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## Structure Reports

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# 5-Amino-1-(4-nitrophenyl)-1*H*-pyrazole-3-carbonitrile

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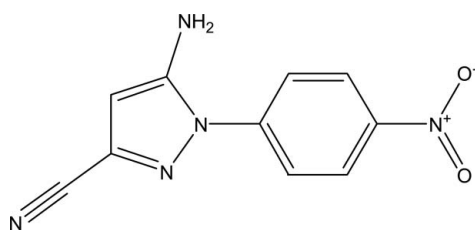
Received 23 November 2011; accepted 3 December 2011

 Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å;  $R$  factor = 0.048;  $wR$  factor = 0.123; data-to-parameter ratio = 6.1.

The title compound,  $\text{C}_{10}\text{H}_7\text{N}_5\text{O}_2$ , was synthesized by the reaction of 4-nitroaniline and 2,3-dicyanopropionic acid ethyl ester. In the crystal,  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds link the molecules, forming a three-dimensional network.

## Related literature

*N*-pyrazole derivatives are of great interest because of their chemical and pharmaceutical properties, see: Cheng *et al.* (2008). They also exhibit diverse biological activity such as insecticidal (Zhao *et al.*, 2010) and antifungal activities (Liu *et al.*, 2010). For bond-length data, see: Allen *et al.* (1987).



## Experimental

### Crystal data

$\text{C}_{10}\text{H}_7\text{N}_5\text{O}_2$   
 $M_r = 229.21$   
 Monoclinic,  $Cc$   
 $a = 3.7685$  (2) Å

$b = 27.3441$  (17) Å  
 $c = 10.1294$  (8) Å  
 $\beta = 96.20$  (3)°  
 $V = 1037.70$  (12) Å<sup>3</sup>

$Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.11$  mm<sup>-1</sup>

$T = 293$  K  
 $0.30 \times 0.30 \times 0.10$  mm

### Data collection

Enraf-Nonius CAD-4 diffractometer  
 Absorption correction:  $\psi$  scan  
 (North *et al.*, 1968)  
 $T_{\min} = 0.968$ ,  $T_{\max} = 0.989$   
 2148 measured reflections  
 951 independent reflections

856 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.071$   
 3 standard reflections every 200 reflections  
 intensity decay: 1%

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$   
 $wR(F^2) = 0.123$   
 $S = 1.00$   
 951 reflections  
 155 parameters

2 restraints  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.26$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.31$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N4}-\text{H4B}\cdots\text{O2}^{\text{i}}$	0.86	2.53	3.335 (5)	156
$\text{C4}-\text{H4A}\cdots\text{O1}^{\text{ii}}$	0.93	2.52	3.216 (5)	132

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

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, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

The authors gratefully acknowledge Professor Hua-Qin Wang of the Analysis Center, Nanjing University, for the use of the diffractometer for this research project.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG5146).

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## supporting information

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**5-Amino-1-(4-nitrophenyl)-1H-pyrazole-3-carbonitrile**

Qiang-Hua Jiang, Qiu He, Jian-Qiang Zhang, Yang Yang and Rong Wan

**S1. Comment**

In a variety of biological heterocyclic compounds, *N*-pyrazole derivatives are of great interest because of their chemical and pharmaceutical properties (Cheng *et al.*, 2008). These compounds are known to exhibit diverse biological activities, such as insecticidal (Zhao *et al.*, 2010) and antifungal activities (Liu *et al.*, 2010).

