

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

(E)-N'-(2-Chlorobenzylidene)-1-methyl-4-nitro-1H-pyrrole-2-carbohydrazide

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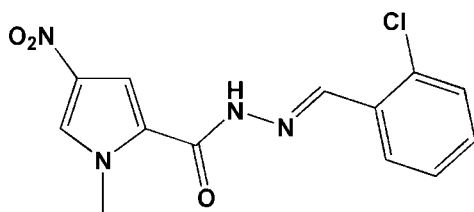
Received 8 December 2013; accepted 18 December 2013

Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.061; wR factor = 0.164; data-to-parameter ratio = 12.8.

In the title compound, $\text{C}_{13}\text{H}_{11}\text{ClN}_4\text{O}_3$, the phenyl and pyrrolyl ring are linked by an acyl-hydrazone ($\text{R}_2\text{C}=\text{N}-\text{N}-\text{CO}-\text{R}$) group, forming a slightly bent molecule: the dihedral angle subtended by the phenyl and pyrrolyl rings is 8.46 (12)°. In the crystal, the three-dimensional supramolecular structure is assembled by $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonding. Molecular sheets are formed parallel to (101) in a herringbone arrangement by weak van der Waals interactions; weak $\pi-\pi$ [centroid-centroid phenyl-phenyl and pyrrolyl-pyrrolyl distances of 3.7816 (3) and 3.8946 (2) Å, respectively] interactions occur between neighbouring sheets.

Related literature

For applications and structures of aroylhydrazones, see: Raja *et al.* (2012); Wang *et al.* (2014).



Experimental

Crystal data

 $\text{C}_{13}\text{H}_{11}\text{ClN}_4\text{O}_3$ $M_r = 306.71$

Monoclinic, $P2_1/c$
 $a = 13.7649$ (13) Å
 $b = 12.4993$ (11) Å
 $c = 8.1263$ (10) Å
 $\beta = 95.523$ (1)°
 $V = 1391.7$ (2) Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.29$ mm⁻¹
 $T = 298$ K
 $0.30 \times 0.20 \times 0.16$ mm

Data collection

Bruker SMART 1000 CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2005)
 $T_{\min} = 0.918$, $T_{\max} = 0.955$

6871 measured reflections
 2452 independent reflections
 1435 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.071$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.061$
 $wR(F^2) = 0.164$
 $S = 1.00$
 2452 reflections

191 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.23$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.33$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N3}-\text{H3}\cdots\text{O1}^i$	0.86	2.14	2.941 (3)	154

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

Data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 1999) and SHELXTL (Sheldrick, 2008); software used to prepare material for publication: PLATON (Spek, 2009) and SHELXTL.

This work was supported by the National-level College Students' Innovative Training Plan Program of the People's Republic of China (grant No. 201310122001) and the Scientific Research Foundation for PhDs of Changzhi University.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FF2124).

References

- Brandenburg, K. (1999). DIAMOND. Crystal Impact GbR, Bonn, Germany.
 Bruker (1999). SMART and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruker (2005). SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
 Raja, D. S., Bhuvanesh, N. S. P. & Natarajan, K. (2012). Dalton Trans. **41**, 4365–4377.
 Sheldrick, G. M. (2008). Acta Cryst. **A64**, 112–122.
 Spek, A. L. (2009). Acta Cryst. **D65**, 148–155.
 Wang, J., Zhao, Y. & Yang, B. (2014). Inorg. Chim. Acta, **409**, 484–496.

supporting information

Acta Cryst. (2014). E70, o99 [https://doi.org/10.1107/S1600536813034119]

(*E*)-*N'*-(2-Chlorobenzylidene)-1-methyl-4-nitro-1*H*-pyrrole-2-carbohydrazide**Jinglin Wang, Rong He, Zhijuan Xin, Huiling Shen and Cairong Wang****S1. Comment**

A great number of aroylhydrazones (AH) have triggered wide interest because of their diverse spectra of biological and pharmaceutical properties (Raja, *et al.*, 2012). In our lab, the AH compound (*E*)-*N'*-(2-hydroxybenzylidene)-1-methyl-4-nitro-1*H*-pyrrole-2-carbohydrazide (*L*) and its transition metal complexes were obtained and characterized. The interaction of these compounds with CT-DNA and pBR322 DNA has been explored (Wang, *et al.*, 2014). The present report is an extension of our earlier studies in this area.

