Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

OPEN ACCESS

ISSN 2056-9890

Crystal structure of ethyl *N*-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)carbamate

Muhammad Danish,[a] Muhammad Nawaz Tahir,[b]* Uzma Anwar[a] and Muhammad Asam Raza[a]

[a]Department of Chemistry, Institute of Natural Sciences, University of Gujrat, Gujrat 50700, Pakistan, and [b]Department of Physics, University of Sargodha, Sargodha, Punjab, Pakistan. *Correspondence e-mail: dmntahir_uos@yahoo.com

Received 23 March 2015; accepted 25 March 2015

Edited by J. Simpson, University of Otago, New Zealand

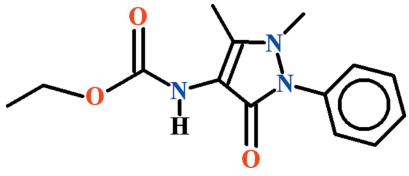
In the title compound, $C_{14}H_{17}N_3O_3$, the dihedral angle between the benzene ring and the five-membered dihydropyrazole ring is 52.26 (9)°. The ethyl ester group is approximately planar (r.m.s. deviation 0.0568 Å) and subtends an angle 67.73 (8)° to the pyrazole ring. In the crystal, molecules are linked by pairs of N—H···O hydrogen bonds, forming inversion dimers with an $R_2^2(10)$ ring motif. Weaker C—H···O contacts link these dimers into a three-dimensional network of molecules stacked along the *a*-axis direction. Offset π–π stacking interactions between the benzene rings [centroid-to-centroid distance = 3.8832 (12) Å] further stabilize the crystal packing.

Keywords: crystal structure; dihydropyrazole; ethyl ester; carbamate; hydrogen bonding; π–π stacking interactions.

CCDC reference: 1056157

1. Related literature

For related structures see: Li *et al.* (2013).



2. Experimental

2.1. Crystal data

$C_{14}H_{17}N_3O_3$ M_r = 275.30

Monoclinic, $P2_1/c$
a = 8.2100 (4) Å
b = 11.4137 (6) Å
c = 15.1594 (8) Å
β = 93.403 (3)°
V = 1418.03 (13) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 296 K
0.38 × 0.34 × 0.20 mm

2.2. Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.968, T_{max} = 0.983
11712 measured reflections
3098 independent reflections
2368 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.127
S = 1.06
3098 reflections
185 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···O1^{i}	0.86	1.99	2.8223 (17)	164
C10—H10A···O1^{ii}	0.96	2.56	3.343 (2)	139
C11—H11B···O2^{iii}	0.96	2.66	3.576 (2)	161

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014*/6 (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON*.

Acknowledgements

The authors acknowledge the provision of funds for purchase of the diffractometer and encouragement by Dr Muhammad Akram Chaudhary, Vice Chancellor, University of Sargodha, Pakistan.

Supporting information for this paper is available from the IUCr electronic archives (Reference: SJ5447).

References

Bruker (2005). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Li, Y., Liu, Y., Wang, H., Xiong, X., Wei, P. & Li, F. (2013). *Molecules*, **18**, 877–893.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supporting information

Acta Cryst. (2015). E**71**, o267 [doi:10.1107/S2056989015006106]

Crystal structure of ethyl *N*-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)carbamate

Muhammad Danish, Muhammad Nawaz Tahir, Uzma Anwar and Muhammad Asam Raza

S1. Comment

The title compound (I), (Fig. 1) has been synthesized to examine its DNA binding potential and anti-microbial activity. The crystal structures of two closely related compounds, methyl (1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)carbamate and methyl (1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)methylcarbamate monohydrate have been reported previously (Li *et al.*, 2013).

