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## Structure Reports

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# Ethyl 1-(6-chloro-3-pyridylmethyl)-5-methyl-1*H*-1,2,3-triazole-4-carboxylate

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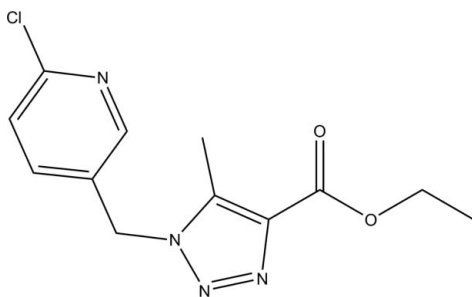
Received 17 October 2008; accepted 21 October 2008

Key indicators: single-crystal X-ray study;  $T = 291$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.039;  $wR$  factor = 0.105; data-to-parameter ratio = 14.1.

In the title compound,  $\text{C}_{12}\text{H}_{13}\text{ClN}_4\text{O}_2$ , the triazole ring carries methyl and ethoxycarbonyl groups, and is bound *via* a methylene bridge to a chloropyridine unit. There is evidence for significant electron delocalization in the triazolyl system. Intramolecular  $\text{C}-\text{H}\cdots\text{O}$  and intermolecular  $\text{C}-\text{H}\cdots\text{N}$  hydrogen bonds stabilize the structure.

## Related literature

For applications of triazoles, see: Abu-Orabi *et al.* (1989); Fan & Katritzky (1996); Dehne (1994); Wang *et al.* (1998). For bond-length data, see: Sasada (1984).



## Experimental

### Crystal data

$\text{C}_{12}\text{H}_{13}\text{ClN}_4\text{O}_2$   
 $M_r = 280.71$

Monoclinic,  $P2_1/c$   
 $a = 24.984$  (4) Å

$b = 4.3919$  (8) Å  
 $c = 12.040$  (2) Å  
 $\beta = 94.415$  (2)°  
 $V = 1317.2$  (4) Å<sup>3</sup>  
 $Z = 4$

Mo  $K\alpha$  radiation  
 $\mu = 0.29$  mm<sup>-1</sup>  
 $T = 291$  (2) K  
 $0.46 \times 0.38 \times 0.33$  mm

### Data collection

Bruker SMART APEX CCD area-detector diffractometer  
Absorption correction: none  
9219 measured reflections

2450 independent reflections  
1991 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.023$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$   
 $wR(F^2) = 0.105$   
 $S = 1.05$   
2450 reflections

174 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.18$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.23$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C5}-\text{H5}\cdots\text{N3}^{\text{i}}$	0.93	2.57	3.479 (3)	164
$\text{C9}-\text{H9A}\cdots\text{N4}^{\text{ii}}$	0.96	2.59	3.523 (3)	164
$\text{C9}-\text{H9B}\cdots\text{O2}$	0.96	2.54	3.114 (3)	119

Symmetry codes: (i)  $x, -y + \frac{5}{2}, z + \frac{1}{2}$ ; (ii)  $x, -y + \frac{3}{2}, z + \frac{1}{2}$ .

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; 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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2655).

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## supporting information

*Acta Cryst.* (2008). E64, o2351 [doi:10.1107/S1600536808034430]

**Ethyl 1-(6-chloro-3-pyridylmethyl)-5-methyl-1*H*-1,2,3-triazole-4-carboxylate**

**Tian-Jia Hua, Feng-Mei Sun, Wen-Ju Liu and Yong-Nian Qu**

**S1. Comment**

[1,2,3]-Triazoles have been widely used in pharmaceuticals, agrochemicals, dyes, photographic materials, and in corrosion inhibition (Fan & Katritzky, 1996; Dehne, 1994; Abu-Orabi *et al.*, 1989). Since the structure-activity relationship is very useful in the rational design of pharmaceuticals and agrochemicals. We report here the crystal structure of the title compound, (I) (Fig. 1), which was synthesized by introducing pyridine rings into a 1,2,3-triazole molecular framework.

The C—N bonds are significantly shorter than a normal single C—N bond [1.47 Å; Sasada, 1984], and closer to the value for a C=N bond [1.28 Å; Wang *et al.*, 1998]. This indicates significant electron delocalization in the triazolyl system.

