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rac-1-(Furan-2-ylmethyl)-*N*-nitro-5-(oxolan-2-ylmethyl)-1,3,5-triazinan-2-imine

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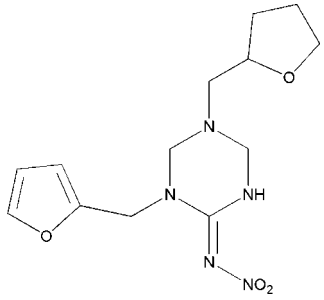
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.066; wR factor = 0.164; data-to-parameter ratio = 14.4.

In the title compound $C_{13}H_{19}N_5O_4$, which belongs to the insecticidally active neonicotinoid group of compounds, the triazane ring exhibits a half-chair conformation. The large discrepancy between the two nitro O—N—N bond angles [116.1 (2) and 123.98 (19)°] may be attributed to intramolecular N—H···O hydrogen bonding involving one of the nitro O atoms as the acceptor. The delocalization of the electrons extends as far as the nitro group, forming coplanar π-electron networks. In the crystal, inversion dimers lined by pairs of N—H···O hydrogen bonds occur.

Related literature

For general background to neonicotinoids, see: Kagabu *et al.* (2005); Peter & Ralf (2008); Riley & Merz (2007); Tian *et al.* (2007); Tomizawa *et al.* (2000). For the synthesis, see: Zhu *et al.* (2010).



Experimental

Crystal data

$C_{13}H_{19}N_5O_4$
M_r = 309.33
Monoclinic, $P2_1/n$
a = 11.1898 (12) Å
b = 9.262 (1) Å
c = 14.4863 (15) Å
β = 99.276 (2)°
V = 1481.7 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 298 K
0.16 × 0.12 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
9196 measured reflections
2902 independent reflections
2615 reflections with $I > 2\sigma(I)$
R_{int} = 0.054

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.164
S = 1.18
2902 reflections
202 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O3	0.82 (3)	1.97 (3)	2.563 (3)	128 (2)
N2—H2···O1^{i}	0.82 (3)	2.43 (3)	3.035 (3)	132 (2)

Symmetry code: (i) $-x, -y+2, -z$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); 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*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZS2064).

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supporting information

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rac-1-(Furan-2-ylmethyl)-*N*-nitro-5-(oxolan-2-ylmethyl)-1,3,5-triazinan-2-imine

Chuan-Wen Sun, Xu-Bo Ma and Hong-Fei Bu

S1. Comment

In recent years, the neonicotinoids have been the fastest-growing class of insecticides used in modern crop protection (Tomizawa *et al.*, 2000; Kagabu *et al.*, 2005; Tian *et al.*, 2007; Peter & Ralf, 2008). We report here crystal structure of one of these compounds, $C_{13}H_{19}N_5O_4$, the title compound (I). In the structure of (I) (Fig. 1), the triazine ring exhibits a half-chair conformation with a dihedral angle of 50.62° between plane A (C8, N3, C7, N2, C6) and plane B (C6, N1, C8). The bond angles C8–N1–C6, N1–C6–N2, C6–N2–C7, N2–C7–N3, C7–N3–C8 and N3–C8–N1 are 108.15 (19), 111.20 (18), 122.69 (19), 118.54 (19), 119.94 (18) and 111.98 (18)° respectively, in turn indicating asymmetry and strong tensility in the 1,3,5-hexahydrotriazine ring. The large discrepancy between the nitro O3–N5–N4 and O4–N5–N4 bond angles [116.1 (2) and 123.98 (19)° respectively] may be attributed to the intramolecular N2–H···O3 hydrogen bond (Table 1). There is also a single intermolecular N–H···O hydrogen bond associated with N2 (Fig. 2).