In the title compound (Fig. 1), C₁₃H₁₁ClN₄O₃, the phenyl and pyrrolyl ring are linked by acyl-hydrazone ($R_2C=N-N-CO-R$) to form a slightly bent molecule. The dihedral angle between the phenyl (C8—C13) and pyrrolyl rings (C2—C5, N1) is 8.46 (12)°.

As shown in Figure 2, the herringbone molecular sheet of the title compound is formed by weak van-der-Waals interactions along (101) plane.

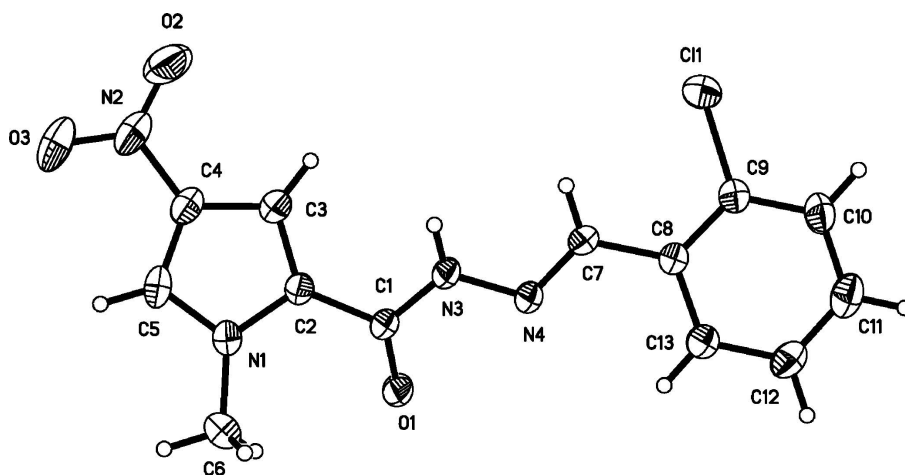
The three-dimensional supramolecular structure (Fig. 3) is assembled by N3—H3[⋯]O1ⁱ hydrogen bonding (pink dotted lines) and weak Cg1[⋯]Cg1ⁱⁱ (Cg1 is the centroid of the phenyl ring) and Cg2[⋯]Cg2ⁱⁱⁱ (Cg2 is the centroid of the pyrrolyl ring) interactions (black dotted lines) between the neighbouring molecular sheets [symmetry code: (i) $x, 3/2 - y, 1/2 + z$; (ii) $1 - x, 2 - y, 2 - z$; (iii) $-x, 1 - y, 2 - z$]. The data of hydrogen-bond geometry are given in Table 1.

