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4-Nitrophthalonitrile

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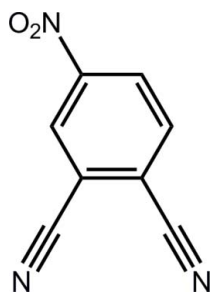
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.001$ Å; R factor = 0.030; wR factor = 0.088; data-to-parameter ratio = 12.6.

In the title compound, $\text{C}_8\text{H}_3\text{N}_3\text{O}_2$ (systematic name: 4-nitrobenzene-1,2-dicarbonitrile), the nitro group is twisted out of the plane of the benzene ring to which it is attached [$\text{O}-\text{N}-\text{C}_{\text{ring}}-\text{C}_{\text{ring}}$ torsion angle = 9.80 (13°)]. In the crystal packing, supramolecular layers with a zigzag topology in the ac plane are sustained by $\text{C}-\text{H}\cdots\text{N}$ interactions.

Related literature

For background to the synthesis of functional phthalocyanines, see: Chin *et al.* (2012). For a related structure, see: Lin *et al.* (2006). For the synthesis, see: Rasmussen *et al.* (1978).



Experimental

Crystal data

 $\text{C}_8\text{H}_3\text{N}_3\text{O}_2$
 $M_r = 173.13$
Orthorhombic, $Pbca$
 $a = 12.8642$ (3) Å $b = 9.2013$ (2) Å
 $c = 13.2578$ (3) Å
 $V = 1569.29$ (6) Å³
 $Z = 8$ Cu $K\alpha$ radiation
 $\mu = 0.94$ mm⁻¹ $T = 100$ K
 $0.35 \times 0.30 \times 0.25$ mm

Data collection

Agilent SuperNova Dual diffractometer with an Atlas detector
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2013)
 $T_{\text{min}} = 0.626$, $T_{\text{max}} = 1.000$ 7104 measured reflections
1638 independent reflections
1556 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.016$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.088$
 $S = 1.10$
1638 reflections130 parameters
All H-atom parameters refined
 $\Delta\rho_{\text{max}} = 0.21$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.24$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C2}-\text{H2}\cdots\text{N3}^{\text{i}}$	0.962 (14)	2.621 (14)	3.3880 (13)	136.9 (11)
$\text{C3}-\text{H3}\cdots\text{N2}^{\text{ii}}$	0.950 (14)	2.554 (14)	3.3955 (13)	147.8 (10)
$\text{C6}-\text{H6}\cdots\text{N3}^{\text{iii}}$	0.943 (13)	2.457 (13)	3.3412 (13)	156.1 (10)

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

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; 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 *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: WM5005).

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supporting information

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4-Nitrophthalonitrile

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S1. Chemical context

As part of our on-going study of functional phthalocyanines, we have previously reported the synthesis and structure of 4-(prop-2-yn-1-yloxy)benzene-1,2-dicarbonitrile prepared from 4-nitrophthalonitrile (Chin *et al.*, 2012). We now report the structure of the latter.

S2. Structural commentary

In the title compound (Fig. 1), the nitro group is slightly twisted out of the plane of the benzene ring to which it is attached as seen in the value of the O1—N1—C1—C6 torsion angle of 9.80 (13)°. A similar small twist was found in the structure of the most closely related compound in the literature, *i.e.* 4-bromo-5-nitrophthalonitrile (Lin *et al.*, 2006).

S3. Supramolecular features

Supramolecular layers (Fig. 2) sustained by C—H...N interactions which form 22-membered {...NC₄N...HC₂H...NC₃H...NC₅H} synthons (Table 1) features in the crystal packing. The layers have a zigzag topology and extend parallel to the *ac* plane and stack along the *b* axis (Fig. 3).

S4. Synthesis and crystallization

The title compound was prepared by a literature procedure (Rasmussen *et al.*, 1978). Thionyl chloride (4.3 ml, 0.56 mmol) was added drop wise with stirring over 5 minutes to 4-nitrophthalamide (2.83 g, 13.5 mmol) in dry DMF (10.4 ml, 0.20 mmol) at 263 to 258 K (salt-ice bath). After 4 h, the homogenous yellow solution was poured onto excess ice-water with vigorous stirring. The precipitate was vacuum filtered, washed with cold water and dried. Crystals for the X-ray study were grown from slow evaporation from its methanol solution. Yield = 1.92 g (68 %), M.pt: 408–413 K (lit. 413–415 K). IR (KBr) ν/cm^{-1} : 2924, 2241, 1610, 1587, 1538, 1463, 1356, 1297, 1076, 931, 855, 802, 745, 718.