In (I), the C1—C6 benzene ring and dihydropyrazol-3-one system, O1/N1/N2/N3/C7—C9 are planar with *r.m.s.* deviations of 0.0037 and 0.0398 Å, respectively. The dihedral angle between the two systems is 53.64 (5)°. The ethyl ester group, C12/C13/C14/O2/O3, is also planar (*r.m.s.* deviation 0.0568 Å) and subtends an angle 67.73 (8)° to the pyrazole ring. In the crystal structure classical N3—H3A···O1 hydrogen bonds form inversion dimers (Table 1, Fig. 2) with $R_2^2(10)$ ring motifs. Weaker C10–H10A···O1 and C11–H11B···O2 contacts link these dimers into a three dimensional network of molecules stacked along the a axis direction. Offset $\pi\cdots\pi$ stacking interactions between the benzene rings with Cg2···Cg2^{i} = 3.8832 (12) Å further stabilise the crystal packing (Cg2 is the centroid of the C1—C6 benzene ring; i = 2 - *x*, -*y*, 1 - *z*).

S2. Experimental

4-aminoantipyrene (2 g, 9.84 mmole) was dissolved in 50 ml dimethyl formamide and anhydrous potassium carbonate (0.68 g, 4.92 mmole) was added with continuous stirring over 50 minutes. Ethyl chloroformate (1.3 ml) was added drop-wise with stirring over three minutes at 323 K. TLC monitoring showed the reaction to be complete in almost 4 h. The reaction mixture was then cooled to room temperature and transferred to crushed ice leading to the formation of a precipitate. This was separated by filtration and recrystallized from aqueous ethanol to yield (I) as light yellow plates.

Melting point: 477–479 K.

S3. Refinement

The H-atoms were positioned geometrically (N–H = 0.86, C–H = 0.93–0.97 Å) and refined as riding with U_{iso}(H) = 1.2U$_{eq}$(C, N).

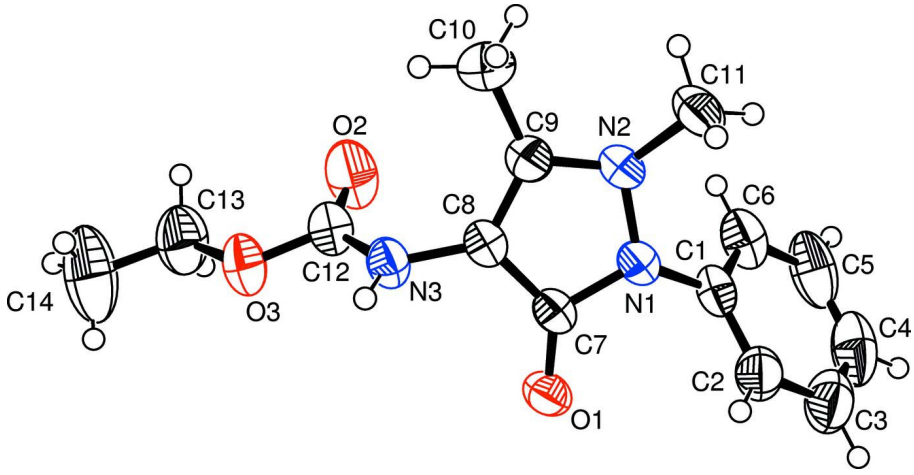


Figure 1

View of the asymmetric unit of title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small circles of arbitrary radii.