S2. Experimental

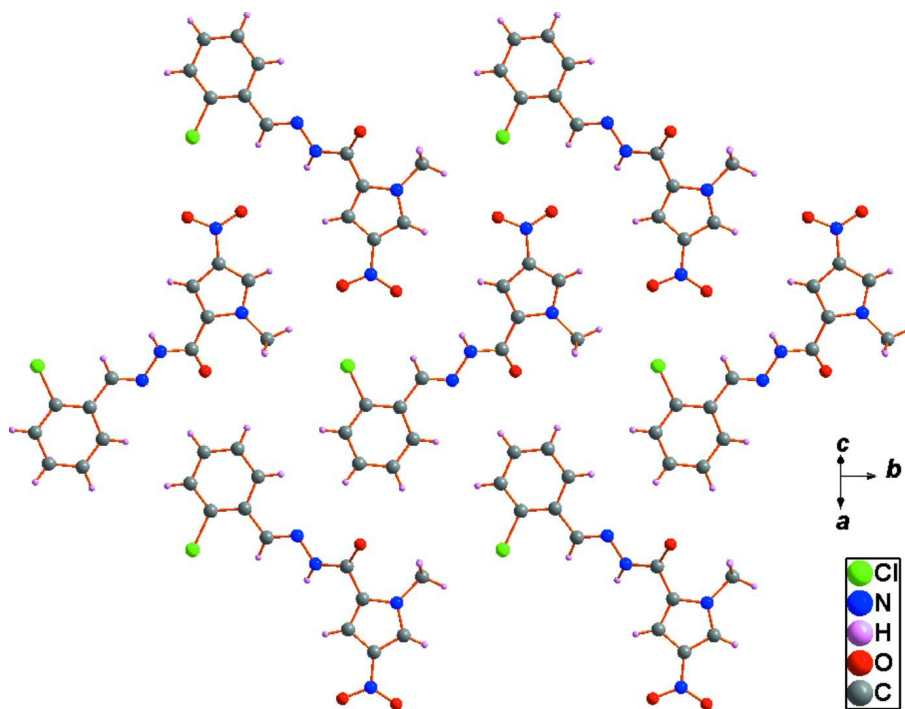
Single crystals of the title compound were obtained accidentally in the attempted synthesis of a Ni complex. (*E*)-*N'*-(2-hydroxybenzylidene)-1-methyl-4-nitro-1*H*-pyrrole-2-carbohydrazide (*L*) was synthesized according to literature procedures (Wang *et al.*, 2014). Sodium methoxide (250 μ L, 3%, g/V) was added to solution of *L* (0.50 mmol, 0.144 g) in 15 ml MeOH and was heated to reflux. NiCl₂·6H₂O (0.50 mmol, 0.119 g) was then added to the refluxing mixture and further refluxed for 2 h. The reaction mixture was cooled and was allowed to stir at room temperature overnight. The mixture was filtered and washed with methanol. The L—Ni complex is not achieved as predicted. However, orange single crystals of the title compound suitable for X-ray analysis were obtained after several days from the mother liquor by slow evaporation.

S3. Refinement

H atoms attached to C atoms are placed in geometrically idealized position, with N—H=0.86 Å, C—H=0.93 and 0.96 Å, for CH and CH₃ groups, respectively, and with $U_{iso}(H) = k \times U_{eq}(\text{parent C-atom})$, where $k = 1.5$ for CH₃ H-atoms and =1.2 for other H-atoms.

**Figure 1**

The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are presented as small spheres of arbitrary radius.

**Figure 2**

The two-dimensional herringbone layer in the crystal structure of title compound.

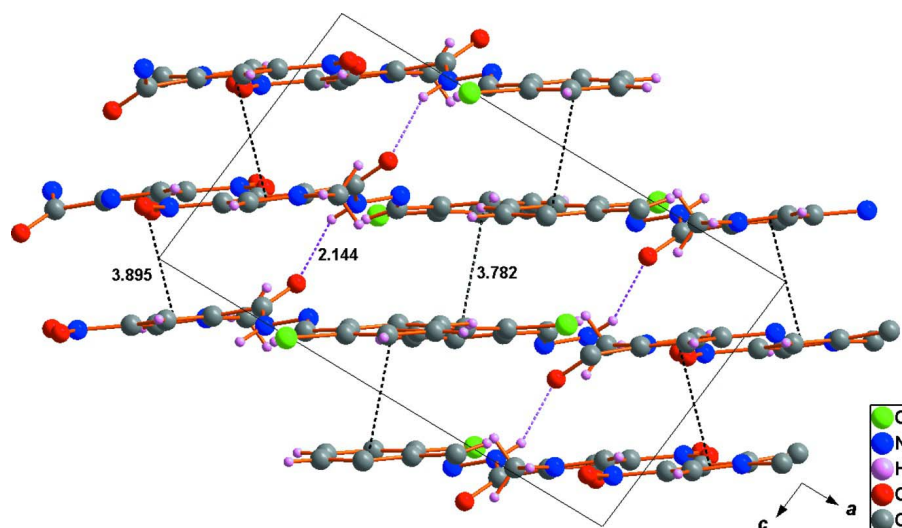


Figure 3

Packing of the title compound viewed along the b axis. The three-dimensional supramolecular structure is assembled by N–H \cdots O hydrogen bonding (pink dotted lines) and weak $\pi\cdots\pi$ interactions (black dotted lines) between the neighbouring molecular sheets (all distances in Å).