S5. Refinement

All hydrogen atoms were refined freely.

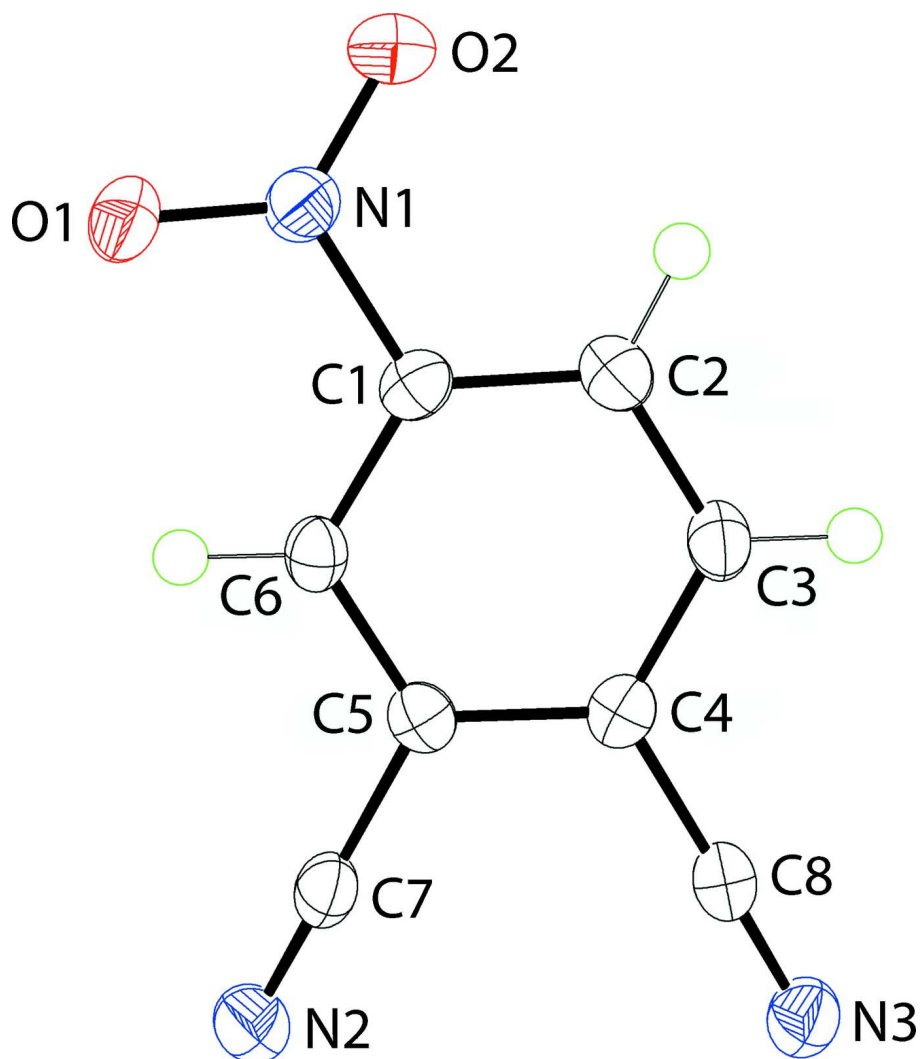


Figure 1

The molecular structure of the title compound showing the atom-labelling scheme and displacement ellipsoids at the 70% probability level.