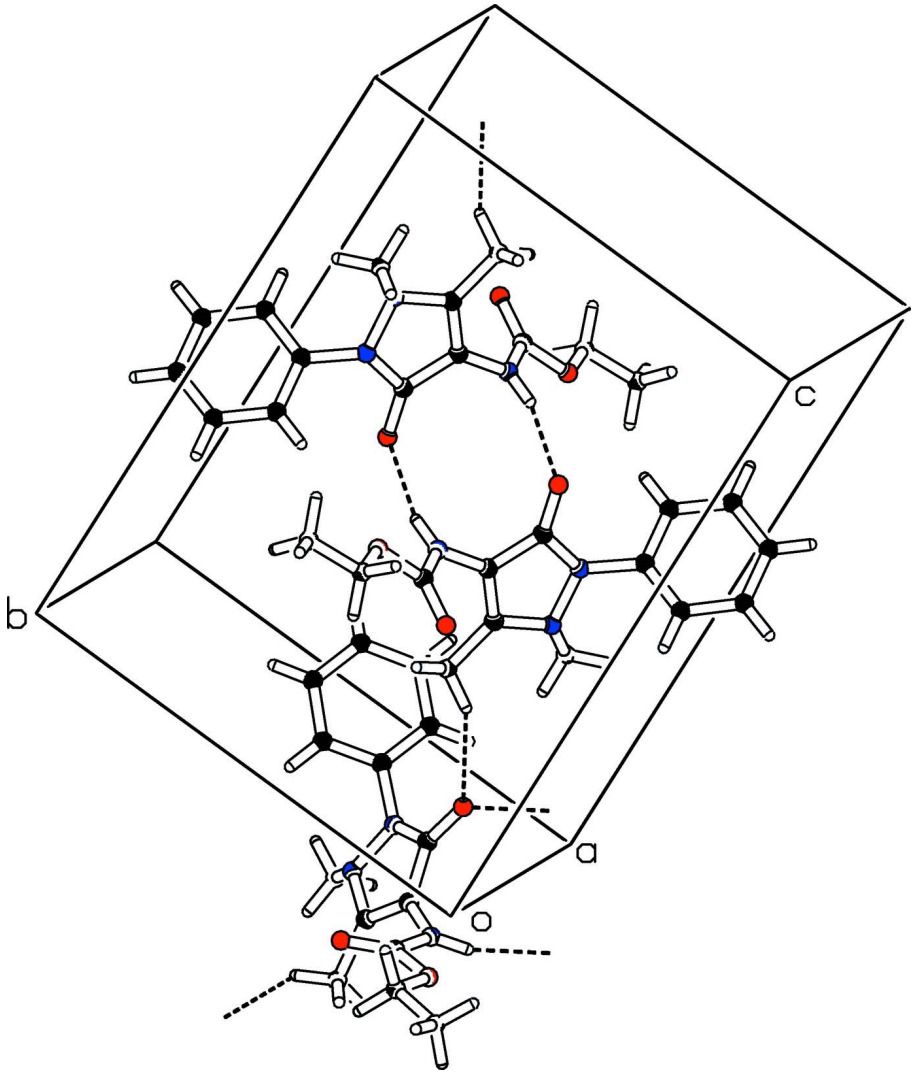


Figure 2

The crystal packing of (I), viewed along the *a* axis, with hydrogen bonds shown as dashed lines.

Ethyl *N*-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)carbamate

Crystal data

$C_{14}H_{17}N_3O_3$
$M_r = 275.30$
Monoclinic, $P2_1/c$
$a = 8.2100$ (4) Å
$b = 11.4137$ (6) Å
$c = 15.1594$ (8) Å
$\beta = 93.403$ (3)°
$V = 1418.03$ (13) Å^3
$Z = 4$
$F(000) = 584$
$D_x = 1.290$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2368 reflections
$\theta = 2.2$–27.0°
$\mu = 0.09$ mm^{-1}
$T = 296$ K
Plate, light yellow
0.38 × 0.34 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 7.80 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.968, T_{max} = 0.983
11712 measured reflections
3098 independent reflections
2368 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 27.0°, θ_{min} = 2.2°
h = −10→10
k = −14→13
l = −19→19