(E)-*N'*-(2-Chlorobenzylidene)-1-methyl-4-nitro-1*H*-pyrrole-2-carbohydrazone

Crystal data

$C_{13}H_{11}ClN_4O_3$

$M_r = 306.71$

Monoclinic, $P2_1/c$

$a = 13.7649$ (13) Å

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$c = 8.1263$ (10) Å

$\beta = 95.523$ (1)°

$V = 1391.7$ (2) Å³

$Z = 4$

$F(000) = 632$

$D_x = 1.464$ Mg m⁻³

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

Cell parameters from 1539 reflections

$\theta = 3.0$ – 25.2 °

$\mu = 0.29$ mm⁻¹

$T = 298$ K

Block, yellow

$0.30 \times 0.20 \times 0.16$ mm

Data collection

Bruker SMART 1000 CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

phi and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2005)

$T_{\min} = 0.918$, $T_{\max} = 0.955$

6871 measured reflections

2452 independent reflections

1435 reflections with $I > 2\sigma(I)$

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

$\theta_{\max} = 25.0$ °, $\theta_{\min} = 1.5$ °

$h = -15 \rightarrow 16$

$k = -14 \rightarrow 14$

$l = -6 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.061$

$wR(F^2) = 0.164$

$S = 1.00$

2452 reflections

191 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
 $w = 1/[\sigma^2(F_o^2) + (0.0787P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.23 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.33 \text{ e } \text{\AA}^{-3}$