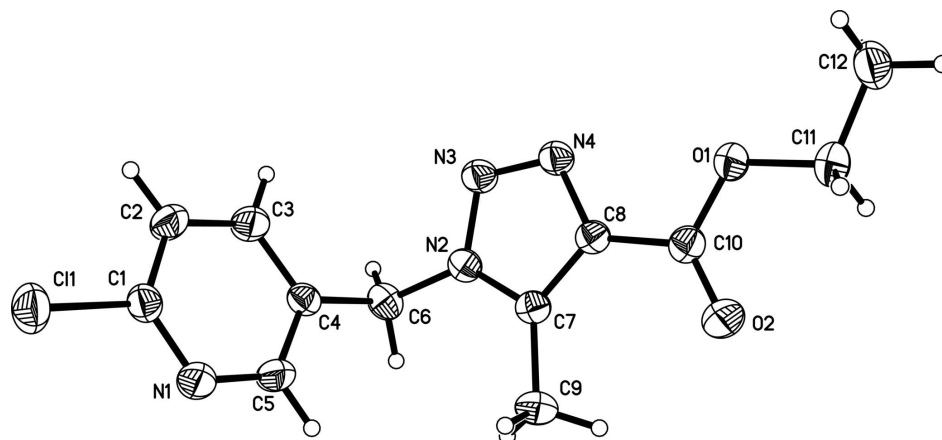
Intramolecular C—H···O and intermolecular C—H···N hydrogen bonds contribute strongly to the stability of the molecular configuration (Table 1, Fig. 2).

**S2. Experimental**

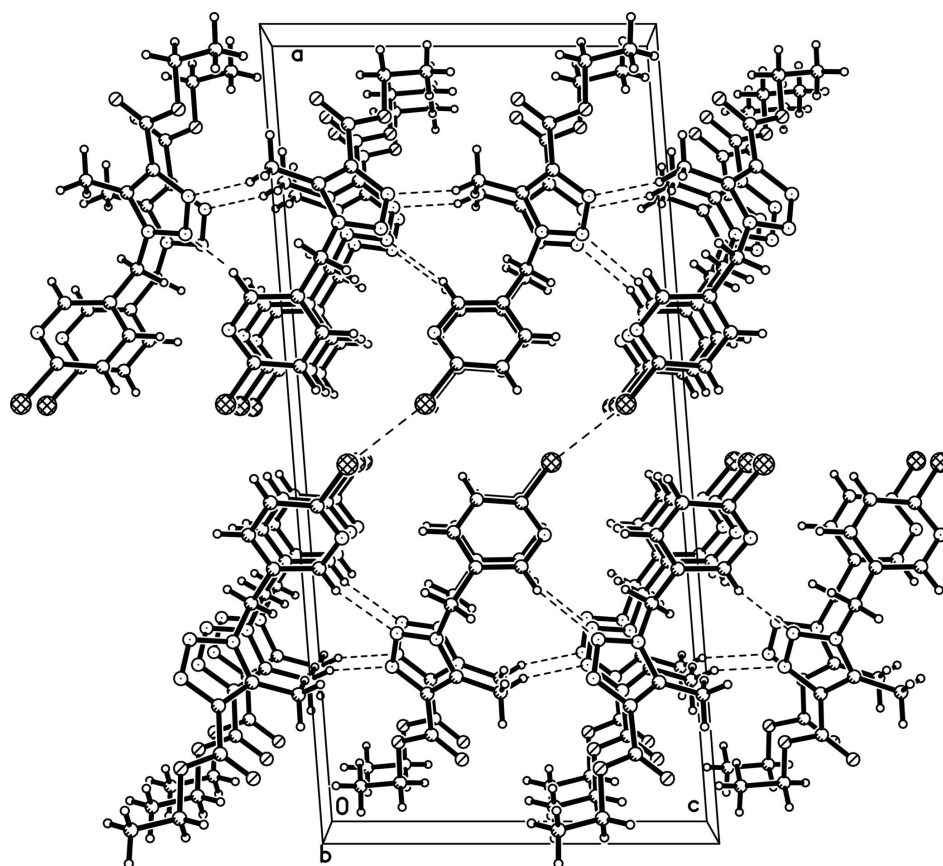
Ethyl acetylacetate (2 mmol) and 5-azidomethyl-2-chloropyridine (2 mmol) were added to a suspension of milled potassium carbonate (2 mmol) in DMSO (10 ml). The mixture was stirred at room temperature for 6 h (monitored by thin-layer chromatography) and poured to water (50 ml). The solid was collected by filtration, washed with water and diethyl ether, respectively, and dried to give 0.52 g of the title compound (yield 91%). Colourless crystals of (I) suitable for X-ray structure analysis were grown from acetone and petroleum ether (2:1, *v/v*).

