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Crystal structure of (*E*)-*N*′-benzylidene-1-methyl-4-nitro-1*H*-pyrrole-2-carbohydrazide

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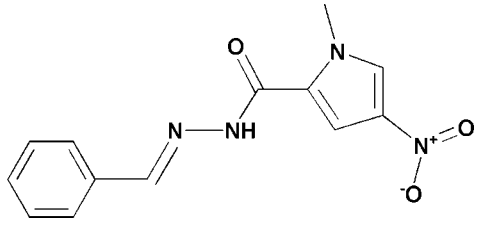
In the title compound, $C_{13}H_{12}N_4O_3$, the dihedral angle between the planes of the pyrrole and benzene rings is 7.47 (1)°. In the crystal, molecules are arranged in sheets lying parallel to (101). Neighbouring sheets are linked by N—H···O hydrogen bonds, weak π–π [centroid–centroid distance between the pyrrole rings = 3.765 (11) Å] and C—H···π interactions, forming a three-dimensional structure.

Keywords: crystal structure; pyrrole-2-carbohydrazide; aroylhydrazones; hydrogen bonding; π–π interactions.

CCDC reference: 1018158

1. Related literature

For applications and structures of aroylhydrazones, see: Krishnamoorthy *et al.* (2012); Raja *et al.* (2012); Wang *et al.* (2014). For similar structures, see: Wang *et al.* (2011, 2014). For π–π interactions, see: Janiak (2000).



2. Experimental

2.1. Crystal data

$C_{13}H_{12}N_4O_3$
M_r = 272.27
Monoclinic, $P2_1/c$
a = 13.030 (3) Å
b = 11.900 (3) Å
c = 8.331 (2) Å
β = 95.409 (3)°
V = 1285.92 (17) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 298 K
0.32 × 0.20 × 0.17 mm

2.2. Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.968, T_{max} = 0.983
6283 measured reflections
2248 independent reflections
1382 reflections with $I > 2\sigma(I)$
R_{int} = 0.043

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.135
S = 1.03
2248 reflections
182 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

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

Cg is the centroid of the C8–C13 ring.

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O1^{i}	0.86	2.13	2.942 (2)	158
C6—H6B···Cg^{i}	0.96	2.70	3.590 (3)	154

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

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: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* and *DIAMOND* (Brandenburg, 2005).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: BT6990).

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supporting information

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Crystal structure of (*E*)-*N*′-benzylidene-1-methyl-4-nitro-1*H*-pyrrole-2-carbohydrazide

Zhijun Wang, Chengyong Zhou, Lei Yan and Jinglin Wang

S1. Comment

Hydrazones and analogous compounds have attracted attention from researchers due to their well known chelating capability and structural flexibility (Krishnamoorthy, *et al.*, 2012; Raja, *et al.*, 2012). In our lab, a series of asymmetric N-heterocyclic substituted hydrazones and their metal complexes were obtained and characterized (Wang *et al.*, 2011). The interactions of these compounds with CT-DNA and pBR322 DNA has been explored (Wang *et al.*, 2014). The present work is an extension of our earlier studies.

In the title compound (Fig. 1) the phenyl and pyrrolyl ring are linked by an acyl-hydrazone moiety. The dihedral angle between the phenyl and pyrrolyl rings is 7.47 (1)°.

As shown in Figure 2, molecules of the title compound form sheet parallel to the (101) plane.

The neighbouring sheets are linked by N–H···O hydrogen bonds, weak $\pi\cdots\pi$ interactions between pyrrolyl rings and C–H···π interactions (Figure 3). These interactions result in the formation of a three-dimensional network (Fig. 4).