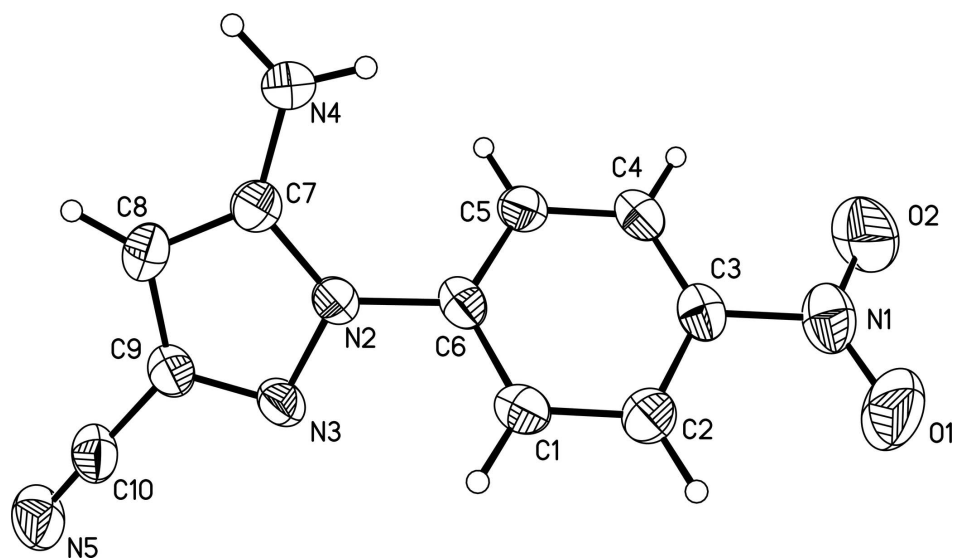
Here we report the crystal structure of the title compound, (I). In the molecule of the title compound (Fig. 1), the bond lengths and angles are within normal ranges (Allen *et al.*, 1987). Rings A (C1—C6), B (N2/N3/C9/C8/C7) are, of course, planar. The dihedral angle between them is A/B = 34.3 (1) Å. In the crystal structure, intermolecular N—H···O and C—H···O hydrogen bonds (Table 1) link the molecules to form a three-dimensional network (Fig. 2), in which they may be effective in the stabilization of the structure.

**S2. Experimental**

Sodium nitrite (1.49 g) was dissolved in 10 ml water, then the solution was added dropwise to a mixture of 4-nitrophenyl-amino (0.02 mol) and 36.5% aq. HCl (5 ml) at 0–5°C. After the addition, the above reaction mixture was stirred for 10 min at 0–5°C. 2,3-Dicyano-propionic acid ethyl ester (0.02 mol) was added dropwise and stirred for 2 hr at room temperature. The reaction mixture was extracted with dichloromethane and the pH was adjusted to 9 with ammonia. The aqueous layer was removed and the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated and precipitated. The pure compound (I) was obtained by recrystallization from ethanol. Crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of an acetone solution.