**S3. Refinement**

H atoms were placed at calculated positions, with C—H distances of 0.93 (aromatic CH), 0.97 (CH<sub>3</sub>) and 0.97 Å (CH<sub>2</sub>). They were refined using a riding model, for methyl H atoms,  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ ; for all other H atoms,  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

**Figure 1**

View of the molecular structure of (I), showing the atom labelling scheme and with displacement ellipsoids drawn at the 50% probability level.

**Figure 2**

A partial view of the crystal packing of (I), showing the formation of C—H...O and C—H...N hydrogen-bonds (dashed lines).

**Ethyl 1-(6-chloro-3-pyridylmethyl)-5-methyl-1H-1,2,3- triazole-4-carboxylate***Crystal data*C<sub>12</sub>H<sub>13</sub>ClN<sub>4</sub>O<sub>2</sub> $M_r = 280.71$ Monoclinic,  $P2_1/c$ 

Hall symbol: -P 2ybc

 $a = 24.984 (4) \text{ \AA}$  $b = 4.3919 (8) \text{ \AA}$  $c = 12.040 (2) \text{ \AA}$  $\beta = 94.415 (2)^\circ$  $V = 1317.2 (4) \text{ \AA}^3$  $Z = 4$  $F(000) = 584$  $D_x = 1.416 \text{ Mg m}^{-3}$ Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ 

Cell parameters from 3288 reflections

 $\theta = 3.3\text{--}25.5^\circ$  $\mu = 0.29 \text{ mm}^{-1}$  $T = 291 \text{ K}$ 

Block, colourless

 $0.46 \times 0.38 \times 0.33 \text{ mm}$ *Data collection*Bruker SMART APEX CCD area-detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 $\varphi$  and  $\omega$  scans

9219 measured reflections

2450 independent reflections

1991 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.023$  $\theta_{\text{max}} = 25.5^\circ$ ,  $\theta_{\text{min}} = 3.3^\circ$  $h = -30 \rightarrow 29$  $k = -5 \rightarrow 5$  $l = -14 \rightarrow 14$ *Refinement*Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.039$  $wR(F^2) = 0.105$  $S = 1.05$ 

2450 reflections

174 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methodsSecondary atom site location: difference Fourier  
mapHydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0461P)^2 + 0.4886P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\text{max}} < 0.001$  $\Delta\rho_{\text{max}} = 0.19 \text{ e \AA}^{-3}$  $\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$ *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 ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.46436 (2)	0.66788 (16)	0.65329 (5)	0.0704 (2)
O1	0.11409 (5)	0.5500 (3)	0.20263 (11)	0.0531 (4)
O2	0.09737 (6)	0.7643 (4)	0.36514 (13)	0.0737 (5)