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.127
S = 1.06
3098 reflections
185 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
$w = 1/[\sigma^2(F_o^2) + (0.0592P)^2 + 0.2848P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Extinction correction: *SHELXL*, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.027 (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}
O1	0.54493 (13)	0.33953 (9)	0.54004 (6)	0.0503 (3)
O2	0.13321 (16)	0.32771 (12)	0.33957 (11)	0.0819 (5)
O3	0.09391 (13)	0.51504 (10)	0.38192 (8)	0.0617 (3)
N1	0.65770 (15)	0.23072 (11)	0.42996 (8)	0.0458 (3)
N2	0.62265 (16)	0.21412 (12)	0.33892 (8)	0.0510 (3)
N3	0.34531 (15)	0.44615 (11)	0.38501 (8)	0.0480 (3)
H3A	0.3728	0.5172	0.3977	0.058*
C1	0.72550 (18)	0.13738 (13)	0.48290 (10)	0.0472 (4)
C2	0.8305 (2)	0.16528 (17)	0.55395 (11)	0.0592 (4)
H2	0.8595	0.2428	0.5653	0.071*
C3	0.8922 (3)	0.0764 (2)	0.60812 (14)	0.0791 (6)
H3	0.9628	0.0945	0.6565	0.095*
C4	0.8508 (3)	−0.0376 (2)	0.59139 (18)	0.0851 (7)
H4	0.8924	−0.0967	0.6285	0.102*

C5	0.7481 (3)	−0.06516 (17)	0.52008 (19)	0.0841 (7)
H5	0.7216	−0.1431	0.5085	0.101*
C6	0.6830 (2)	0.02230 (15)	0.46480 (14)	0.0639 (5)
H6	0.6122	0.0038	0.4166	0.077*
C7	0.55368 (17)	0.31534 (12)	0.46080 (9)	0.0406 (3)
C8	0.46691 (17)	0.35940 (13)	0.38352 (9)	0.0430 (3)
C9	0.51590 (19)	0.30017 (14)	0.31216 (10)	0.0487 (4)
C10	0.4694 (3)	0.3221 (2)	0.21696 (12)	0.0755 (6)
H10A	0.4626	0.2489	0.1858	0.113*
H10B	0.5502	0.3709	0.1921	0.113*
H10C	0.3654	0.3607	0.2117	0.113*
C11	0.7583 (2)	0.17664 (16)	0.28711 (12)	0.0621 (5)
H11A	0.7971	0.1016	0.3078	0.093*
H11B	0.8452	0.2329	0.2937	0.093*
H11C	0.7217	0.1709	0.2259	0.093*
C12	0.1866 (2)	0.42031 (14)	0.36699 (11)	0.0528 (4)
C13	−0.0815 (2)	0.4956 (2)	0.37242 (17)	0.0818 (6)
H13A	−0.1108	0.4609	0.3152	0.098*
H13B	−0.1145	0.4424	0.4179	0.098*
C14	−0.1628 (3)	0.6069 (3)	0.3803 (2)	0.1237 (11)
H14A	−0.2786	0.5946	0.3798	0.186*
H14B	−0.1381	0.6563	0.3316	0.186*
H14C	−0.1259	0.6438	0.4348	0.186*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0619 (7)	0.0475 (6)	0.0425 (6)	0.0067 (5)	0.0099 (5)	−0.0044 (4)
O2	0.0552 (7)	0.0589 (9)	0.1307 (13)	−0.0026 (6)	−0.0010 (8)	−0.0187 (8)
O3	0.0453 (6)	0.0558 (7)	0.0849 (8)	0.0115 (5)	0.0113 (6)	0.0010 (6)
N1	0.0493 (7)	0.0440 (7)	0.0445 (7)	0.0090 (6)	0.0050 (5)	−0.0052 (5)
N2	0.0517 (7)	0.0558 (8)	0.0458 (7)	0.0106 (6)	0.0067 (6)	−0.0112 (6)
N3	0.0459 (7)	0.0395 (7)	0.0586 (8)	0.0054 (5)	0.0037 (6)	−0.0030 (5)
C1	0.0421 (7)	0.0439 (8)	0.0568 (9)	0.0089 (6)	0.0134 (6)	0.0019 (7)
C2	0.0558 (9)	0.0613 (11)	0.0607 (10)	0.0102 (8)	0.0043 (8)	0.0035 (8)
C3	0.0691 (12)	0.0960 (17)	0.0724 (12)	0.0247 (12)	0.0054 (10)	0.0187 (11)
C4	0.0744 (14)	0.0786 (15)	0.1049 (17)	0.0307 (12)	0.0268 (13)	0.0369 (13)
C5	0.0725 (13)	0.0453 (11)	0.138 (2)	0.0119 (10)	0.0371 (14)	0.0176 (12)
C6	0.0542 (10)	0.0488 (10)	0.0901 (13)	0.0032 (8)	0.0156 (9)	−0.0036 (9)
C7	0.0411 (7)	0.0350 (7)	0.0464 (8)	−0.0002 (6)	0.0086 (6)	−0.0038 (6)
C8	0.0423 (7)	0.0396 (8)	0.0476 (8)	0.0030 (6)	0.0067 (6)	−0.0019 (6)
C9	0.0472 (8)	0.0521 (9)	0.0470 (8)	0.0031 (7)	0.0029 (6)	−0.0056 (6)
C10	0.0805 (13)	0.0979 (16)	0.0474 (10)	0.0178 (11)	−0.0019 (9)	−0.0074 (9)
C11	0.0611 (10)	0.0664 (11)	0.0605 (10)	0.0110 (9)	0.0174 (8)	−0.0146 (8)
C12	0.0487 (8)	0.0479 (9)	0.0622 (10)	0.0056 (7)	0.0067 (7)	0.0021 (7)
C13	0.0470 (10)	0.0869 (15)	0.1121 (17)	0.0083 (10)	0.0091 (10)	0.0007 (13)
C14	0.0581 (13)	0.105 (2)	0.211 (3)	0.0252 (14)	0.0337 (17)	0.016 (2)