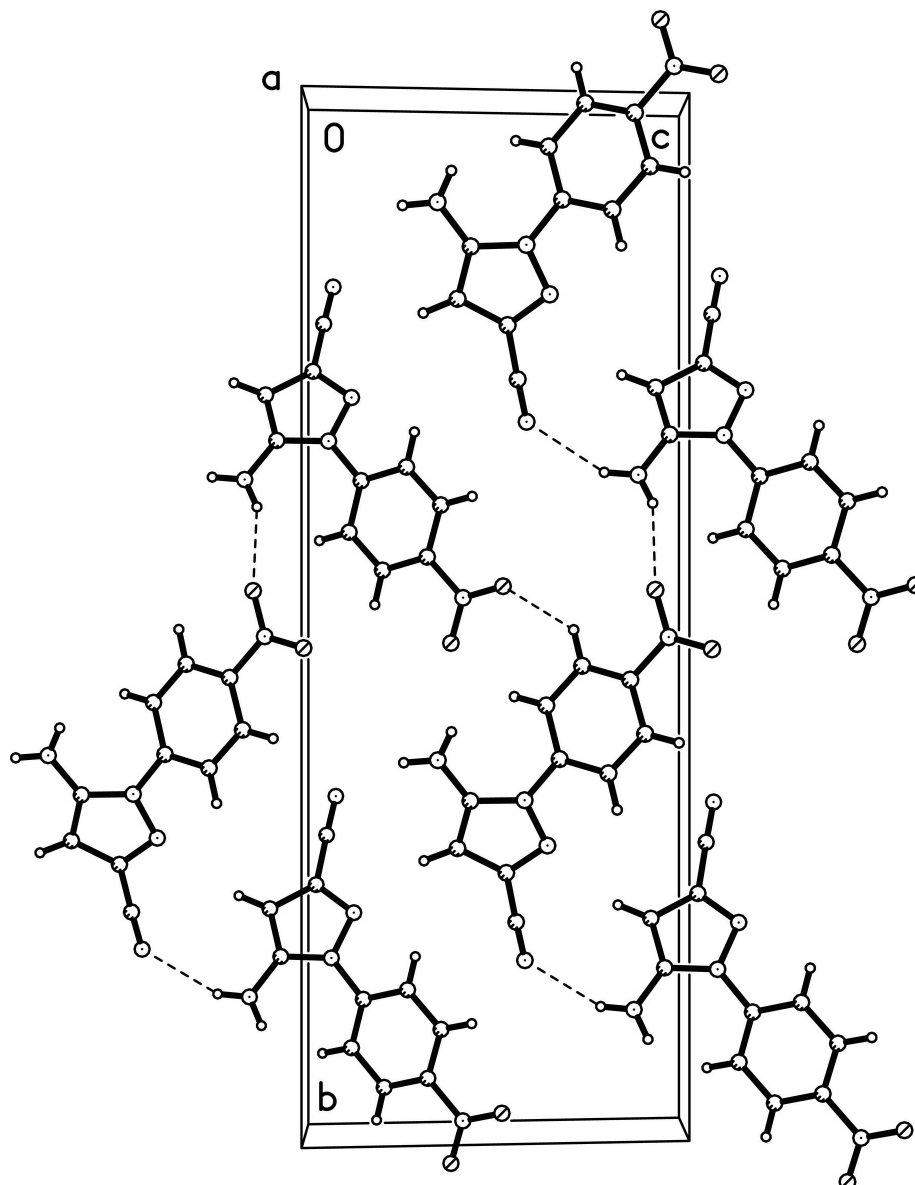
**S3. Refinement**

All H atoms were positioned geometrically, with N—H = 0.86 Å and C—H = 0.93 Å, and constrained to ride on their parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ .



**Figure 1**

The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.



**Figure 2**

A partial packing diagram for (I). Hydrogen bonds are shown as dashed lines.

### 5-Amino-1-(4-nitrophenyl)-1H-pyrazole-3-carbonitrile

#### Crystal data

$C_{10}H_7N_5O_2$

$M_r = 229.21$

Monoclinic,  $Cc$

Hall symbol:  $C -2yc$

$a = 3.7685$  (2) Å

$b = 27.3441$  (17) Å

$c = 10.1294$  (8) Å

$\beta = 96.20$  (3)°

$V = 1037.70$  (12) Å<sup>3</sup>

$Z = 4$

$F(000) = 472$

$D_x = 1.467$  Mg m<sup>-3</sup>

Melting point = 498–501 K

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 25 reflections

$\theta = 9\text{--}13^\circ$

$\mu = 0.11$  mm<sup>-1</sup>

$T = 293$  K

Block, yellow

$0.30 \times 0.30 \times 0.10$  mm

*Data collection*

Enraf–Nonius CAD-4  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega/2\theta$  scans

Absorption correction:  $\psi$  scan  
(North *et al.*, 1968)

$T_{\min} = 0.968$ ,  $T_{\max} = 0.989$

2148 measured reflections

951 independent reflections

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

$R_{\text{int}} = 0.071$

$\theta_{\max} = 25.4^\circ$ ,  $\theta_{\min} = 2.5^\circ$

$h = 0 \rightarrow 4$

$k = -32 \rightarrow 32$

$l = -12 \rightarrow 12$

3 standard reflections every 200 reflections

intensity decay: 1%

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.048$

$wR(F^2) = 0.123$

$S = 1.00$

951 reflections

155 parameters

2 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.093P)^2]$

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

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

$\Delta\rho_{\max} = 0.26 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$

Extinction correction: *SHELXL97* (Sheldrick,  
2008),  $F_c^* = kFc[1 + 0.001x \text{Fc}^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.017 (6)