N1	0.37666 (7)	0.9857 (5)	0.61900 (13)	0.0649 (5)
N2	0.25163 (6)	1.1289 (3)	0.32725 (12)	0.0424 (4)
N3	0.25643 (6)	0.9861 (4)	0.22765 (12)	0.0489 (4)
N4	0.21318 (6)	0.8240 (4)	0.20603 (13)	0.0471 (4)
C1	0.41512 (7)	0.8561 (5)	0.56801 (16)	0.0484 (5)
C2	0.41911 (8)	0.8610 (6)	0.45476 (17)	0.0593 (6)
H2	0.4473	0.7647	0.4228	0.071*
C3	0.37992 (8)	1.0133 (6)	0.39049 (16)	0.0576 (6)
H3	0.3814	1.0215	0.3136	0.069*
C4	0.33851 (7)	1.1538 (4)	0.43968 (14)	0.0426 (4)
C5	0.33924 (9)	1.1340 (6)	0.55394 (16)	0.0625 (6)
H5	0.3118	1.2305	0.5885	0.075*
C6	0.29525 (8)	1.3267 (5)	0.37236 (17)	0.0507 (5)
H6A	0.2806	1.4811	0.4191	0.061*
H6B	0.3109	1.4293	0.3113	0.061*
C7	0.20468 (7)	1.0550 (4)	0.36960 (14)	0.0415 (4)
C8	0.18046 (7)	0.8611 (4)	0.29077 (14)	0.0413 (4)
C9	0.18798 (9)	1.1716 (5)	0.47790 (16)	0.0597 (6)
H9A	0.2023	1.0422	0.5372	0.090*
H9B	0.1495	1.1728	0.4764	0.090*
H9C	0.2013	1.3748	0.4899	0.090*
C10	0.12697 (8)	0.7226 (5)	0.29187 (16)	0.0477 (5)
C11	0.06017 (8)	0.4189 (6)	0.19684 (19)	0.0606 (6)
H11A	0.0336	0.5791	0.1999	0.073*
H11B	0.0567	0.2824	0.2592	0.073*
C12	0.05159 (10)	0.2481 (6)	0.0894 (2)	0.0700 (7)
H12A	0.0555	0.3845	0.0283	0.105*
H12B	0.0161	0.1623	0.0833	0.105*
H12C	0.0776	0.0878	0.0878	0.105*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C11	0.0538 (3)	0.0928 (5)	0.0629 (4)	0.0083 (3)	-0.0057 (2)	0.0110 (3)
O1	0.0436 (7)	0.0630 (9)	0.0533 (8)	-0.0077 (6)	0.0074 (6)	-0.0061 (7)
O2	0.0623 (9)	0.1011 (13)	0.0607 (9)	-0.0154 (9)	0.0240 (8)	-0.0149 (9)
N1	0.0567 (10)	0.1005 (15)	0.0377 (9)	0.0146 (10)	0.0050 (8)	-0.0002 (10)
N2	0.0477 (8)	0.0423 (8)	0.0367 (8)	0.0002 (7)	0.0010 (6)	0.0047 (7)
N3	0.0515 (9)	0.0565 (10)	0.0392 (8)	-0.0032 (8)	0.0071 (7)	-0.0004 (7)
N4	0.0486 (9)	0.0538 (10)	0.0391 (8)	-0.0028 (8)	0.0047 (7)	-0.0002 (7)
C1	0.0432 (10)	0.0573 (12)	0.0444 (10)	-0.0048 (9)	0.0015 (8)	0.0010 (9)
C2	0.0496 (11)	0.0821 (16)	0.0476 (11)	0.0122 (11)	0.0130 (9)	-0.0023 (11)
C3	0.0568 (12)	0.0809 (16)	0.0362 (10)	0.0054 (11)	0.0110 (9)	0.0024 (10)
C4	0.0457 (10)	0.0429 (10)	0.0392 (10)	-0.0068 (8)	0.0029 (7)	-0.0024 (8)
C5	0.0570 (12)	0.0909 (17)	0.0404 (11)	0.0193 (12)	0.0078 (9)	-0.0083 (11)
C6	0.0559 (11)	0.0436 (11)	0.0515 (11)	-0.0048 (9)	-0.0017 (9)	0.0015 (9)
C7	0.0480 (10)	0.0422 (10)	0.0342 (9)	0.0067 (8)	0.0022 (7)	0.0066 (8)
C8	0.0448 (10)	0.0443 (10)	0.0349 (9)	0.0038 (8)	0.0034 (7)	0.0052 (8)

C9	0.0690 (13)	0.0692 (15)	0.0416 (11)	0.0010 (12)	0.0092 (9)	-0.0065 (10)
C10	0.0468 (10)	0.0517 (11)	0.0447 (10)	0.0020 (9)	0.0050 (8)	0.0046 (9)
C11	0.0448 (11)	0.0683 (14)	0.0692 (14)	-0.0100 (10)	0.0085 (10)	-0.0011 (11)
C12	0.0587 (13)	0.0816 (17)	0.0690 (15)	-0.0187 (12)	0.0004 (11)	-0.0038 (13)