S2. Experimental

The precursor 1-methyl-4-nitro-1*H*-pyrrole-2-carbohydrazide was synthesized according to literature procedures (Wang *et al.*, 2011). Similar to the synthesis of (*E*)-1-methyl-4-nitro-*N*′-(pyridin-2-ylmethylene)-1*H*-pyrrole-2-carbohydrazide, the reaction of the precursor and benzaldehyde in a 1:1 molar ratio gave the title compound as a yellowish powder in 80% yield. Anal. Calc. (%) for $C_{13}H_{12}N_4O_3$: C 57.35, H 4.44, N 20.58; found: C 57.31, H 4.51, N 20.55. The powder of the title compound was dissolved in *N*,*N*-dimethyl formamide and the yellow crystals were collected after slow evaporation at room temperature for about two weeks.

S3. Refinement

H atoms were placed in geometrically idealized positions, with N–H=0.86 Å, $C_{aromatic}$–H=0.93, C_{methyl}–H 0.96 Å, and with U_{iso}(H) = $k \times U_{eq}$(parent C-atom), where k = 1.5 for methyl H-atoms and 1.2 for other H-atoms.

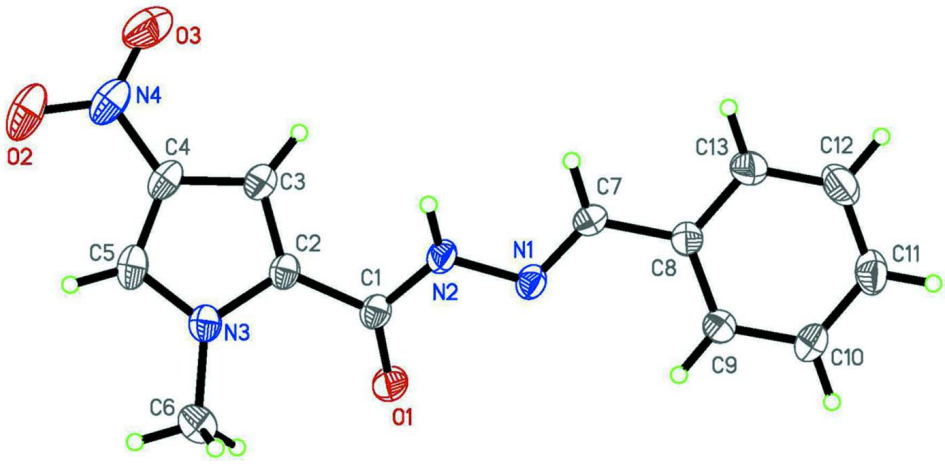

Figure 1

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

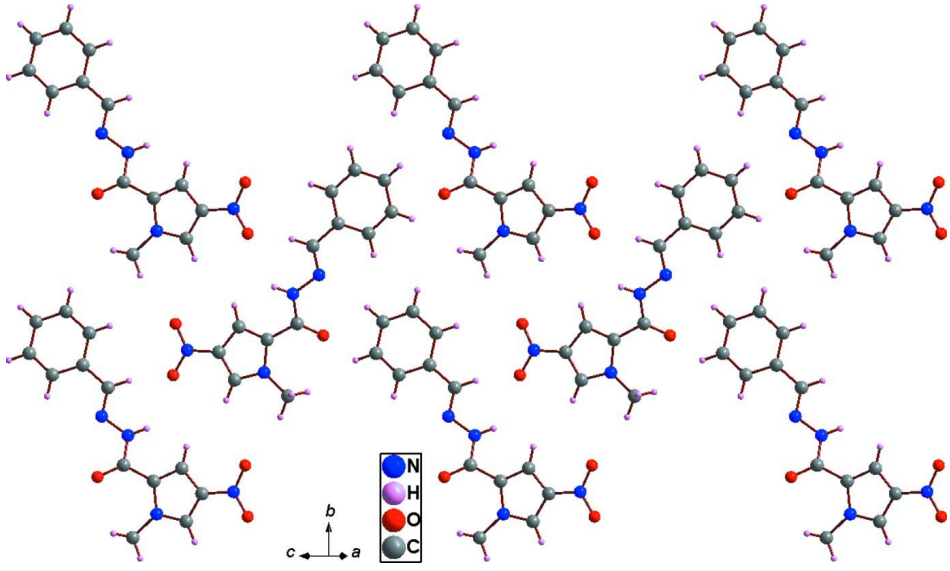

Figure 2

Molecules of the title compound forming planes parallel to the (101) plane.

