Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

4-[(1*RS*,5*RS*,7*SR*)-5-Methyl-2,4-dioxo-3,6-diazabicyclo[3.2.1]octan-7-yl]benzonitrile

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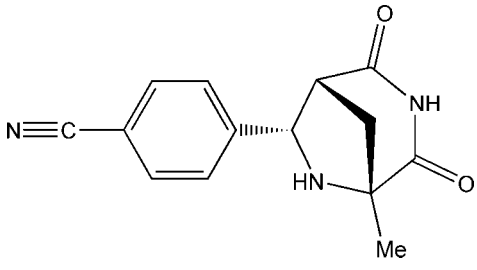
Received 28 April 2012; accepted 4 May 2012

Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.002 Å; R factor = 0.040; wR factor = 0.110; data-to-parameter ratio = 13.1.

In the title compound, $C_{14}H_{13}N_3O_2$, the relative stereochemistry of the three stereogenic C atoms has been determined. In the crystal, N—H···O hydrogen bonds link the molecules into chains of inversion dimers running along the b axis.

Related literature

For general background to chemistry affording a bridged 3,6-diazabicyclo[3.2.1]octane scaffold, substituted at the 3, 5, 6, and 7 positions, and the biological activity of this class of compounds, see: Kudryavtsev (2010).



Experimental

Crystal data

$C_{14}H_{13}N_3O_2$
M_r = 255.27
Monoclinic, $P2_1/c$
a = 14.8572 (13) Å
b = 6.2269 (6) Å
c = 13.1215 (12) Å
β = 95.568 (1)°
V = 1208.20 (19) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 150 K
0.40 × 0.15 × 0.10 mm

Data collection

Bruker SMART APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.962, T_{max} = 0.990
11909 measured reflections
2924 independent reflections
2601 reflections with $I > 2\sigma(I)$
R_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.110
S = 1.06
2924 reflections
224 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.35 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···O2^{i}	0.899 (18)	2.368 (19)	3.2377 (14)	162.8 (15)
N1—H1···O1^{ii}	0.877 (17)	2.032 (17)	2.9019 (14)	171.3 (15)

Symmetry codes: (i) $x, y+1, z$; (ii) $-x, -y+1, -z+1$.

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This study was partially supported by the Russian Foundation for Basic Research (project Nos. 11–03–00630_ a and 11–03–91375-ST_a) and State Contract No. 11.519.11.2032.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FF2066).

References

Bruker (2008). *APEX2*, *SADABS* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Kudryavtsev, K. V. (2010). *Russ. J. Org. Chem.* **46**, 372–379.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2012). E**68**, o1718 [doi:10.1107/S1600536812020156]

4-[(1*RS*,5*RS*,7*SR*)-5-Methyl-2,4-dioxo-3,6-diazabicyclo[3.2.1]octan-7-yl]benzonitrile

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Comment

In the title compound, 4-cyanophenyl substituent occupies *endo* position (Fig. 1). The –C(=O)NHC(=O)- system is planar within 0.046 (3) Å. The adjacent molecules are combined into double centrosymmetric chains along *b*-axis by N—H···O=C hydrogen bonds (Fig. 2). These chains are linked by weak van der Waals interactions.

3,6-Diazabicyclo[3.2.1]octanes are of interest as a structural motif for enzymes inhibitors. Synthesis of substituted 3,6-diazabicyclo[3.2.1]octane is based on copper(I) catalyzed intramolecular imide formation (Kudryavtsev (2010), Fig. 3).

Experimental

(2*SR*,4*SR*,5*RS*)-Methyl 4-carbamoyl-5-(4-cyanophenyl)-2-methylpyrrolidine-2-carboxylate (0.862 g, 3.0 mmol) was dissolved in 30 ml of DMF, 0.054 g (0.6 mmol) of CuCN were added, and the mixture was stirred under argon at 413 K during 6 h. The solvent was distilled off under reduced pressure, and the residue was dissolved in 20 ml of AcOEt, washed with saturated solution of $NaHCO_3$ (2 *x* 7 ml). Organic phase was dried under Na_2SO_4, concentrated and recrystallized from hexane–ethyl acetate. 4-((1*RS*,5*RS*,7*SR*- 5-methyl-2,4-dioxo-3,6-diazabicyclo[3.2.1]octan-7-yl)benzonitrile. Yield 0.490 g (64%), colourless crystals, m.p. 497–499 K. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.38 (s, 3H, CH_3), 2.00 (dd, *J* 11.8, 4.0, 1H, H-8a), 2.31 (d, *J* 11.8, 1H, H-8 b), 3.37 (br.s, 1H, H-1), 3.59 (d, *J* 7.8, 1H, N(6)H), 4.93 (dd, *J* 7.8, 5.8, 1H, H-7), 7.55 (d, *J* 8.3, 2H, Ar), 7.73 (d, *J* 8.3, 2H, Ar), 10.42(s, 1H, N(3)H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 18.73, 40.82, 52.78, 62.73, 63.09, 109.99, 119.42, 128.01 (2 C), 132.33 (2 C), 147.52, 174.04, 176.39. Anal. Calcd. for $C_{14}H_{13}N_3O_2$: C, 65.87; H, 5.13; N, 16.46. Found: C, 65.92; H, 5.17; N,16.63. The crystals were obtained by slow evaporation of saturated solution in hexane–ethyl acetate (2:3) mixture at ambient temperature.

