Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Ethyl 2-(3-chloro-2-pyridyl)-5-oxopyrazolidine-3-carboxylate

Hai-Jun Tan,[a] Hai-Bing He,[a] Ming Xia,[a] Xiang-Ning Zhang[b] and Hong-Jun Zhu[a]*

[a]Department of Applied Chemistry, College of Science, Nanjing University of Technology, Nanjing 210009, People's Republic of China, and [b]Jiangsu Pesticide Research Institute Co Ltd, Nanjing 210036, People's Republic of China
Correspondence e-mail: zhuhj@njut.edu.cn

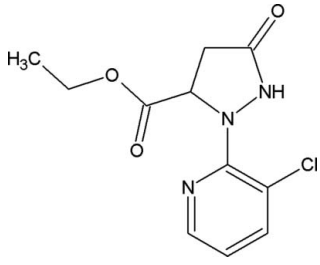
Received 20 May 2009; accepted 1 June 2009

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.043; wR factor = 0.110; data-to-parameter ratio = 13.9.

In the molecule of the title compound, $C_{11}H_{12}ClN_3O_3$, the five membered ring adopts an envelope conformation. In the crystal structure, intermolecular N—H···O hydrogen bonds link the molecules into centrosymmetric dimers.

Related literature

For the synthetic procedure, see: Lahm *et al.* (2007). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{11}H_{12}ClN_3O_3$
M_r = 269.69
Orthorhombic, *Pbca*
a = 15.488 (3) Å
b = 10.009 (2) Å
c = 16.249 (3) Å
V = 2518.9 (8) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.31 mm^{-1}
T = 298 K
0.30 × 0.20 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.913, T_{max} = 0.970
4453 measured reflections
2273 independent reflections
1635 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.110
S = 1.03
2273 reflections
164 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O2^{i}	0.86	2.14	2.910 (3)	149

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1985); 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: *SHELXTL*.

The authors thank Dr Shan Liu and Dr Rui Liu of the College of Science, Nanjing University of Technology, for useful discussions and the Center of Testing and Analysis, Nanjing University, for support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2697).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1-19.
Enraf–Nonius (1985). *CAD-4 Software*. Enraf–Nonius, Delft. The Netherlands.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
Lahm, G. P., Stevenson, T. M., Selby, T. P., Freudenberger, J. H., Cordova, D., Flexner, L., Bellin, C. A., Dubas, C. M., Smith, B. K., Hughes, K. A., Hollingshaus, J. G., Clark, C. E. & Benner, E. A. (2007). *Bioorg. Med. Chem. Lett.* **17**, 6274–6279.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

Acta Cryst. (2009). E**65**, o1495 [doi:10.1107/S1600536809020789]

Ethyl 2-(3-chloro-2-pyridyl)-5-oxopyrazolidine-3-carboxylate

Hai-Jun Tan, Hai-Bing He, Ming Xia, Xiang-Ning Zhang and Hong-Jun Zhu

S1. Comment

The title compound is one of the most important intermediates used for the synthesis of Rynaxypyre, a new insecticidal anthranilic diamide as a potent and selective ryanodine receptor activator (Lahm *et al.*, 2007). We report herein the crystal structure of the title compound.

In the molecule of the title compound (Fig 1), the bond lengths (Allen *et al.*, 1987) and angles are within normal ranges. Ring B (N3/C7-C11) is, of course, planar. Ring A (N1/N2/C4-C6) adopts envelope conformation with atom C4 displaced by -0.375 (3) Å from the plane of the other ring atoms.

In the crystal structure, intermolecular N-H···O hydrogen bonds (Table 1) link the molecules into centrosymmetric dimers (Fig. 2), in which they may be effective in the stabilization of the structure.

S2. Experimental

The title compound was synthesized according to a literature method (Lahm *et al.*, 2007). Crystals suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution.

S3. Refinement

H atoms were positioned geometrically, with N-H = 0.86 Å (for NH) and C-H = 0.93, 0.98, 0.97 and 0.96 Å for aromatic, methine, methylene and methyl H, respectively, and constrained to ride on their parent atoms, with $U_{iso}(H) = xU_{eq}(C,N)$, where x = 1.5 for methyl H and x = 1.2 for all other H atoms.