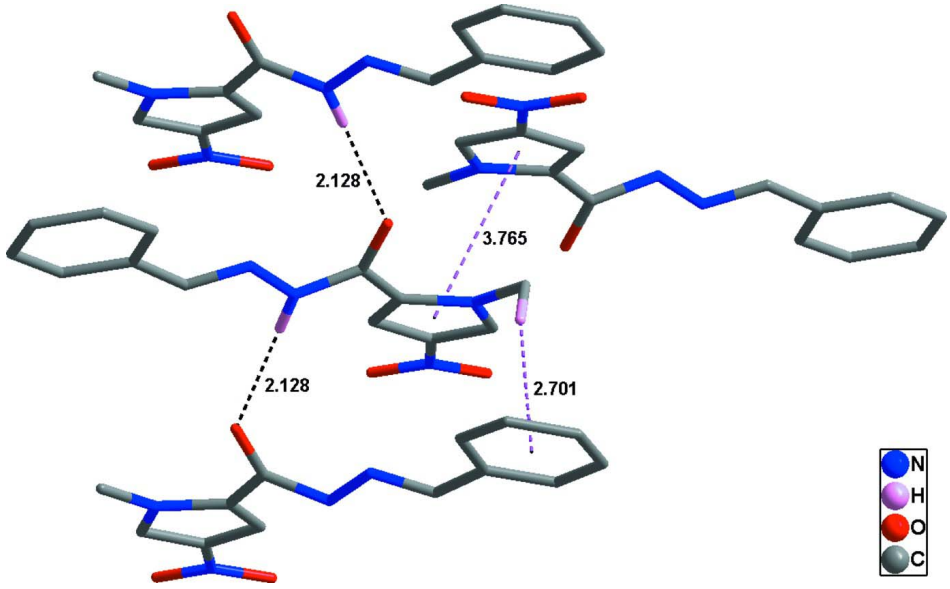

Figure 3

The intermolecular N–H···O hydrogen bonds (black dotted lines), $\pi\cdots\pi$ and C–H···π interactions (pink dotted lines) between adjacent sheets (H atoms not involved in hydrogen bonds have been omitted for clarity, all distances in Å).

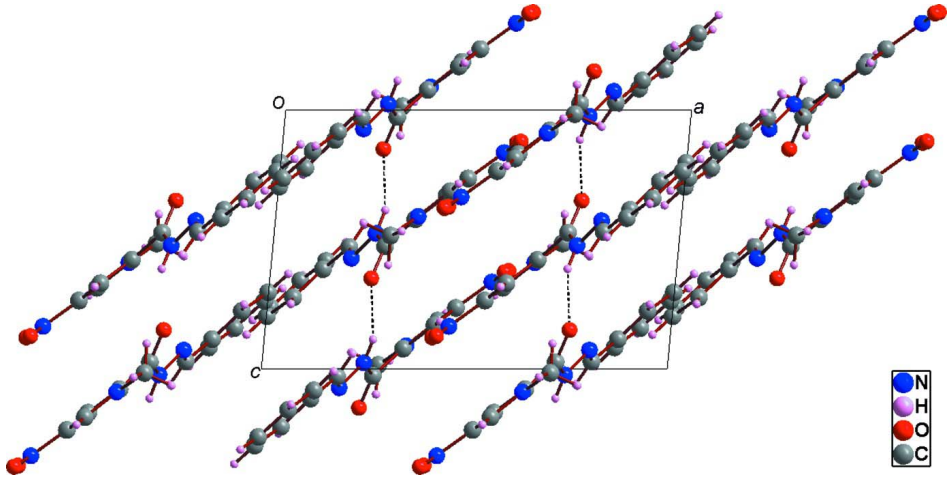

Figure 4

Packing of the title compound viewed along the *b* axis.