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.6000 (9)	0.14112 (13)	0.7685 (3)	0.0345 (8)
H1A	0.6497	0.1737	0.7890	0.041*
N1	0.7783 (9)	0.01800 (13)	0.9127 (4)	0.0495 (9)
O1	0.9593 (11)	0.02857 (14)	1.0134 (4)	0.0782 (13)
N2	0.2632 (8)	0.16762 (10)	0.5653 (3)	0.0343 (7)
C2	0.7254 (10)	0.10486 (14)	0.8562 (4)	0.0370 (8)
H2A	0.8616	0.1124	0.9357	0.044*
O2	0.6973 (13)	-0.02441 (11)	0.8819 (4)	0.0763 (12)
C3	0.6406 (9)	0.05648 (13)	0.8214 (3)	0.0347 (8)
N3	0.1670 (9)	0.21026 (11)	0.6233 (3)	0.0362 (7)
C4	0.4432 (9)	0.04433 (12)	0.7061 (4)	0.0361 (8)
H4A	0.3940	0.0117	0.6858	0.043*
N4	0.2620 (12)	0.13064 (12)	0.3498 (3)	0.0517 (9)
H4B	0.3581	0.1043	0.3834	0.062*

H4C	0.2109	0.1331	0.2652	0.062*
C5	0.3155 (9)	0.08073 (14)	0.6189 (3)	0.0353 (8)
H5A	0.1748	0.0731	0.5405	0.042*
N5	-0.2189 (12)	0.32149 (13)	0.5701 (4)	0.0571 (10)
C6	0.4020 (9)	0.12921 (12)	0.6510 (4)	0.0316 (7)
C7	0.1906 (10)	0.16856 (13)	0.4306 (4)	0.0367 (8)
C8	0.0411 (12)	0.21334 (14)	0.3985 (4)	0.0412 (8)
H8A	-0.0359	0.2255	0.3146	0.049*
C9	0.0310 (9)	0.23653 (12)	0.5213 (4)	0.0347 (8)
C10	-0.1059 (10)	0.28392 (14)	0.5470 (4)	0.0411 (9)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0409 (17)	0.0288 (16)	0.0351 (16)	-0.0030 (14)	0.0102 (15)	-0.0032 (14)
N1	0.050 (2)	0.0475 (19)	0.053 (2)	0.0072 (16)	0.0127 (18)	0.0160 (16)
O1	0.094 (3)	0.070 (2)	0.065 (2)	0.005 (2)	-0.021 (2)	0.0227 (19)
N2	0.0461 (16)	0.0256 (14)	0.0317 (14)	0.0020 (13)	0.0072 (12)	0.0000 (12)
C2	0.0424 (18)	0.0389 (18)	0.0305 (16)	0.0005 (16)	0.0073 (14)	0.0026 (14)
O2	0.111 (3)	0.0379 (17)	0.079 (2)	0.0041 (19)	0.010 (2)	0.0194 (16)
C3	0.0330 (17)	0.0337 (17)	0.0394 (17)	0.0046 (15)	0.0129 (15)	0.0066 (15)
N3	0.0488 (17)	0.0255 (14)	0.0357 (15)	0.0032 (12)	0.0108 (13)	-0.0018 (10)
C4	0.0400 (19)	0.0275 (17)	0.0427 (18)	0.0031 (14)	0.0135 (16)	0.0008 (14)
N4	0.090 (3)	0.0352 (16)	0.0300 (14)	0.0101 (17)	0.0084 (16)	-0.0028 (12)
C5	0.0416 (19)	0.0306 (18)	0.0340 (17)	-0.0001 (14)	0.0053 (15)	-0.0029 (12)
N5	0.080 (3)	0.0384 (18)	0.055 (2)	0.0178 (19)	0.0208 (19)	0.0037 (16)
C6	0.0351 (16)	0.0261 (15)	0.0360 (17)	0.0022 (14)	0.0145 (14)	0.0033 (13)
C7	0.0441 (19)	0.0337 (17)	0.0332 (16)	-0.0010 (15)	0.0091 (15)	0.0011 (14)
C8	0.050 (2)	0.0407 (18)	0.0330 (17)	0.0015 (16)	0.0047 (15)	0.0086 (14)
C9	0.0379 (18)	0.0289 (17)	0.0383 (17)	0.0014 (15)	0.0090 (14)	0.0023 (13)
C10	0.049 (2)	0.036 (2)	0.0410 (19)	0.0059 (17)	0.0150 (17)	0.0075 (15)