Interestingly, due to the transfer of the lone-pair of electrons from the hetero-N atoms to the C7═N4 double bond, the C7–N2 and C7–N3 bond lengths (1.327 (3) Å and 1.338 (3) Å), are both remarkably shorter than the pure C–N single bond (1.49 Å), but close to the C═C value (1.33 Å). The delocalization of the electrons extends as far as the electron-withdrawing nitro group, forming a coplanar π-electron network. A six-membered plane C (C7, N4, N5, O3, H2 and N2) is established by the intramolecular N2–H···O3 hydrogen bond. In addition, planes A and C form an enlarged plane D (comprising C6, C8, N3, C7, N2, H2, N4, O3 and O4).

S2. Experimental

The title compound was prepared by the literature method (Zhu *et al.*, 2010) and was recrystallized from ethanol-water (10:1), giving colorless crystals (yield 79.6%). ^{1}HNMR($CDCl_3$, 400 Hz): 9.61 (1*H*, s, NH), 7.37–7.36 (2*H*, d, *J* = 0.8 Hz, furan—H), 6.38–6.34 (3*H*,m,furan—H), 4.49–4.47(6*H*, m, CH_2—furan, triazine–H), 3.97–3.85 (2*H*, m, CH_2—tetrahydrofuran), 3.53–3.12 (3*H*, m, tetrahydrofuran—H) 1.86–1.64(4*H*, m, tetrahydrofuran—H); IR(KBr, cm^{-1}) 3278(N—H), 1588 (C═N), 1195 (C—O—C), 1060 (C—N), Anal.: calcd. for $C_{13}H_{19}N_5O_4$: C 50.48, H 6.19, N 22.64%; found, C 51.03, H 6.17, N 22.75%.

S3. Refinement

H atoms bonded to C were positioned geometrically [C—H = 0.93 Å (aromatic), 0.97 Å (methylene) and 0.98Å (methine)] and refined in riding modes [U_{iso}(H) = 1.2U_{eq}(C). H atoms bonded to N were found in Fourier difference maps and refined with the constraints of N—H = 0.82 (3)Å and U_{iso}(H) = 1.2U_{eq}(N).

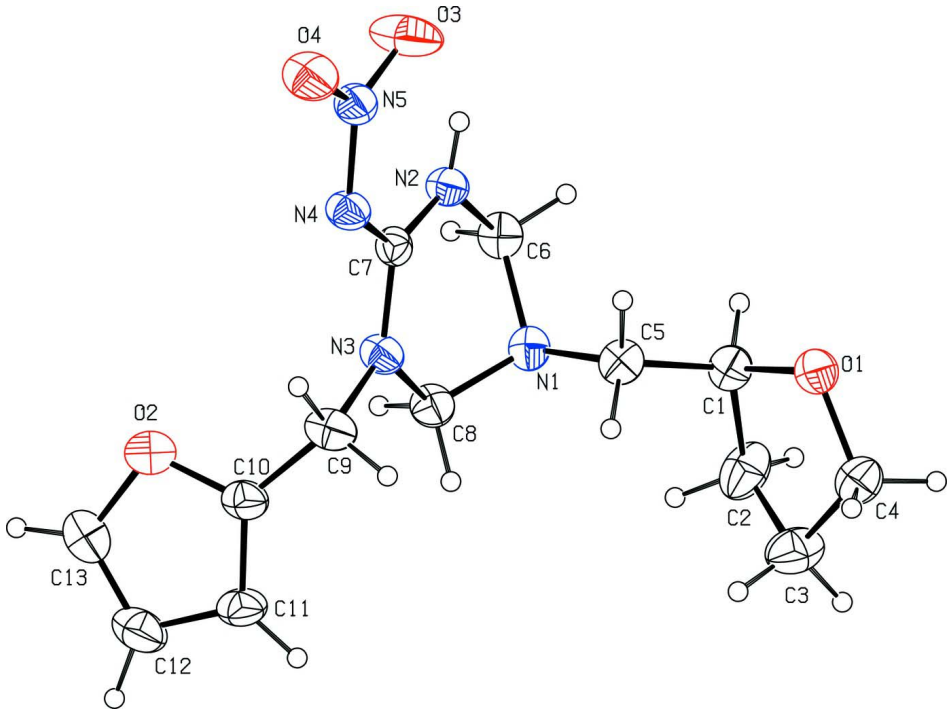

Figure 1

The molecular structure of (I), showing the atom-numbering scheme with non-H atoms shown as 50% probability displacement ellipsoids.