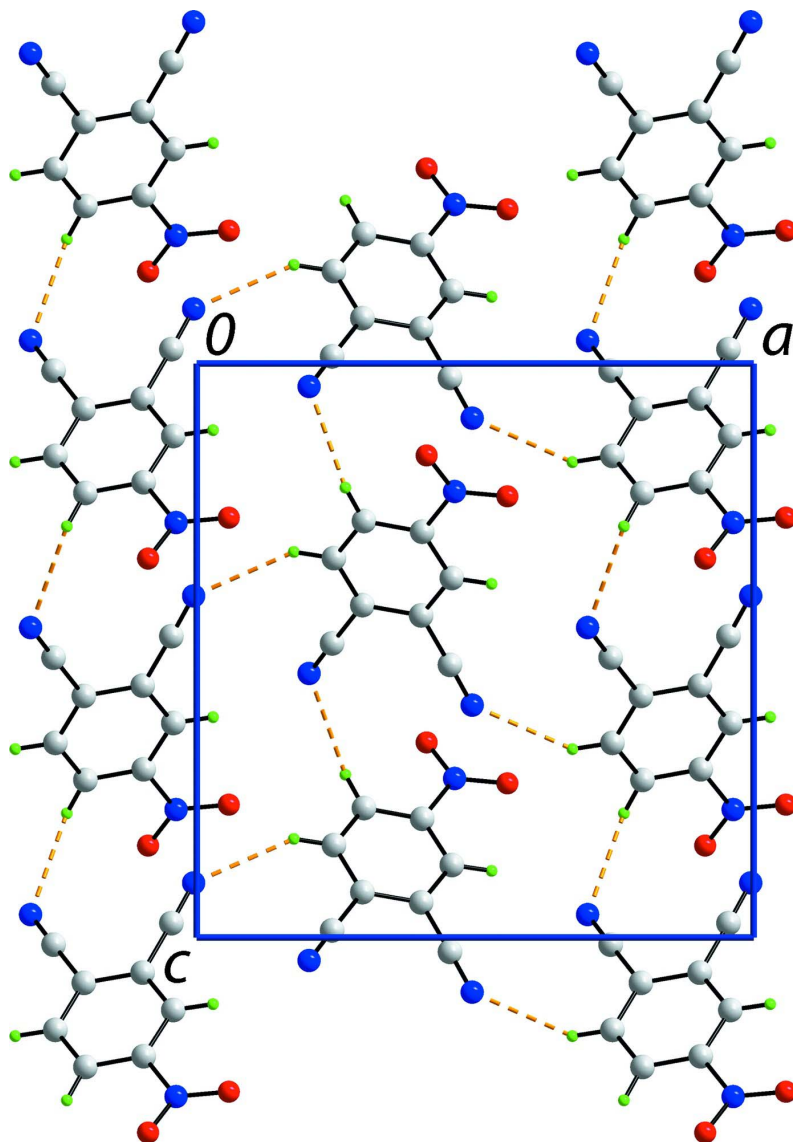


Figure 2

A view of the supramolecular layer in the title compound, sustained by C—H...N interactions shown as orange dashed lines.

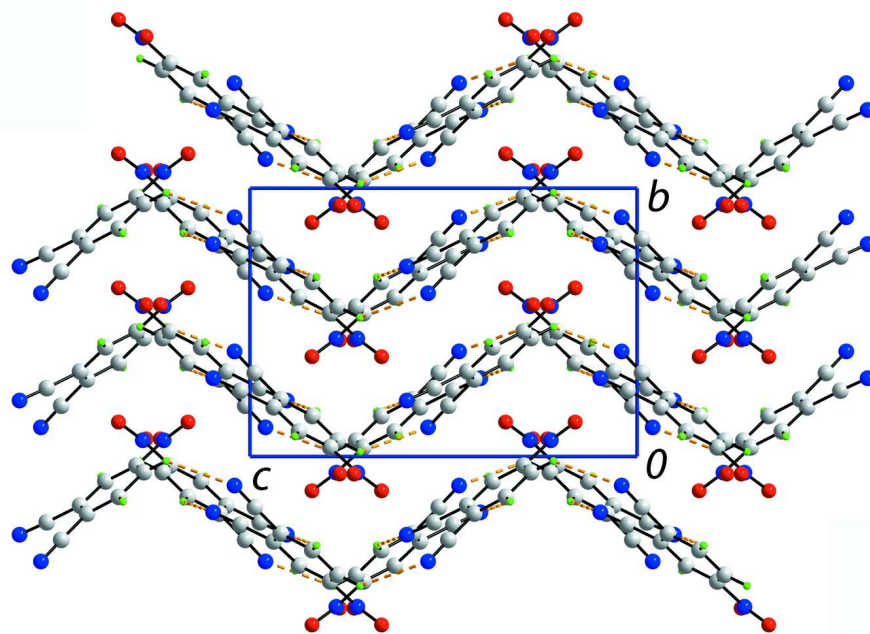


Figure 3

A view of the unit-cell contents of the title compound in projection down the a axis. The C—H...N interactions are shown as orange dashed lines.