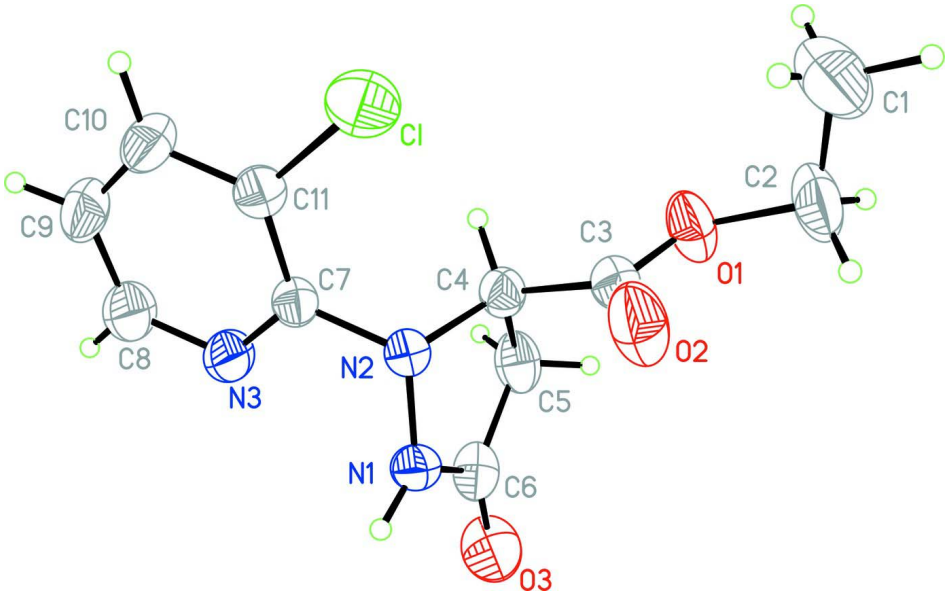


Figure 1

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

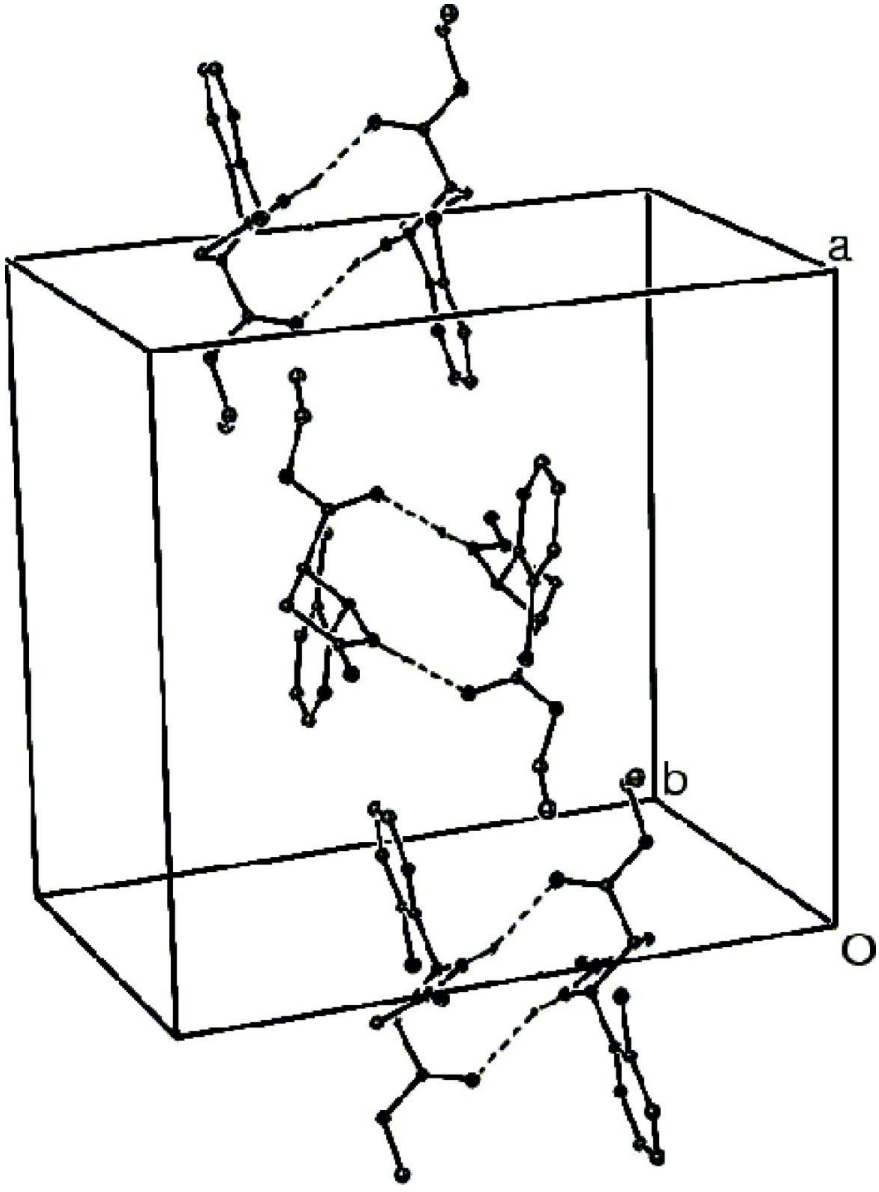


Figure 2

A partial packing diagram of the title compound. Hydrogen bonds are shown as dashed lines.

Ethyl 2-(3-chloro-2-pyridyl)-5-oxopyrazolidine-3-carboxylate

Crystal data

$C_{11}H_{12}ClN_3O_3$
$M_r = 269.69$
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
$a = 15.488$ (3) Å
$b = 10.009$ (2) Å
$c = 16.249$ (3) Å
$V = 2518.9$ (8) Å^3
$Z = 8$
$F(000) = 1120$
$D_x = 1.422$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 0.9$–$1.0°$
$\mu = 0.31$ mm^{-1}
$T = 298$ K
Block, colorless
0.30 × 0.20 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.913, T_{max} = 0.970
4453 measured reflections
2273 independent reflections
1635 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 25.3°, θ_{min} = 2.5°
h = 0→18
k = 0→12
l = −19→19
3 standard reflections every 120 min
intensity decay: none

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.110