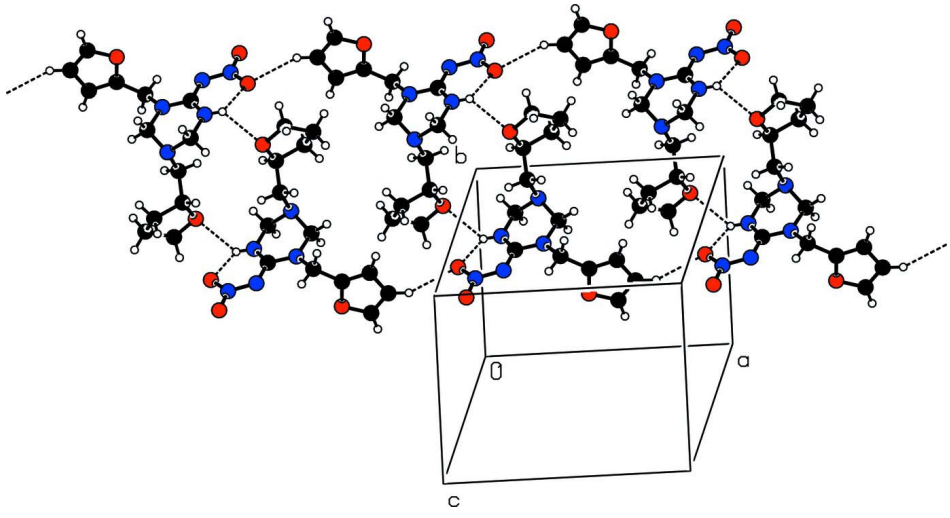

Figure 2

A perspective view of the packing of the title compound (I). Hydrogen bonds are shown as dashed lines.

rac-1-(Furan-2-ylmethyl)-*N*-nitro-5-(oxolan-2-ylmethyl)- 1,3,5-triazinan-2-imine

Crystal data

$C_{13}H_{19}N_5O_4$
M_r = 309.33
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 11.1898 (12) Å
b = 9.262 (1) Å

c = 14.4863 (15) Å
β = 99.276 (2)°
V = 1481.7 (3) Å^3
Z = 4
F(000) = 656
D_x = 1.387 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å

Cell parameters from 4051 reflections
θ = 2.5–28.3°
μ = 0.11 mm^{-1}
T = 298 K
Block, colorless
0.16 × 0.12 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
9196 measured reflections
2902 independent reflections

2615 reflections with $I > 2\sigma(I)$
R_{int} = 0.054
θ_{max} = 26.0°, θ_{min} = 2.1°
h = −12→13
k = −9→11
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.164
S = 1.18
2902 reflections
202 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 atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0599P)^2 + 0.7103P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.1890 (2)	1.0871 (3)	−0.01634 (16)	0.0487 (6)
H1	0.1262	1.0589	−0.0684	0.058*
C2	0.2996 (3)	1.1394 (3)	−0.0536 (2)	0.0696 (8)
H2A	0.3568	1.0614	−0.0561	0.084*
H2B	0.2777	1.1802	−0.1157	0.084*
C3	0.3511 (3)	1.2516 (4)	0.0146 (2)	0.0736 (9)
H3A	0.3924	1.3257	−0.0156	0.088*
H3B	0.4078	1.2094	0.0651	0.088*
C4	0.2436 (3)	1.3124 (3)	0.0502 (2)	0.0615 (7)
H4A	0.2630	1.3307	0.1169	0.074*