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.29032 (9)	1.16858 (8)	1.00653 (18)	0.1044 (6)
N1	0.14340 (19)	0.51021 (19)	1.0868 (3)	0.0508 (7)
N2	-0.0430 (2)	0.5940 (3)	1.3388 (4)	0.0712 (9)
N3	0.24317 (19)	0.7725 (2)	1.0085 (3)	0.0512 (8)
H3	0.2231	0.7996	1.0964	0.061*
N4	0.30201 (18)	0.83156 (19)	0.9133 (3)	0.0470 (7)
O1	0.24317 (17)	0.62828 (16)	0.8366 (3)	0.0587 (7)
O2	-0.0656 (2)	0.6852 (3)	1.3780 (4)	0.1057 (12)
O3	-0.08399 (19)	0.5122 (3)	1.3789 (3)	0.0907 (9)
C1	0.2175 (2)	0.6716 (2)	0.9618 (4)	0.0465 (8)
C2	0.1506 (2)	0.6203 (2)	1.0708 (4)	0.0451 (8)
C3	0.0829 (2)	0.6674 (3)	1.1612 (4)	0.0514 (8)
H3A	0.0711	0.7403	1.1715	0.062*
C4	0.0352 (2)	0.5839 (3)	1.2344 (4)	0.0561 (9)
C5	0.0737 (2)	0.4884 (3)	1.1897 (4)	0.0573 (9)
H5	0.0554	0.4209	1.2235	0.069*
C6	0.2046 (3)	0.4285 (3)	1.0169 (5)	0.0659 (10)
H6A	0.2708	0.4362	1.0642	0.099*
H6B	0.2017	0.4376	0.8992	0.099*
H6C	0.1810	0.3586	1.0416	0.099*
C7	0.3117 (2)	0.9297 (2)	0.9548 (4)	0.0483 (8)
H7	0.2764	0.9569	1.0373	0.058*
C8	0.3779 (2)	1.0000 (2)	0.8743 (4)	0.0467 (8)
C9	0.3778 (2)	1.1102 (2)	0.8944 (4)	0.0571 (9)
C10	0.4438 (3)	1.1761 (3)	0.8256 (5)	0.0698 (11)
H10	0.4413	1.2498	0.8406	0.084*
C11	0.5133 (3)	1.1319 (3)	0.7348 (5)	0.0698 (11)
H11	0.5587	1.1756	0.6900	0.084*
C12	0.5154 (3)	1.0231 (3)	0.7108 (5)	0.0659 (10)
H12	0.5620	0.9933	0.6491	0.079*
C13	0.4481 (2)	0.9577 (3)	0.7784 (4)	0.0568 (9)
H13	0.4497	0.8843	0.7598	0.068*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.1002 (9)	0.0517 (6)	0.1730 (14)	0.0028 (6)	0.0731 (9)	-0.0179 (7)
N1	0.0553 (16)	0.0427 (14)	0.0560 (18)	-0.0065 (13)	0.0130 (13)	0.0045 (13)
N2	0.057 (2)	0.102 (3)	0.057 (2)	-0.019 (2)	0.0189 (16)	0.0023 (19)
N3	0.0646 (18)	0.0459 (15)	0.0477 (17)	-0.0109 (13)	0.0286 (14)	-0.0042 (12)
N4	0.0549 (16)	0.0436 (15)	0.0455 (16)	-0.0057 (13)	0.0199 (13)	0.0025 (11)
O1	0.0821 (17)	0.0499 (12)	0.0490 (14)	-0.0105 (12)	0.0310 (12)	-0.0064 (11)
O2	0.088 (2)	0.121 (3)	0.117 (3)	-0.010 (2)	0.056 (2)	-0.027 (2)
O3	0.0637 (17)	0.134 (3)	0.077 (2)	-0.0337 (18)	0.0193 (14)	0.0198 (18)
C1	0.053 (2)	0.0444 (17)	0.045 (2)	-0.0027 (15)	0.0197 (15)	0.0023 (14)
C2	0.0476 (18)	0.0425 (16)	0.047 (2)	-0.0063 (14)	0.0123 (15)	-0.0010 (14)
C3	0.0496 (19)	0.0530 (18)	0.054 (2)	-0.0032 (16)	0.0153 (16)	-0.0007 (16)
C4	0.0516 (19)	0.069 (2)	0.050 (2)	-0.0095 (18)	0.0160 (16)	0.0016 (17)
C5	0.059 (2)	0.059 (2)	0.055 (2)	-0.0168 (18)	0.0113 (17)	0.0151 (17)
C6	0.075 (3)	0.0447 (18)	0.079 (3)	0.0036 (18)	0.014 (2)	0.0010 (18)
C7	0.0515 (19)	0.0442 (18)	0.053 (2)	-0.0001 (15)	0.0227 (16)	-0.0005 (15)
C8	0.0473 (18)	0.0431 (16)	0.052 (2)	-0.0039 (15)	0.0150 (15)	0.0006 (14)
C9	0.056 (2)	0.0442 (18)	0.074 (3)	-0.0032 (16)	0.0199 (18)	0.0008 (17)
C10	0.068 (2)	0.0459 (19)	0.098 (3)	-0.0110 (18)	0.021 (2)	0.0092 (19)
C11	0.061 (2)	0.076 (3)	0.074 (3)	-0.013 (2)	0.016 (2)	0.018 (2)
C12	0.063 (2)	0.075 (3)	0.064 (3)	-0.002 (2)	0.0284 (19)	0.003 (2)
C13	0.064 (2)	0.0502 (19)	0.059 (2)	-0.0029 (17)	0.0220 (18)	0.0008 (16)

Geometric parameters (\AA , $^\circ$)

C11—C9	1.739 (3)	C5—H5	0.9300
N1—C5	1.359 (4)	C6—H6A	0.9600
N1—C2	1.387 (4)	C6—H6B	0.9600
N1—C6	1.472 (4)	C6—H6C	0.9600
N2—O3	1.227 (4)	C7—C8	1.465 (4)
N2—O2	1.232 (4)	C7—H7	0.9300
N2—C4	1.439 (4)	C8—C9	1.387 (4)
N3—C1	1.354 (4)	C8—C13	1.402 (4)
N3—N4	1.386 (3)	C9—C10	1.383 (5)
N3—H3	0.8600	C10—C11	1.379 (5)
N4—C7	1.276 (4)	C10—H10	0.9300
O1—C1	1.234 (3)	C11—C12	1.374 (5)
C1—C2	1.483 (4)	C11—H11	0.9300
C2—C3	1.374 (4)	C12—C13	1.388 (4)
C3—C4	1.397 (4)	C12—H12	0.9300
C3—H3A	0.9300	C13—H13	0.9300
C4—C5	1.369 (5)		
C5—N1—C2	108.5 (3)	N1—C6—H6B	109.5
C5—N1—C6	124.2 (3)	H6A—C6—H6B	109.5
C2—N1—C6	127.1 (2)	N1—C6—H6C	109.5