S = 1.03
2273 reflections
164 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
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0473P)^2 + 0.824P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Extinction correction: *SHELXL*, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0065 (7)

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}
Cl	0.45523 (4)	0.14184 (7)	0.43566 (5)	0.0629 (3)
O1	0.30427 (10)	0.43898 (19)	0.31272 (11)	0.0561 (5)
O2	0.34478 (11)	0.4578 (2)	0.44373 (11)	0.0597 (5)
O3	0.55616 (12)	0.7407 (2)	0.33051 (13)	0.0667 (6)
N1	0.54947 (12)	0.55100 (18)	0.40815 (12)	0.0372 (5)
H1A	0.5776	0.5814	0.4497	0.045*
N2	0.51613 (11)	0.41865 (17)	0.40548 (11)	0.0328 (4)
N3	0.66149 (12)	0.3566 (2)	0.37919 (13)	0.0456 (5)
C1	0.1756 (2)	0.3232 (4)	0.3592 (2)	0.0876 (11)
H1B	0.1163	0.3358	0.3745	0.131*
H1C	0.2069	0.2863	0.4049	0.131*
H1D	0.1789	0.2631	0.3133	0.131*
C2	0.21401 (15)	0.4539 (3)	0.3359 (2)	0.0666 (9)
H2A	0.1820	0.4915	0.2902	0.080*