Geometric parameters (Å, º)

O1—C7	1.2387 (17)	C4—H4	0.9300
O2—C12	1.208 (2)	C5—C6	1.390 (3)
O3—C12	1.3489 (19)	C5—H5	0.9300
O3—C13	1.456 (2)	C6—H6	0.9300
N1—C7	1.3886 (18)	C7—C8	1.426 (2)
N1—N2	1.4057 (17)	C8—C9	1.357 (2)
N1—C1	1.4269 (19)	C9—C10	1.492 (2)
N2—C9	1.362 (2)	C10—H10A	0.9600
N2—C11	1.4645 (19)	C10—H10B	0.9600
N3—C12	1.348 (2)	C10—H10C	0.9600
N3—C8	1.4072 (18)	C11—H11A	0.9600
N3—H3A	0.8600	C11—H11B	0.9600
C1—C2	1.376 (2)	C11—H11C	0.9600
C1—C6	1.383 (2)	C13—C14	1.443 (3)
C2—C3	1.382 (3)	C13—H13A	0.9700
C2—H2	0.9300	C13—H13B	0.9700
C3—C4	1.365 (3)	C14—H14A	0.9600
C3—H3	0.9300	C14—H14B	0.9600
C4—C5	1.367 (4)	C14—H14C	0.9600
C12—O3—C13	115.20 (15)	C9—C8—C7	108.79 (13)
C7—N1—N2	109.28 (11)	N3—C8—C7	123.72 (12)
C7—N1—C1	123.86 (12)	C8—C9—N2	109.74 (13)
N2—N1—C1	120.12 (12)	C8—C9—C10	128.08 (15)
C9—N2—N1	106.61 (11)	N2—C9—C10	122.17 (14)
C9—N2—C11	123.19 (14)	C9—C10—H10A	109.5
N1—N2—C11	116.61 (13)	C9—C10—H10B	109.5
C12—N3—C8	121.39 (13)	H10A—C10—H10B	109.5
C12—N3—H3A	119.3	C9—C10—H10C	109.5
C8—N3—H3A	119.3	H10A—C10—H10C	109.5
C2—C1—C6	120.94 (16)	H10B—C10—H10C	109.5
C2—C1—N1	118.21 (15)	N2—C11—H11A	109.5
C6—C1—N1	120.81 (15)	N2—C11—H11B	109.5
C1—C2—C3	119.05 (19)	H11A—C11—H11B	109.5
C1—C2—H2	120.5	N2—C11—H11C	109.5
C3—C2—H2	120.5	H11A—C11—H11C	109.5
C4—C3—C2	120.7 (2)	H11B—C11—H11C	109.5
C4—C3—H3	119.6	O2—C12—N3	125.98 (15)
C2—C3—H3	119.6	O2—C12—O3	124.21 (15)
C3—C4—C5	120.1 (2)	N3—C12—O3	109.79 (14)
C3—C4—H4	120.0	C14—C13—O3	108.53 (19)
C5—C4—H4	120.0	C14—C13—H13A	110.0
C4—C5—C6	120.6 (2)	O3—C13—H13A	110.0
C4—C5—H5	119.7	C14—C13—H13B	110.0
C6—C5—H5	119.7	O3—C13—H13B	110.0
C1—C6—C5	118.6 (2)	H13A—C13—H13B	108.4