*Geometric parameters (Å, °)*

C11—C1	1.748 (2)	C4—C6	1.505 (3)
O1—C10	1.334 (2)	C5—H5	0.9300
O1—C11	1.462 (2)	C6—H6A	0.9700
O2—C10	1.208 (2)	C6—H6B	0.9700
N1—C1	1.310 (3)	C7—C8	1.380 (3)
N1—C5	1.341 (3)	C7—C9	1.490 (3)
N2—C7	1.354 (2)	C8—C10	1.469 (3)
N2—N3	1.367 (2)	C9—H9A	0.9600
N2—C6	1.465 (2)	C9—H9B	0.9600
N3—N4	1.303 (2)	C9—H9C	0.9600
N4—C8	1.365 (2)	C11—C12	1.496 (3)
C1—C2	1.375 (3)	C11—H11A	0.9700
C2—C3	1.374 (3)	C11—H11B	0.9700
C2—H2	0.9300	C12—H12A	0.9600
C3—C4	1.377 (3)	C12—H12B	0.9600
C3—H3	0.9300	C12—H12C	0.9600
C4—C5	1.377 (3)		
C10—O1—C11	115.24 (15)	N2—C7—C8	103.62 (15)
C1—N1—C5	116.16 (17)	N2—C7—C9	123.82 (17)
C7—N2—N3	110.96 (15)	C8—C7—C9	132.56 (18)
C7—N2—C6	130.06 (16)	N4—C8—C7	109.36 (16)
N3—N2—C6	118.97 (15)	N4—C8—C10	123.69 (16)
N4—N3—N2	107.36 (14)	C7—C8—C10	126.89 (16)
N3—N4—C8	108.69 (15)	C7—C9—H9A	109.5
N1—C1—C2	124.75 (19)	C7—C9—H9B	109.5
N1—C1—C11	116.01 (15)	H9A—C9—H9B	109.5
C2—C1—C11	119.23 (16)	C7—C9—H9C	109.5
C3—C2—C1	117.59 (18)	H9A—C9—H9C	109.5
C3—C2—H2	121.2	H9B—C9—H9C	109.5
C1—C2—H2	121.2	O2—C10—O1	123.45 (18)
C2—C3—C4	120.15 (18)	O2—C10—C8	123.52 (19)
C2—C3—H3	119.9	O1—C10—C8	113.02 (16)
C4—C3—H3	119.9	O1—C11—C12	107.99 (17)
C5—C4—C3	116.66 (18)	O1—C11—H11A	110.1
C5—C4—C6	121.56 (17)	C12—C11—H11A	110.1
C3—C4—C6	121.77 (17)	O1—C11—H11B	110.1
N1—C5—C4	124.68 (19)	C12—C11—H11B	110.1
N1—C5—H5	117.7	H11A—C11—H11B	108.4
C4—C5—H5	117.7	C11—C12—H12A	109.5
N2—C6—C4	112.53 (15)	C11—C12—H12B	109.5

N2—C6—H6A	109.1	H12A—C12—H12B	109.5
C4—C6—H6A	109.1	C11—C12—H12C	109.5
N2—C6—H6B	109.1	H12A—C12—H12C	109.5
C4—C6—H6B	109.1	H12B—C12—H12C	109.5
H6A—C6—H6B	107.8		
C7—N2—N3—N4	0.3 (2)	N3—N2—C7—C8	-0.43 (19)
C6—N2—N3—N4	179.64 (15)	C6—N2—C7—C8	-179.72 (17)
N2—N3—N4—C8	0.0 (2)	N3—N2—C7—C9	179.32 (17)
C5—N1—C1—C2	-0.5 (3)	C6—N2—C7—C9	0.0 (3)
C5—N1—C1—C11	179.07 (18)	N3—N4—C8—C7	-0.3 (2)
N1—C1—C2—C3	0.1 (4)	N3—N4—C8—C10	177.11 (17)
C11—C1—C2—C3	-179.46 (17)	N2—C7—C8—N4	0.5 (2)
C1—C2—C3—C4	-0.1 (3)	C9—C7—C8—N4	-179.3 (2)
C2—C3—C4—C5	0.5 (3)	N2—C7—C8—C10	-176.87 (17)
C2—C3—C4—C6	179.1 (2)	C9—C7—C8—C10	3.4 (3)
C1—N1—C5—C4	1.0 (4)	C11—O1—C10—O2	1.9 (3)
C3—C4—C5—N1	-1.0 (4)	C11—O1—C10—C8	-177.09 (17)
C6—C4—C5—N1	-179.6 (2)	N4—C8—C10—O2	-177.4 (2)
C7—N2—C6—C4	93.0 (2)	C7—C8—C10—O2	-0.4 (3)
N3—N2—C6—C4	-86.3 (2)	N4—C8—C10—O1	1.6 (3)
C5—C4—C6—N2	-96.2 (2)	C7—C8—C10—O1	178.57 (17)
C3—C4—C6—N2	85.3 (2)	C10—O1—C11—C12	176.97 (19)

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>
C5—H5...N3 <sup>i</sup>	0.93	2.57	3.479 (3)	164
C9—H9 <i>A</i> ...N4 <sup>ii</sup>	0.96	2.59	3.523 (3)	164
C9—H9 <i>B</i> ...O2	0.96	2.54	3.114 (3)	119

Symmetry codes: (i) *x*, -*y*+5/2, *z*+1/2; (ii) *x*, -*y*+3/2, *z*+1/2.