(*E*)-*N*′-Benzylidene-1-methyl-4-nitro-1*H*-pyrrole-2-carbohydrazide

Crystal data

$C_{13}H_{12}N_4O_3$
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β = 95.409 (3)°
V = 1285.92 (17) Å^3
Z = 4
F(000) = 568
D_x = 1.406 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1529 reflections
θ = 2.3–24.0°
μ = 0.10 mm^{-1}

T = 298 K
Block, yellow

0.32 × 0.20 × 0.17 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} = 0.968, T_{max} = 0.983

6283 measured reflections
2248 independent reflections
1382 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 25.0°, θ_{min} = 2.3°
h = −13→15
k = −14→14
l = −9→9

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.135
S = 1.03
2248 reflections
182 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
$w = 1/[\sigma^2(F_o^2) + (0.0571P)^2 + 0.2921P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
N1	0.80415 (15)	0.34342 (17)	0.4275 (2)	0.0409 (5)
N2	0.74919 (15)	0.27603 (17)	0.5233 (2)	0.0435 (6)
H2	0.7314	0.3006	0.6138	0.052*
N3	0.64881 (15)	−0.00154 (17)	0.5892 (2)	0.0436 (6)
N4	0.45223 (18)	0.0771 (3)	0.8358 (3)	0.0618 (7)
O1	0.75036 (14)	0.12934 (15)	0.3497 (2)	0.0540 (5)
O2	0.41349 (15)	−0.0109 (2)	0.8783 (2)	0.0804 (7)
O3	0.42286 (18)	0.1703 (2)	0.8735 (3)	0.0916 (8)
C1	0.72375 (18)	0.1713 (2)	0.4734 (3)	0.0397 (6)
C2	0.65549 (18)	0.1145 (2)	0.5783 (3)	0.0386 (6)
C3	0.58369 (18)	0.1601 (2)	0.6690 (3)	0.0441 (7)
H3	0.5704	0.2361	0.6829	0.053*
C4	0.53470 (19)	0.0704 (2)	0.7359 (3)	0.0469 (7)
C5	0.57607 (19)	−0.0277 (2)	0.6867 (3)	0.0502 (7)