H2B	0.2096	0.5152	0.3820	0.080*
C3	0.36204 (14)	0.4419 (2)	0.37295 (15)	0.0389 (6)
C4	0.45184 (14)	0.4216 (2)	0.33772 (13)	0.0363 (5)
H4A	0.4542	0.3381	0.3063	0.044*
C5	0.48079 (15)	0.5388 (3)	0.28374 (15)	0.0471 (6)
H5A	0.5154	0.5078	0.2378	0.056*
H5B	0.4315	0.5878	0.2627	0.056*
C6	0.53378 (15)	0.6246 (3)	0.34130 (15)	0.0434 (6)
C7	0.58184 (14)	0.3194 (2)	0.39697 (13)	0.0332 (5)
C8	0.72260 (16)	0.2612 (3)	0.37550 (18)	0.0565 (8)
H8A	0.7790	0.2872	0.3639	0.068*
C9	0.70658 (18)	0.1279 (3)	0.38781 (17)	0.0548 (7)
H9A	0.7509	0.0655	0.3842	0.066*
C10	0.62367 (17)	0.0884 (3)	0.40552 (16)	0.0490 (6)
H10A	0.6104	−0.0013	0.4134	0.059*
C11	0.56048 (14)	0.1858 (2)	0.41127 (15)	0.0389 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl	0.0487 (4)	0.0514 (4)	0.0885 (6)	−0.0128 (3)	0.0079 (4)	0.0135 (4)
O1	0.0322 (9)	0.0815 (14)	0.0546 (11)	0.0039 (9)	−0.0095 (8)	−0.0041 (10)
O2	0.0367 (10)	0.0944 (16)	0.0479 (11)	0.0071 (10)	0.0002 (8)	−0.0127 (11)
O3	0.0629 (12)	0.0508 (12)	0.0864 (16)	−0.0110 (10)	−0.0068 (10)	0.0283 (11)
N1	0.0399 (10)	0.0307 (10)	0.0411 (11)	−0.0008 (8)	−0.0056 (9)	−0.0020 (9)
N2	0.0301 (9)	0.0308 (10)	0.0374 (10)	0.0009 (8)	−0.0036 (8)	−0.0011 (8)
N3	0.0314 (10)	0.0402 (12)	0.0650 (14)	0.0003 (9)	0.0035 (10)	−0.0027 (10)
C1	0.0537 (19)	0.097 (3)	0.112 (3)	−0.0200 (19)	0.0081 (19)	−0.017 (2)
C2	0.0295 (13)	0.087 (2)	0.084 (2)	0.0059 (14)	−0.0081 (14)	−0.0055 (18)
C3	0.0339 (12)	0.0399 (14)	0.0429 (14)	0.0027 (10)	−0.0047 (11)	−0.0039 (11)
C4	0.0342 (11)	0.0409 (13)	0.0339 (12)	0.0046 (10)	−0.0039 (9)	−0.0051 (10)
C5	0.0389 (13)	0.0647 (17)	0.0377 (13)	0.0061 (12)	−0.0017 (10)	0.0091 (12)
C6	0.0364 (13)	0.0465 (16)	0.0474 (15)	0.0045 (11)	0.0034 (11)	0.0107 (12)
C7	0.0318 (11)	0.0340 (12)	0.0337 (12)	0.0022 (10)	−0.0027 (10)	−0.0002 (10)
C8	0.0323 (12)	0.0542 (18)	0.083 (2)	0.0046 (12)	0.0019 (13)	−0.0045 (15)
C9	0.0498 (16)	0.0481 (16)	0.0666 (19)	0.0201 (13)	−0.0077 (14)	−0.0037 (13)
C10	0.0581 (16)	0.0342 (13)	0.0548 (15)	0.0072 (13)	−0.0068 (13)	0.0069 (12)
C11	0.0379 (13)	0.0351 (13)	0.0439 (14)	−0.0019 (10)	−0.0037 (10)	0.0032 (11)

Geometric parameters (Å, º)

Cl—C11	1.735 (2)	C2—H2A	0.9700
O1—C2	1.456 (3)	C2—H2B	0.9700
O1—C3	1.326 (3)	C3—C4	1.518 (3)
O2—C3	1.191 (3)	C4—C5	1.531 (3)
O3—C6	1.226 (3)	C4—H4A	0.9800
N1—N2	1.422 (2)	C5—C6	1.512 (4)
N1—C6	1.335 (3)	C5—H5A	0.9700

N1—H1A	0.8600	C5—H5B	0.9700
N2—C4	1.485 (3)	C7—C11	1.396 (3)
N2—C7	1.429 (3)	C8—C9	1.372 (4)
N3—C7	1.321 (3)	C8—H8A	0.9300
N3—C8	1.346 (3)	C9—C10	1.374 (4)
C1—C2	1.485 (4)	C9—H9A	0.9300
C1—H1B	0.9600	C10—C11	1.385 (3)
C1—H1C	0.9600	C10—H10A	0.9300
C1—H1D	0.9600		