Refinement

All hydrogen atoms were located in a difference Fourier map and refined with isotropic thermal parameters.

Computing details

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT* (Bruker, 2008); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

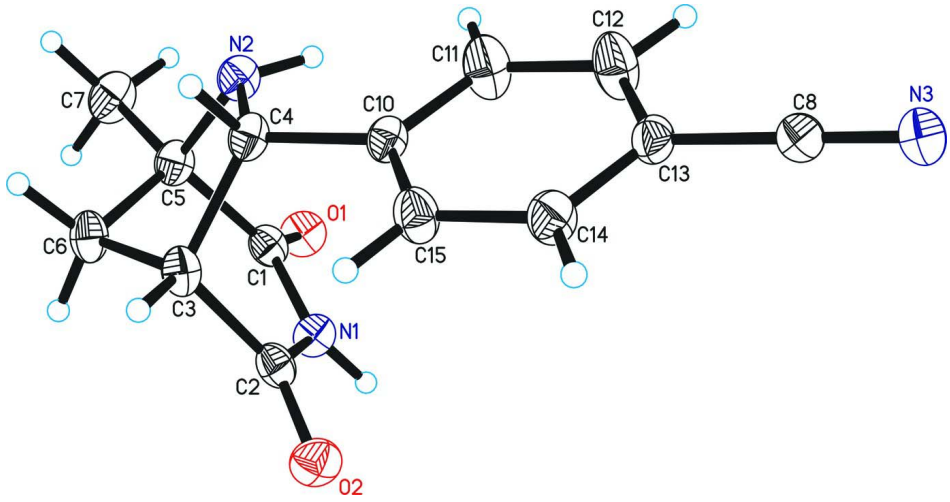

Figure 1

The molecular structure of the title compound, showing the numbering scheme adopted. Displacement ellipsoids are shown at the 50% probability level.