4-Nitrobenzene-1,2-dicarbonitrile

Crystal data

$C_8H_3N_3O_2$

$M_r = 173.13$

Orthorhombic, $Pbca$

Hall symbol: $-P\ 2ac\ 2ab$

$a = 12.8642\ (3)\ \text{\AA}$

$b = 9.2013\ (2)\ \text{\AA}$

$c = 13.2578\ (3)\ \text{\AA}$

$V = 1569.29\ (6)\ \text{\AA}^3$

$Z = 8$

$F(000) = 704$

$D_x = 1.466\ \text{Mg m}^{-3}$

Cu $K\alpha$ radiation, $\lambda = 1.54184\ \text{\AA}$

Cell parameters from 4240 reflections

$\theta = 3.3\text{--}76.1^\circ$

$\mu = 0.94\ \text{mm}^{-1}$

$T = 100\ \text{K}$

Prism, colourless

$0.35 \times 0.30 \times 0.25\ \text{mm}$

Data collection

Agilent SuperNova Dual

diffractometer with an Atlas detector

Radiation source: SuperNova (Cu) X-ray

Source

Mirror monochromator

Detector resolution: $10.4041\ \text{pixels mm}^{-1}$

ω scan

Absorption correction: multi-scan

(*CrysAlis PRO*; Agilent, 2013)

$T_{\min} = 0.626$, $T_{\max} = 1.000$

7104 measured reflections

1638 independent reflections

1556 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$

$\theta_{\max} = 76.3^\circ$, $\theta_{\min} = 6.7^\circ$

$h = -8 \rightarrow 16$

$k = -10 \rightarrow 11$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.088$

$S = 1.10$

1638 reflections

130 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0522P)^2 + 0.3777P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.21 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.55783 (6)	0.56540 (8)	0.23140 (6)	0.0224 (2)
O2	0.41285 (6)	0.62811 (9)	0.16017 (6)	0.0284 (2)
N1	0.46305 (7)	0.56035 (9)	0.22296 (6)	0.0185 (2)
N2	0.49465 (7)	0.20831 (10)	0.59515 (7)	0.0245 (2)
N3	0.20184 (7)	0.10850 (10)	0.54001 (7)	0.0214 (2)
C1	0.40488 (7)	0.46610 (10)	0.29308 (7)	0.0159 (2)
C2	0.30038 (8)	0.44112 (11)	0.27448 (7)	0.0185 (2)
C3	0.24639 (7)	0.34933 (11)	0.33907 (7)	0.0183 (2)
C4	0.29752 (7)	0.28688 (10)	0.42094 (7)	0.0158 (2)
C5	0.40307 (7)	0.31687 (10)	0.43884 (7)	0.0152 (2)
C6	0.45807 (7)	0.40675 (10)	0.37365 (7)	0.0156 (2)
C7	0.45469 (7)	0.25464 (10)	0.52497 (7)	0.0176 (2)
C8	0.24319 (7)	0.18890 (10)	0.48760 (7)	0.0173 (2)
H2	0.2670 (11)	0.4827 (16)	0.2163 (10)	0.027 (3)*
H3	0.1745 (11)	0.3317 (13)	0.3282 (9)	0.020 (3)*
H6	0.5294 (10)	0.4254 (13)	0.3839 (9)	0.017 (3)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0156 (4)	0.0246 (4)	0.0271 (4)	-0.0022 (3)	0.0032 (3)	0.0031 (3)
O2	0.0248 (4)	0.0300 (4)	0.0304 (4)	-0.0019 (3)	-0.0029 (3)	0.0151 (3)
N1	0.0177 (4)	0.0174 (4)	0.0204 (4)	-0.0004 (3)	0.0013 (3)	0.0015 (3)
N2	0.0198 (4)	0.0303 (5)	0.0235 (5)	0.0001 (3)	-0.0016 (3)	0.0064 (4)
N3	0.0183 (4)	0.0241 (4)	0.0217 (4)	-0.0026 (3)	0.0008 (3)	0.0014 (3)