O3—N2—O2	124.7 (3)	H6A—C6—H6C	109.5
O3—N2—C4	118.2 (4)	H6B—C6—H6C	109.5
O2—N2—C4	117.1 (3)	N4—C7—C8	120.8 (3)
C1—N3—N4	119.4 (2)	N4—C7—H7	119.6
C1—N3—H3	120.3	C8—C7—H7	119.6
N4—N3—H3	120.3	C9—C8—C13	116.7 (3)
C7—N4—N3	114.6 (2)	C9—C8—C7	122.4 (3)
O1—C1—N3	123.5 (3)	C13—C8—C7	120.9 (3)
O1—C1—C2	123.1 (3)	C10—C9—C8	122.4 (3)
N3—C1—C2	113.3 (3)	C10—C9—C11	118.5 (3)
C3—C2—N1	108.5 (3)	C8—C9—C11	119.1 (2)
C3—C2—C1	128.8 (3)	C11—C10—C9	119.6 (3)
N1—C2—C1	122.6 (3)	C11—C10—H10	120.2
C2—C3—C4	106.1 (3)	C9—C10—H10	120.2
C2—C3—H3A	126.9	C12—C11—C10	119.8 (3)
C4—C3—H3A	126.9	C12—C11—H11	120.1
C5—C4—C3	109.2 (3)	C10—C11—H11	120.1
C5—C4—N2	124.3 (3)	C11—C12—C13	120.2 (3)
C3—C4—N2	126.4 (3)	C11—C12—H12	119.9
N1—C5—C4	107.6 (3)	C13—C12—H12	119.9
N1—C5—H5	126.2	C12—C13—C8	121.3 (3)
C4—C5—H5	126.2	C12—C13—H13	119.4
N1—C6—H6A	109.5	C8—C13—H13	119.4
C1—N3—N4—C7	171.3 (3)	C2—N1—C5—C4	1.7 (4)
N4—N3—C1—O1	-0.5 (5)	C6—N1—C5—C4	177.5 (3)
N4—N3—C1—C2	-177.2 (3)	C3—C4—C5—N1	-1.2 (4)
C5—N1—C2—C3	-1.6 (4)	N2—C4—C5—N1	178.0 (3)
C6—N1—C2—C3	-177.2 (3)	N3—N4—C7—C8	175.1 (3)
C5—N1—C2—C1	-177.7 (3)	N4—C7—C8—C9	168.3 (3)
C6—N1—C2—C1	6.7 (5)	N4—C7—C8—C13	-14.7 (5)
O1—C1—C2—C3	-147.4 (4)	C13—C8—C9—C10	-0.6 (6)
N3—C1—C2—C3	29.3 (5)	C7—C8—C9—C10	176.4 (4)
O1—C1—C2—N1	27.9 (5)	C13—C8—C9—C11	178.0 (3)
N3—C1—C2—N1	-155.5 (3)	C7—C8—C9—C11	-4.9 (5)
N1—C2—C3—C4	0.8 (4)	C8—C9—C10—C11	-0.7 (6)
C1—C2—C3—C4	176.6 (3)	C11—C9—C10—C11	-179.4 (3)
C2—C3—C4—C5	0.3 (4)	C9—C10—C11—C12	1.2 (6)
C2—C3—C4—N2	-178.9 (3)	C10—C11—C12—C13	-0.4 (6)
O3—N2—C4—C5	-6.7 (6)	C11—C12—C13—C8	-1.0 (6)
O2—N2—C4—C5	175.1 (4)	C9—C8—C13—C12	1.5 (5)
O3—N2—C4—C3	172.3 (3)	C7—C8—C13—C12	-175.6 (3)
O2—N2—C4—C3	-5.9 (6)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
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N3—H3 \cdots O1 ⁱ	0.86	2.14	2.941 (3)	154
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Symmetry code: (i) $x, -y+3/2, z+1/2$.