H5	0.5572	−0.0998	0.7156	0.060*
C6	0.7129 (2)	−0.0846 (2)	0.5155 (3)	0.0560 (8)
H6A	0.6865	−0.1586	0.5319	0.084*
H6B	0.7825	−0.0796	0.5644	0.084*
H6C	0.7117	−0.0700	0.4020	0.084*
C7	0.81171 (19)	0.4454 (2)	0.4711 (3)	0.0419 (6)
H7	0.7786	0.4697	0.5589	0.050*
C8	0.87158 (18)	0.5250 (2)	0.3853 (3)	0.0388 (6)
C9	0.93840 (19)	0.4903 (2)	0.2762 (3)	0.0467 (7)
H9	0.9426	0.4143	0.2512	0.056*
C10	0.9988 (2)	0.5662 (2)	0.2040 (3)	0.0530 (8)
H10	1.0445	0.5413	0.1324	0.064*
C11	0.9919 (2)	0.6776 (3)	0.2370 (3)	0.0604 (8)
H11	1.0330	0.7290	0.1885	0.072*
C12	0.9246 (3)	0.7139 (2)	0.3416 (4)	0.0724 (10)
H12	0.9186	0.7903	0.3620	0.087*
C13	0.8655 (2)	0.6380 (2)	0.4170 (3)	0.0587 (8)
H13	0.8210	0.6635	0.4901	0.070*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0444 (12)	0.0449 (13)	0.0346 (12)	−0.0062 (10)	0.0097 (10)	0.0028 (10)
N2	0.0533 (13)	0.0436 (12)	0.0362 (13)	−0.0105 (10)	0.0172 (10)	−0.0027 (10)
N3	0.0437 (13)	0.0442 (13)	0.0428 (13)	−0.0056 (10)	0.0024 (10)	0.0019 (11)
N4	0.0421 (14)	0.096 (2)	0.0474 (15)	−0.0117 (15)	0.0069 (12)	0.0073 (16)
O1	0.0735 (13)	0.0526 (11)	0.0388 (11)	−0.0083 (10)	0.0211 (10)	−0.0081 (9)
O2	0.0547 (13)	0.1207 (19)	0.0668 (15)	−0.0377 (13)	0.0107 (11)	0.0153 (14)
O3	0.0764 (17)	0.112 (2)	0.0932 (19)	0.0082 (15)	0.0433 (14)	−0.0026 (17)
C1	0.0425 (15)	0.0449 (16)	0.0319 (15)	−0.0037 (12)	0.0039 (12)	0.0031 (13)
C2	0.0400 (14)	0.0439 (15)	0.0316 (14)	−0.0057 (12)	0.0009 (11)	0.0038 (12)
C3	0.0436 (15)	0.0507 (16)	0.0385 (16)	−0.0035 (13)	0.0065 (13)	0.0029 (13)
C4	0.0354 (14)	0.0679 (19)	0.0379 (16)	−0.0091 (14)	0.0054 (12)	0.0040 (14)
C5	0.0473 (17)	0.0566 (18)	0.0455 (17)	−0.0171 (14)	−0.0013 (14)	0.0101 (14)
C6	0.0604 (19)	0.0455 (16)	0.061 (2)	0.0004 (14)	0.0017 (15)	−0.0036 (14)
C7	0.0439 (15)	0.0466 (16)	0.0367 (15)	0.0009 (13)	0.0115 (12)	−0.0018 (13)
C8	0.0417 (14)	0.0402 (15)	0.0343 (15)	−0.0041 (11)	0.0023 (12)	0.0002 (12)
C9	0.0474 (16)	0.0388 (15)	0.0552 (17)	0.0036 (12)	0.0116 (14)	0.0038 (13)
C10	0.0493 (16)	0.0574 (19)	0.0547 (19)	−0.0070 (14)	0.0177 (14)	0.0038 (15)
C11	0.075 (2)	0.0553 (19)	0.0521 (19)	−0.0224 (16)	0.0116 (16)	0.0043 (15)
C12	0.110 (3)	0.0413 (17)	0.069 (2)	−0.0147 (18)	0.025 (2)	−0.0071 (16)
C13	0.078 (2)	0.0486 (18)	0.0523 (19)	−0.0055 (15)	0.0238 (16)	−0.0101 (15)

Geometric parameters (Å, º)

N1—C7	1.268 (3)	C6—H6A	0.9600
N1—N2	1.379 (3)	C6—H6B	0.9600
N2—C1	1.346 (3)	C6—H6C	0.9600

N2—H2	0.8600	C7—C8	1.456 (3)
N3—C5	1.342 (3)	C7—H7	0.9300
N3—C2	1.386 (3)	C8—C13	1.374 (3)
N3—C6	1.466 (3)	C8—C9	1.380 (3)
N4—O3	1.224 (3)	C9—C10	1.374 (3)
N4—O2	1.230 (3)	C9—H9	0.9300
N4—C4	1.422 (3)	C10—C11	1.359 (4)
O1—C1	1.224 (3)	C10—H10	0.9300
C1—C2	1.469 (3)	C11—C12	1.363 (4)
C2—C3	1.369 (3)	C11—H11	0.9300
C3—C4	1.387 (3)	C12—C13	1.376 (4)
C3—H3	0.9300	C12—H12	0.9300
C4—C5	1.365 (4)	C13—H13	0.9300
C5—H5	0.9300		