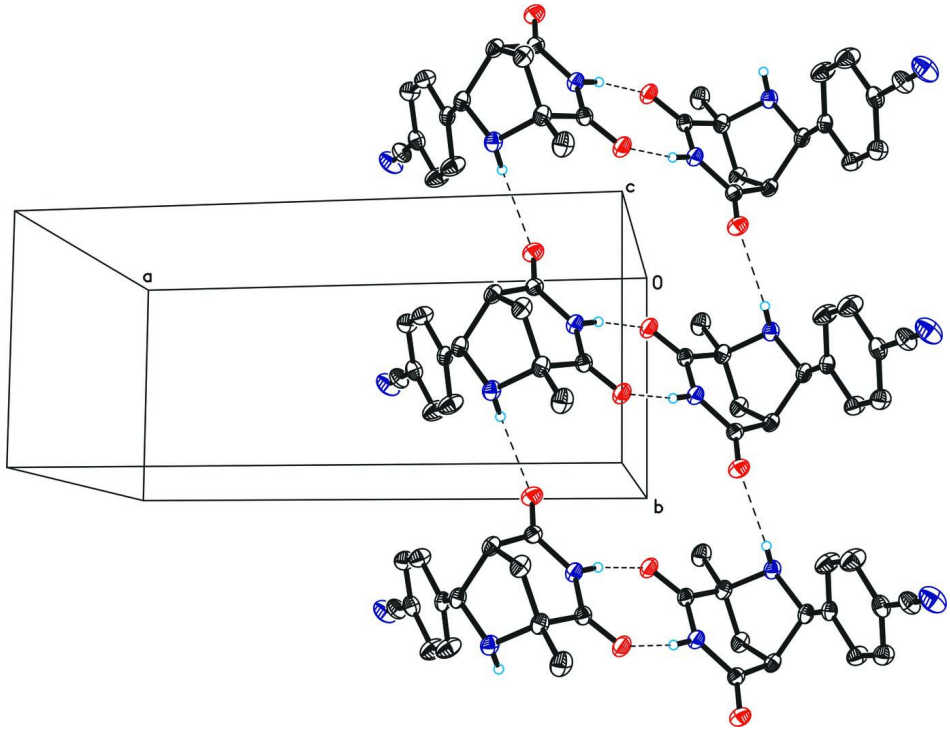

Figure 2

Hydrogen-bonded chains along *b*-axis in the structure of the title compound. H-bonds are shown as dashed lines.

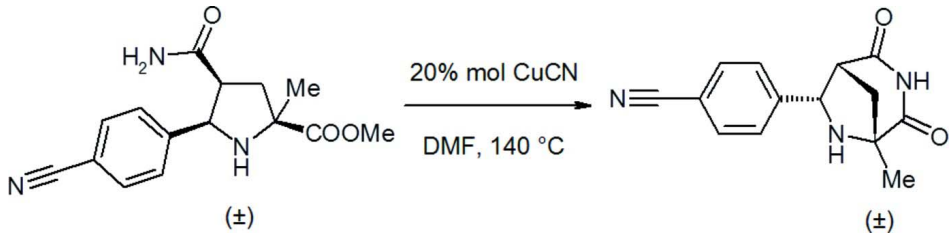

Figure 3

Synthetic scheme.

4-[(1*RS*,5*RS*,7*SR*)-5-Methyl-2,4-dioxo-3,6- diazabicyclo[3.2.1]octan-7-yl]benzonitrile

Crystal data

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Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 14.8572$ (13) Å
$b = 6.2269$ (6) Å
$c = 13.1215$ (12) Å
$\beta = 95.568$ (1)°
$V = 1208.20$ (19) Å^3
$Z = 4$
$F(000) = 536$
$D_x = 1.403$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5466 reflections
$\theta = 2.3$–$31.0°$
$\mu = 0.10$ mm^{-1}
$T = 150$ K
Block, colourless
0.40 × 0.15 × 0.10 mm

Data collection

Bruker SMART APEXII diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min} = 0.962$, $T_{max} = 0.990$
11909 measured reflections
2924 independent reflections
2601 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 28.0°$, $\theta_{min} = 2.8°$
$h = -19 \rightarrow 19$
$k = -8 \rightarrow 8$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.110$
$S = 1.06$
2924 reflections
224 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0568P)^2 + 0.4568P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.35$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.01850 (6)	0.66158 (14)	0.61099 (7)	0.0262 (2)
O2	0.17560 (6)	0.06107 (15)	0.54975 (7)	0.0271 (2)
N1	0.10075 (7)	0.36899 (17)	0.57715 (8)	0.0213 (2)
N2	0.23232 (7)	0.66162 (17)	0.70043 (8)	0.0218 (2)
N3	0.47535 (9)	0.5189 (2)	0.21483 (9)	0.0350 (3)
C1	0.08167 (7)	0.54263 (19)	0.63735 (9)	0.0205 (2)
C2	0.16886 (8)	0.22065 (19)	0.60194 (9)	0.0203 (2)
C3	0.23153 (8)	0.27578 (19)	0.69563 (9)	0.0208 (2)
C4	0.28953 (8)	0.47800 (19)	0.67574 (8)	0.0202 (2)
C5	0.14651 (8)	0.5781 (2)	0.73407 (9)	0.0218 (2)
C6	0.17531 (8)	0.3600 (2)	0.77908 (9)	0.0237 (3)
C7	0.10602 (9)	0.7300 (2)	0.80748 (11)	0.0302 (3)
C8	0.44462 (9)	0.5099 (2)	0.29149 (9)	0.0262 (3)
C10	0.32690 (7)	0.48798 (19)	0.57236 (8)	0.0193 (2)
C11	0.32273 (10)	0.6744 (2)	0.51302 (11)	0.0326 (3)
C12	0.36129 (10)	0.6806 (2)	0.42077 (11)	0.0340 (3)
C13	0.40462 (8)	0.5001 (2)	0.38726 (9)	0.0227 (3)
C14	0.41036 (9)	0.3136 (2)	0.44601 (10)	0.0257 (3)
C15	0.37150 (9)	0.3091 (2)	0.53770 (10)	0.0251 (3)
H4	0.3428 (10)	0.470 (2)	0.7280 (12)	0.023 (4)*
H62	0.2141 (10)	0.378 (3)	0.8439 (12)	0.027 (4)*
H3	0.2689 (11)	0.147 (3)	0.7158 (12)	0.029 (4)*
H1	0.0636 (11)	0.346 (3)	0.5222 (13)	0.027 (4)*
H61	0.1244 (10)	0.265 (2)	0.7877 (11)	0.021 (3)*
H14	0.4399 (11)	0.192 (3)	0.4254 (13)	0.031 (4)*
H73	0.0524 (12)	0.658 (3)	0.8305 (14)	0.039 (5)*
H15	0.3758 (12)	0.181 (3)	0.5765 (13)	0.038 (4)*
H2	0.2219 (11)	0.755 (3)	0.6484 (14)	0.035 (4)*
H72	0.0885 (11)	0.867 (3)	0.7734 (13)	0.035 (4)*
H71	0.1509 (12)	0.751 (3)	0.8687 (15)	0.042 (5)*
H12	0.3569 (14)	0.814 (3)	0.3768 (16)	0.055 (6)*
H11	0.2931 (13)	0.803 (3)	0.5349 (14)	0.043 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0212 (4)	0.0265 (5)	0.0309 (5)	0.0070 (3)	0.0025 (3)	−0.0009 (4)
O2	0.0292 (5)	0.0226 (4)	0.0297 (5)	0.0053 (4)	0.0045 (4)	−0.0035 (4)
N1	0.0191 (5)	0.0226 (5)	0.0221 (5)	0.0035 (4)	0.0016 (4)	−0.0014 (4)
N2	0.0200 (5)	0.0243 (5)	0.0219 (5)	0.0024 (4)	0.0064 (4)	−0.0021 (4)
N3	0.0419 (7)	0.0385 (7)	0.0266 (6)	−0.0124 (5)	0.0137 (5)	−0.0029 (5)
C1	0.0175 (5)	0.0220 (5)	0.0231 (5)	0.0011 (4)	0.0072 (4)	0.0012 (4)