H4B	0.2191	1.4027	0.0188	0.074*
C5	0.2134 (2)	0.9639 (3)	0.05245 (16)	0.0473 (6)
H5A	0.2792	0.9902	0.1017	0.057*
H5B	0.1420	0.9468	0.0809	0.057*
C6	0.1429 (2)	0.7399 (3)	−0.02488 (15)	0.0482 (6)
H6A	0.1663	0.6655	−0.0656	0.058*
H6B	0.0791	0.7970	−0.0608	0.058*
C7	0.16647 (19)	0.6493 (2)	0.13610 (15)	0.0382 (5)
C8	0.3341 (2)	0.7465 (3)	0.06578 (16)	0.0476 (6)
H8A	0.4025	0.8074	0.0900	0.057*
H8B	0.3630	0.6705	0.0290	0.057*
C9	0.3679 (2)	0.6694 (3)	0.23428 (16)	0.0532 (6)
H9A	0.3267	0.6217	0.2798	0.064*
H9B	0.3899	0.7657	0.2574	0.064*
C10	0.4795 (2)	0.5882 (3)	0.22556 (16)	0.0482 (6)
C11	0.5939 (2)	0.6300 (3)	0.23025 (18)	0.0540 (6)
H11	0.6233	0.7234	0.2408	0.065*
C12	0.6623 (2)	0.5070 (4)	0.2163 (2)	0.0693 (8)
H12	0.7454	0.5036	0.2161	0.083*
C13	0.5869 (3)	0.3982 (4)	0.2035 (3)	0.0808 (10)
H13	0.6081	0.3034	0.1925	0.097*
N1	0.24528 (17)	0.8309 (2)	0.00685 (12)	0.0440 (5)
N2	0.09726 (18)	0.6721 (2)	0.05406 (13)	0.0434 (5)
H2	0.024 (2)	0.659 (3)	0.0503 (18)	0.052*
N3	0.28447 (16)	0.6810 (2)	0.14521 (12)	0.0442 (5)
N4	0.13154 (16)	0.5958 (2)	0.21520 (13)	0.0463 (5)
N5	0.01557 (17)	0.5609 (2)	0.21385 (14)	0.0486 (5)
O1	0.14841 (15)	1.20885 (19)	0.03162 (12)	0.0540 (5)
O2	0.47092 (18)	0.4451 (2)	0.20884 (18)	0.0799 (7)
O3	−0.06477 (17)	0.5800 (3)	0.14598 (15)	0.0902 (8)
O4	−0.00984 (17)	0.5099 (2)	0.28658 (14)	0.0709 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0558 (14)	0.0487 (14)	0.0407 (12)	−0.0013 (11)	0.0050 (10)	0.0002 (10)
C2	0.092 (2)	0.0565 (17)	0.0706 (18)	−0.0087 (16)	0.0424 (17)	0.0028 (14)
C3	0.0628 (17)	0.078 (2)	0.084 (2)	−0.0169 (16)	0.0242 (16)	−0.0094 (17)
C4	0.0651 (17)	0.0516 (16)	0.0669 (17)	−0.0046 (13)	0.0075 (13)	−0.0092 (13)
C5	0.0543 (14)	0.0514 (14)	0.0384 (11)	−0.0023 (11)	0.0141 (10)	0.0002 (10)
C6	0.0558 (14)	0.0530 (14)	0.0361 (11)	0.0010 (11)	0.0086 (10)	−0.0008 (10)
C7	0.0385 (11)	0.0360 (11)	0.0409 (11)	0.0031 (9)	0.0088 (9)	−0.0005 (9)
C8	0.0448 (12)	0.0543 (14)	0.0470 (12)	0.0011 (11)	0.0175 (10)	0.0064 (11)
C9	0.0432 (13)	0.0758 (18)	0.0407 (12)	−0.0032 (12)	0.0072 (10)	0.0061 (12)
C10	0.0418 (12)	0.0613 (16)	0.0393 (11)	−0.0063 (11)	0.0004 (9)	0.0113 (11)
C11	0.0406 (12)	0.0648 (16)	0.0580 (14)	−0.0129 (12)	0.0121 (11)	0.0088 (12)
C12	0.0416 (14)	0.093 (2)	0.0730 (18)	0.0042 (15)	0.0090 (13)	0.0168 (17)
C13	0.0614 (18)	0.069 (2)	0.108 (3)	0.0143 (17)	0.0027 (17)	0.0073 (19)