C7—N1—N2	114.9 (2)	N3—C6—H6B	109.5
C1—N2—N1	119.1 (2)	H6A—C6—H6B	109.5
C1—N2—H2	120.5	N3—C6—H6C	109.5
N1—N2—H2	120.5	H6A—C6—H6C	109.5
C5—N3—C2	108.8 (2)	H6B—C6—H6C	109.5
C5—N3—C6	124.1 (2)	N1—C7—C8	120.8 (2)
C2—N3—C6	127.0 (2)	N1—C7—H7	119.6
O3—N4—O2	123.5 (3)	C8—C7—H7	119.6
O3—N4—C4	118.2 (3)	C13—C8—C9	118.1 (2)
O2—N4—C4	118.3 (3)	C13—C8—C7	119.9 (2)
O1—C1—N2	123.8 (2)	C9—C8—C7	121.9 (2)
O1—C1—C2	123.3 (2)	C10—C9—C8	121.0 (2)
N2—C1—C2	112.8 (2)	C10—C9—H9	119.5
C3—C2—N3	108.0 (2)	C8—C9—H9	119.5
C3—C2—C1	129.0 (2)	C11—C10—C9	120.1 (3)
N3—C2—C1	122.8 (2)	C11—C10—H10	119.9
C2—C3—C4	106.3 (2)	C9—C10—H10	119.9
C2—C3—H3	126.8	C10—C11—C12	119.8 (3)
C4—C3—H3	126.8	C10—C11—H11	120.1
C5—C4—C3	109.1 (2)	C12—C11—H11	120.1
C5—C4—N4	124.4 (3)	C11—C12—C13	120.4 (3)
C3—C4—N4	126.4 (3)	C11—C12—H12	119.8
N3—C5—C4	107.8 (2)	C13—C12—H12	119.8
N3—C5—H5	126.1	C8—C13—C12	120.6 (3)
C4—C5—H5	126.1	C8—C13—H13	119.7
N3—C6—H6A	109.5	C12—C13—H13	119.7

C7—N1—N2—C1	170.0 (2)	O3—N4—C4—C3	−3.2 (4)
N1—N2—C1—O1	3.3 (4)	O2—N4—C4—C3	176.1 (3)
N1—N2—C1—C2	−173.4 (2)	C2—N3—C5—C4	1.1 (3)
C5—N3—C2—C3	−1.1 (3)	C6—N3—C5—C4	178.1 (2)
C6—N3—C2—C3	−178.0 (2)	C3—C4—C5—N3	−0.7 (3)
C5—N3—C2—C1	−176.4 (2)	N4—C4—C5—N3	177.4 (2)

C6—N3—C2—C1	6.7 (4)	N2—N1—C7—C8	177.2 (2)
O1—C1—C2—C3	−146.8 (3)	N1—C7—C8—C13	169.5 (3)
N2—C1—C2—C3	29.9 (4)	N1—C7—C8—C9	−13.1 (4)
O1—C1—C2—N3	27.4 (4)	C13—C8—C9—C10	1.4 (4)
N2—C1—C2—N3	−155.9 (2)	C7—C8—C9—C10	−176.0 (2)
N3—C2—C3—C4	0.7 (3)	C8—C9—C10—C11	−1.3 (4)
C1—C2—C3—C4	175.6 (2)	C9—C10—C11—C12	−0.2 (5)
C2—C3—C4—C5	0.0 (3)	C10—C11—C12—C13	1.7 (5)
C2—C3—C4—N4	−178.1 (2)	C9—C8—C13—C12	0.0 (4)
O3—N4—C4—C5	179.0 (3)	C7—C8—C13—C12	177.5 (3)
O2—N4—C4—C5	−1.7 (4)	C11—C12—C13—C8	−1.6 (5)

Hydrogen-bond geometry (Å, º)

Cg is the centroid of the C8–C13 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O1^{i}	0.86	2.13	2.942 (2)	158
C6—H6*B*···*Cg*^{i}	0.96	2.70	3.590 (3)	154

Symmetry code: (i) *x*, −*y*+1/2, *z*+1/2.