*Geometric parameters (Å, °)*

C1—C6	1.374 (5)	C4—C5	1.382 (5)
C1—C2	1.381 (5)	C4—H4A	0.9300
C1—H1A	0.9300	N4—C7	1.366 (5)
N1—O1	1.199 (5)	N4—H4B	0.8600
N1—O2	1.231 (5)	N4—H4C	0.8600
N1—C3	1.459 (5)	C5—C6	1.395 (5)
N2—C7	1.363 (5)	C5—H5A	0.9300
N2—N3	1.371 (4)	N5—C10	1.146 (5)
N2—C6	1.425 (4)	C7—C8	1.372 (5)
C2—C3	1.397 (5)	C8—C9	1.400 (5)
C2—H2A	0.9300	C8—H8A	0.9300
C3—C4	1.357 (5)	C9—C10	1.429 (5)
N3—C9	1.316 (5)		

C6—C1—C2	120.2 (3)	C7—N4—H4B	120.0
C6—C1—H1A	119.9	C7—N4—H4C	120.0
C2—C1—H1A	119.9	H4B—N4—H4C	120.0
O1—N1—O2	123.1 (4)	C4—C5—C6	118.6 (3)
O1—N1—C3	119.7 (4)	C4—C5—H5A	120.7
O2—N1—C3	117.2 (4)	C6—C5—H5A	120.7
C7—N2—N3	112.3 (3)	C1—C6—C5	121.2 (3)
C7—N2—C6	130.1 (3)	C1—C6—N2	118.8 (3)
N3—N2—C6	117.6 (3)	C5—C6—N2	119.8 (3)
C1—C2—C3	117.7 (3)	N2—C7—N4	123.7 (3)
C1—C2—H2A	121.2	N2—C7—C8	106.7 (3)
C3—C2—H2A	121.2	N4—C7—C8	129.6 (4)
C4—C3—C2	122.6 (3)	C7—C8—C9	104.1 (3)
C4—C3—N1	119.6 (3)	C7—C8—H8A	128.0
C2—C3—N1	117.8 (3)	C9—C8—H8A	128.0
C9—N3—N2	103.1 (3)	N3—C9—C8	113.9 (3)
C3—C4—C5	119.6 (3)	N3—C9—C10	118.0 (3)
C3—C4—H4A	120.2	C8—C9—C10	128.2 (3)
C5—C4—H4A	120.2	N5—C10—C9	178.4 (4)
C6—C1—C2—C3	-0.6 (5)	C4—C5—C6—N2	-177.7 (3)
C1—C2—C3—C4	0.1 (5)	C7—N2—C6—C1	150.6 (4)
C1—C2—C3—N1	178.9 (3)	N3—N2—C6—C1	-33.0 (5)
O1—N1—C3—C4	178.4 (4)	C7—N2—C6—C5	-33.7 (6)
O2—N1—C3—C4	-2.3 (5)	N3—N2—C6—C5	142.6 (3)
O1—N1—C3—C2	-0.4 (5)	N3—N2—C7—N4	179.8 (4)
O2—N1—C3—C2	178.9 (4)	C6—N2—C7—N4	-3.7 (6)
C7—N2—N3—C9	0.8 (4)	N3—N2—C7—C8	-0.1 (4)
C6—N2—N3—C9	-176.1 (3)	C6—N2—C7—C8	176.4 (4)
C2—C3—C4—C5	-0.7 (5)	N2—C7—C8—C9	-0.7 (4)
N1—C3—C4—C5	-179.4 (3)	N4—C7—C8—C9	179.4 (4)
C3—C4—C5—C6	1.6 (5)	N2—N3—C9—C8	-1.3 (4)
C2—C1—C6—C5	1.6 (5)	N2—N3—C9—C10	178.7 (3)
C2—C1—C6—N2	177.2 (3)	C7—C8—C9—N3	1.3 (5)
C4—C5—C6—C1	-2.1 (5)	C7—C8—C9—C10	-178.7 (4)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N4—H4B $\cdots$ O2 <sup>i</sup>	0.86	2.53	3.335 (5)	156
C4—H4A $\cdots$ O1 <sup>ii</sup>	0.93	2.52	3.216 (5)	132

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