N1	0.0493 (11)	0.0454 (11)	0.0393 (9)	0.0019 (9)	0.0125 (8)	0.0025 (8)
N2	0.0386 (10)	0.0493 (12)	0.0416 (10)	−0.0025 (9)	0.0046 (8)	0.0033 (8)
N3	0.0370 (10)	0.0562 (12)	0.0403 (10)	0.0008 (8)	0.0091 (8)	0.0102 (8)
N4	0.0369 (10)	0.0568 (12)	0.0465 (10)	−0.0022 (9)	0.0099 (8)	0.0112 (9)
N5	0.0423 (11)	0.0519 (12)	0.0523 (12)	−0.0010 (9)	0.0101 (9)	0.0095 (9)
O1	0.0495 (10)	0.0493 (10)	0.0636 (11)	0.0033 (8)	0.0104 (8)	−0.0040 (8)
O2	0.0524 (12)	0.0665 (14)	0.1163 (19)	−0.0084 (10)	−0.0001 (11)	0.0061 (12)
O3	0.0461 (11)	0.154 (2)	0.0675 (13)	−0.0258 (13)	0.0006 (10)	0.0314 (14)
O4	0.0549 (11)	0.0947 (16)	0.0677 (12)	−0.0047 (10)	0.0235 (9)	0.0345 (11)

Geometric parameters (Å, º)

C1—O1	1.436 (3)	C7—N4	1.362 (3)
C1—C2	1.508 (4)	C8—N1	1.433 (3)
C1—C5	1.510 (3)	C8—N3	1.485 (3)
C1—H1	0.9800	C8—H8A	0.9700
C2—C3	1.485 (4)	C8—H8B	0.9700
C2—H2A	0.9700	C9—N3	1.469 (3)
C2—H2B	0.9700	C9—C10	1.481 (3)
C3—C4	1.494 (4)	C9—H9A	0.9700
C3—H3A	0.9700	C9—H9B	0.9700
C3—H3B	0.9700	C10—C11	1.329 (3)
C4—O1	1.426 (3)	C10—O2	1.348 (3)
C4—H4A	0.9700	C11—C12	1.405 (4)
C4—H4B	0.9700	C11—H11	0.9300
C5—N1	1.469 (3)	C12—C13	1.309 (4)
C5—H5A	0.9700	C12—H12	0.9300
C5—H5B	0.9700	C13—O2	1.382 (4)
C6—N1	1.436 (3)	C13—H13	0.9300
C6—N2	1.467 (3)	N2—H2	0.82 (3)
C6—H6A	0.9700	N4—N5	1.335 (3)
C6—H6B	0.9700	N5—O4	1.229 (3)
C7—N2	1.327 (3)	N5—O3	1.233 (3)
C7—N3	1.338 (3)		
O1—C1—C2	105.2 (2)	N1—C8—N3	111.98 (18)
O1—C1—C5	108.15 (18)	N1—C8—H8A	109.2
C2—C1—C5	114.1 (2)	N3—C8—H8A	109.2
O1—C1—H1	109.7	N1—C8—H8B	109.2
C2—C1—H1	109.7	N3—C8—H8B	109.2
C5—C1—H1	109.7	H8A—C8—H8B	107.9
C3—C2—C1	103.8 (2)	N3—C9—C10	112.8 (2)
C3—C2—H2A	111.0	N3—C9—H9A	109.0
C1—C2—H2A	111.0	C10—C9—H9A	109.0
C3—C2—H2B	111.0	N3—C9—H9B	109.0
C1—C2—H2B	111.0	C10—C9—H9B	109.0
H2A—C2—H2B	109.0	H9A—C9—H9B	107.8
C2—C3—C4	104.2 (2)	C11—C10—O2	109.6 (2)