C3—O1—C2	117.0 (2)	C3—C4—H4A	110.1
N2—N1—H1A	122.5	C5—C4—H4A	110.1
C6—N1—N2	115.02 (19)	C6—C5—C4	103.85 (18)
C6—N1—H1A	122.5	C6—C5—H5A	111.0
N1—N2—C7	113.08 (17)	C4—C5—H5A	111.0
N1—N2—C4	104.33 (16)	C6—C5—H5B	111.0
C7—N2—C4	114.82 (17)	C4—C5—H5B	111.0
C7—N3—C8	117.8 (2)	H5A—C5—H5B	109.0
C2—C1—H1B	109.5	O3—C6—N1	126.0 (2)
C2—C1—H1C	109.5	O3—C6—C5	127.1 (2)
H1B—C1—H1C	109.5	N1—C6—C5	106.8 (2)
C2—C1—H1D	109.5	N3—C7—C11	121.9 (2)
H1B—C1—H1D	109.5	N3—C7—N2	119.3 (2)
H1C—C1—H1D	109.5	C11—C7—N2	118.7 (2)
O1—C2—C1	111.1 (2)	N3—C8—C9	123.8 (2)
O1—C2—H2A	109.4	N3—C8—H8A	118.1
C1—C2—H2A	109.4	C9—C8—H8A	118.1
O1—C2—H2B	109.4	C8—C9—C10	118.6 (2)
C1—C2—H2B	109.4	C8—C9—H9A	120.7
H2A—C2—H2B	108.0	C10—C9—H9A	120.7
O2—C3—O1	124.3 (2)	C9—C10—C11	118.2 (2)
O2—C3—C4	126.0 (2)	C9—C10—H10A	120.9
O1—C3—C4	109.70 (19)	C11—C10—H10A	120.9
N2—C4—C3	109.73 (17)	C10—C11—C7	119.7 (2)
N2—C4—C5	104.11 (18)	C10—C11—Cl	120.06 (19)
C3—C4—C5	112.46 (19)	C7—C11—Cl	120.25 (17)
N2—C4—H4A	110.1		

C6—N1—N2—C7	108.8 (2)	C4—C5—C6—O3	−164.6 (2)
C6—N1—N2—C4	−16.6 (2)	C4—C5—C6—N1	13.3 (2)
C3—O1—C2—C1	−85.7 (3)	C8—N3—C7—C11	−0.3 (3)
C2—O1—C3—O2	−1.2 (4)	C8—N3—C7—N2	176.9 (2)
C2—O1—C3—C4	178.6 (2)	N1—N2—C7—N3	−10.9 (3)
N1—N2—C4—C3	−97.1 (2)	C4—N2—C7—N3	108.6 (2)
C7—N2—C4—C3	138.54 (19)	N1—N2—C7—C11	166.3 (2)
N1—N2—C4—C5	23.4 (2)	C4—N2—C7—C11	−74.1 (3)
C7—N2—C4—C5	−100.9 (2)	C7—N3—C8—C9	1.1 (4)
O2—C3—C4—N2	2.4 (3)	N3—C8—C9—C10	−0.5 (4)

O1—C3—C4—N2	−177.44 (18)	C8—C9—C10—C11	−0.9 (4)
O2—C3—C4—C5	−113.0 (3)	C9—C10—C11—C7	1.7 (4)
O1—C3—C4—C5	67.2 (2)	C9—C10—C11—Cl	−178.6 (2)
N2—C4—C5—C6	−22.5 (2)	N3—C7—C11—C10	−1.1 (4)
C3—C4—C5—C6	96.2 (2)	N2—C7—C11—C10	−178.3 (2)
N2—N1—C6—O3	179.8 (2)	N3—C7—C11—Cl	179.22 (18)
N2—N1—C6—C5	1.8 (3)	N2—C7—C11—Cl	2.0 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O2^{i}	0.86	2.14	2.910 (3)	149

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.