C1	0.0166 (5)	0.0145 (4)	0.0167 (5)	0.0002 (3)	0.0030 (3)	-0.0003 (3)
C2	0.0176 (5)	0.0204 (5)	0.0174 (5)	0.0014 (3)	-0.0017 (3)	0.0002 (4)
C3	0.0132 (5)	0.0219 (5)	0.0199 (5)	-0.0009 (3)	-0.0010 (3)	-0.0005 (4)
C4	0.0155 (4)	0.0152 (4)	0.0166 (4)	-0.0002 (3)	0.0021 (3)	-0.0022 (3)
C5	0.0152 (4)	0.0144 (4)	0.0159 (4)	0.0021 (3)	-0.0001 (3)	-0.0020 (3)
C6	0.0125 (4)	0.0153 (4)	0.0190 (5)	0.0005 (3)	0.0006 (3)	-0.0021 (4)
C7	0.0135 (4)	0.0185 (5)	0.0208 (5)	-0.0015 (3)	0.0019 (3)	0.0000 (4)
C8	0.0139 (4)	0.0196 (5)	0.0184 (4)	0.0002 (3)	-0.0014 (3)	-0.0023 (4)

Geometric parameters (Å, °)

O1—N1	1.2252 (12)	C2—H2	0.962 (14)
O2—N1	1.2243 (11)	C3—C4	1.3932 (13)
N1—C1	1.4752 (12)	C3—H3	0.949 (13)
N2—C7	1.1453 (13)	C4—C5	1.4057 (13)
N3—C8	1.1459 (13)	C4—C8	1.4431 (13)
C1—C6	1.3811 (14)	C5—C6	1.3898 (13)
C1—C2	1.3859 (14)	C5—C7	1.4397 (13)
C2—C3	1.3889 (14)	C6—H6	0.943 (13)
O2—N1—O1	124.59 (8)	C3—C4—C5	120.44 (9)
O2—N1—C1	117.40 (8)	C3—C4—C8	120.41 (8)
O1—N1—C1	118.01 (8)	C5—C4—C8	119.15 (8)
C6—C1—C2	123.54 (9)	C6—C5—C4	120.23 (9)
C6—C1—N1	117.94 (8)	C6—C5—C7	119.68 (8)
C2—C1—N1	118.52 (9)	C4—C5—C7	120.09 (8)
C1—C2—C3	118.44 (9)	C1—C6—C5	117.66 (9)
C1—C2—H2	120.7 (8)	C1—C6—H6	121.4 (8)
C3—C2—H2	120.8 (8)	C5—C6—H6	120.9 (8)
C2—C3—C4	119.67 (9)	N2—C7—C5	178.04 (11)
C2—C3—H3	119.8 (8)	N3—C8—C4	178.30 (10)
C4—C3—H3	120.5 (8)		
O2—N1—C1—C6	-170.25 (9)	C3—C4—C5—C7	178.52 (9)
O1—N1—C1—C6	9.80 (13)	C8—C4—C5—C7	-2.37 (13)
O2—N1—C1—C2	10.12 (13)	C2—C1—C6—C5	0.25 (14)
O1—N1—C1—C2	-169.82 (9)	N1—C1—C6—C5	-179.36 (8)
C6—C1—C2—C3	-1.26 (15)	C4—C5—C6—C1	1.09 (14)
N1—C1—C2—C3	178.34 (8)	C7—C5—C6—C1	-178.85 (8)
C1—C2—C3—C4	0.91 (15)	C6—C5—C7—N2	96 (3)
C2—C3—C4—C5	0.38 (14)	C4—C5—C7—N2	-84 (3)
C2—C3—C4—C8	-178.71 (9)	C3—C4—C8—N3	122 (3)
C3—C4—C5—C6	-1.41 (14)	C5—C4—C8—N3	-57 (4)
C8—C4—C5—C6	177.69 (8)		

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>
C2—H2···N3 ⁱ	0.962 (14)	2.621 (14)	3.3880 (13)	136.9 (11)
C3—H3···N2 ⁱⁱ	0.950 (14)	2.554 (14)	3.3955 (13)	147.8 (10)
C6—H6···N3 ⁱⁱⁱ	0.943 (13)	2.457 (13)	3.3412 (13)	156.1 (10)

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