C2—C3—H3A	110.9	C11—C10—C9	131.8 (3)
C4—C3—H3A	110.9	O2—C10—C9	118.6 (2)
C2—C3—H3B	110.9	C10—C11—C12	107.4 (3)
C4—C3—H3B	110.9	C10—C11—H11	126.3
H3A—C3—H3B	108.9	C12—C11—H11	126.3
O1—C4—C3	107.4 (2)	C13—C12—C11	106.9 (3)
O1—C4—H4A	110.2	C13—C12—H12	126.6
C3—C4—H4A	110.2	C11—C12—H12	126.6
O1—C4—H4B	110.2	C12—C13—O2	109.9 (3)
C3—C4—H4B	110.2	C12—C13—H13	125.1
H4A—C4—H4B	108.5	O2—C13—H13	125.1
N1—C5—C1	111.59 (18)	C8—N1—C6	108.15 (19)
N1—C5—H5A	109.3	C8—N1—C5	112.63 (19)
C1—C5—H5A	109.3	C6—N1—C5	113.40 (19)
N1—C5—H5B	109.3	C7—N2—C6	122.69 (19)
C1—C5—H5B	109.3	C7—N2—H2	117.9 (18)
H5A—C5—H5B	108.0	C6—N2—H2	118.7 (18)
N1—C6—N2	111.20 (18)	C7—N3—C9	123.22 (18)
N1—C6—H6A	109.4	C7—N3—C8	119.94 (18)
N2—C6—H6A	109.4	C9—N3—C8	116.49 (18)
N1—C6—H6B	109.4	N5—N4—C7	119.09 (19)
N2—C6—H6B	109.4	O4—N5—O3	119.9 (2)
H6A—C6—H6B	108.0	O4—N5—N4	116.1 (2)
N2—C7—N3	118.54 (19)	O3—N5—N4	123.98 (19)
N2—C7—N4	127.3 (2)	C4—O1—C1	109.54 (19)
N3—C7—N4	114.15 (19)	C10—O2—C13	106.2 (2)

O1—C1—C2—C3	29.5 (3)	N1—C6—N2—C7	−25.4 (3)
C5—C1—C2—C3	−88.8 (3)	N2—C7—N3—C9	175.7 (2)
C1—C2—C3—C4	−30.1 (3)	N4—C7—N3—C9	−4.3 (3)
C2—C3—C4—O1	20.2 (3)	N2—C7—N3—C8	2.8 (3)
O1—C1—C5—N1	175.01 (18)	N4—C7—N3—C8	−177.2 (2)
C2—C1—C5—N1	−68.3 (3)	C10—C9—N3—C7	130.5 (2)
N3—C9—C10—C11	110.1 (3)	C10—C9—N3—C8	−56.4 (3)
N3—C9—C10—O2	−69.1 (3)	N1—C8—N3—C7	28.7 (3)
O2—C10—C11—C12	−0.3 (3)	N1—C8—N3—C9	−144.7 (2)
C9—C10—C11—C12	−179.6 (2)	N2—C7—N4—N5	−0.1 (4)
C10—C11—C12—C13	0.3 (3)	N3—C7—N4—N5	179.9 (2)
C11—C12—C13—O2	−0.2 (4)	C7—N4—N5—O4	178.3 (2)
N3—C8—N1—C6	−56.5 (3)	C7—N4—N5—O3	−3.5 (4)
N3—C8—N1—C5	69.6 (2)	C3—C4—O1—C1	−1.6 (3)
N2—C6—N1—C8	54.5 (2)	C2—C1—O1—C4	−17.4 (3)
N2—C6—N1—C5	−71.2 (2)	C5—C1—O1—C4	104.8 (2)
C1—C5—N1—C8	144.4 (2)	C11—C10—O2—C13	0.2 (3)
C1—C5—N1—C6	−92.4 (2)	C9—C10—O2—C13	179.6 (2)
N3—C7—N2—C6	−4.4 (3)	C12—C13—O2—C10	0.0 (4)
N4—C7—N2—C6	175.6 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O3	0.82 (3)	1.97 (3)	2.563 (3)	128 (2)
N2—H2···O1^{i}	0.82 (3)	2.43 (3)	3.035 (3)	132 (2)

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