C1—C6—H6	120.7	C13—C14—H14A	109.5
C5—C6—H6	120.7	C13—C14—H14B	109.5
O1—C7—N1	123.62 (13)	H14A—C14—H14B	109.5
O1—C7—C8	131.54 (13)	C13—C14—H14C	109.5
N1—C7—C8	104.82 (12)	H14A—C14—H14C	109.5
C9—C8—N3	127.41 (14)	H14B—C14—H14C	109.5

C7—N1—N2—C9	9.01 (16)	C12—N3—C8—C9	67.6 (2)
C1—N1—N2—C9	161.31 (13)	C12—N3—C8—C7	−108.89 (18)
C7—N1—N2—C11	151.05 (14)	O1—C7—C8—C9	−177.01 (16)
C1—N1—N2—C11	−56.66 (19)	N1—C7—C8—C9	1.68 (16)
C7—N1—C1—C2	−64.2 (2)	O1—C7—C8—N3	0.0 (3)
N2—N1—C1—C2	147.71 (14)	N1—C7—C8—N3	178.73 (13)
C7—N1—C1—C6	113.91 (17)	N3—C8—C9—N2	−172.97 (14)
N2—N1—C1—C6	−34.2 (2)	C7—C8—C9—N2	3.95 (18)
C6—C1—C2—C3	−0.7 (2)	N3—C8—C9—C10	8.5 (3)
N1—C1—C2—C3	177.40 (15)	C7—C8—C9—C10	−174.57 (18)
C1—C2—C3—C4	0.4 (3)	N1—N2—C9—C8	−7.90 (17)
C2—C3—C4—C5	0.5 (3)	C11—N2—C9—C8	−146.82 (15)
C3—C4—C5—C6	−1.0 (3)	N1—N2—C9—C10	170.73 (16)
C2—C1—C6—C5	0.2 (2)	C11—N2—C9—C10	31.8 (3)
N1—C1—C6—C5	−177.87 (15)	C8—N3—C12—O2	−8.1 (3)
C4—C5—C6—C1	0.7 (3)	C8—N3—C12—O3	173.51 (13)
N2—N1—C7—O1	172.30 (14)	C13—O3—C12—O2	6.8 (3)
C1—N1—C7—O1	21.3 (2)	C13—O3—C12—N3	−174.78 (15)
N2—N1—C7—C8	−6.52 (16)	C12—O3—C13—C14	−173.5 (2)
C1—N1—C7—C8	−157.55 (14)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···O1^{i}	0.86	1.99	2.8223 (17)	164
C10—H10*A*···O1^{ii}	0.96	2.56	3.343 (2)	139
C11—H11*B*···O2^{iii}	0.96	2.66	3.576 (2)	161

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) *x*, −*y*+1/2, *z*−1/2; (iii) *x*+1, *y*, *z*.