0025 (11)	0.0071 (11)	0.0093 (11)
C6	0.0383 (14)	0.0499 (16)	0.0437 (16)	-0.0027 (12)	0.0097 (12)	0.0127 (12)
C7	0.0335 (13)	0.0436 (15)	0.0394 (15)	-0.0050 (11)	0.0071 (10)	0.0094 (11)
C8	0.0426 (15)	0.0563 (17)	0.0391 (15)	-0.0094 (13)	0.0082 (12)	0.0093 (13)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O1—C6	1.215 (3)	C2—C3	1.369 (4)
N1—C1	1.329 (3)	C2—H2	0.9300
N1—C5	1.339 (3)	C3—C4	1.378 (4)
N2—C6	1.365 (3)	C3—H3	0.9300
N2—C7	1.392 (3)	C4—C5	1.378 (4)
N2—H2N	0.86 (3)	C4—H4	0.9300
N3—C8	1.135 (4)	C5—C6	1.493 (4)
C1—C2	1.379 (4)	C7—C7 <sup>i</sup>	1.352 (5)
C1—H1	0.9300	C7—C8	1.438 (4)

C1—N1—C5	116.4 (2)	C5—C4—C3	118.2 (3)
C6—N2—C7	124.1 (2)	C5—C4—H4	120.9
C6—N2—H2N	115 (2)	C3—C4—H4	120.9
C7—N2—H2N	121 (2)	N1—C5—C4	123.9 (3)
N1—C1—C2	123.7 (3)	N1—C5—C6	116.9 (2)
N1—C1—H1	118.1	C4—C5—C6	119.2 (2)
C2—C1—H1	118.1	O1—C6—N2	122.1 (3)
C3—C2—C1	118.8 (3)	O1—C6—C5	123.5 (2)
C3—C2—H2	120.6	N2—C6—C5	114.3 (2)
C1—C2—H2	120.6	C7 <sup>i</sup> —C7—N2	122.5 (3)
C2—C3—C4	118.9 (3)	C7 <sup>i</sup> —C7—C8	117.8 (3)
C2—C3—H3	120.5	N2—C7—C8	119.7 (2)
C4—C3—H3	120.5	N3—C8—C7	171.7 (3)
C5—N1—C1—C2	-1.0 (4)	C7—N2—C6—O1	1.8 (5)
N1—C1—C2—C3	-0.1 (5)	C7—N2—C6—C5	-179.4 (2)
C1—C2—C3—C4	0.7 (5)	N1—C5—C6—O1	168.8 (3)
C2—C3—C4—C5	-0.2 (4)	C4—C5—C6—O1	-10.0 (4)
C1—N1—C5—C4	1.6 (4)	N1—C5—C6—N2	-10.0 (4)
C1—N1—C5—C6	-177.1 (2)	C4—C5—C6—N2	171.2 (3)
C3—C4—C5—N1	-1.0 (4)	C6—N2—C7—C7 <sup>i</sup>	-161.8 (3)
C3—C4—C5—C6	177.7 (3)	C6—N2—C7—C8	19.5 (4)

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

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2N $\cdots$ N1	0.86 (3)	2.23 (3)	2.671 (3)	111 (3)
C2—H2 $\cdots$ N3 <sup>ii</sup>	0.93	2.61	3.354 (4)	138
C4—H4 $\cdots$ O1 <sup>iii</sup>	0.93	2.51	3.274 (4)	140

Symmetry codes: (ii)  $x-1, y-1, z-1$ ; (iii)  $-x+2, -y+1, -z$ .