C2	0.0198 (5)	0.0200 (5)	0.0219 (5)	0.0018 (4)	0.0070 (4)	0.0037 (4)
C3	0.0198 (5)	0.0238 (6)	0.0193 (5)	0.0054 (4)	0.0049 (4)	0.0031 (4)
C4	0.0175 (5)	0.0259 (6)	0.0174 (5)	0.0035 (4)	0.0029 (4)	−0.0009 (4)
C5	0.0200 (5)	0.0262 (6)	0.0200 (5)	0.0033 (4)	0.0062 (4)	−0.0016 (4)
C6	0.0240 (6)	0.0293 (6)	0.0189 (5)	0.0042 (5)	0.0079 (4)	0.0026 (5)
C7	0.0281 (6)	0.0365 (7)	0.0275 (6)	0.0063 (6)	0.0101 (5)	−0.0071 (6)
C8	0.0272 (6)	0.0288 (6)	0.0234 (6)	−0.0068 (5)	0.0055 (5)	−0.0021 (5)
C10	0.0160 (5)	0.0249 (6)	0.0172 (5)	0.0012 (4)	0.0027 (4)	−0.0008 (4)
C11	0.0405 (7)	0.0283 (7)	0.0311 (7)	0.0127 (6)	0.0146 (6)	0.0055 (5)
C12	0.0424 (8)	0.0315 (7)	0.0301 (7)	0.0107 (6)	0.0130 (6)	0.0108 (6)
C13	0.0204 (5)	0.0297 (6)	0.0184 (5)	−0.0040 (5)	0.0041 (4)	−0.0008 (5)
C14	0.0283 (6)	0.0246 (6)	0.0256 (6)	0.0024 (5)	0.0103 (5)	−0.0021 (5)
C15	0.0296 (6)	0.0234 (6)	0.0238 (6)	0.0053 (5)	0.0093 (5)	0.0032 (5)

Geometric parameters (Å, º)

O1—C1	1.2190 (14)	C5—C6	1.5257 (17)
O2—C2	1.2164 (15)	C6—H62	0.986 (16)
N1—C1	1.3845 (15)	C6—H61	0.976 (15)
N1—C2	1.3853 (15)	C7—H73	0.986 (19)
N1—H1	0.877 (17)	C7—H72	0.988 (18)
N2—C4	1.4793 (15)	C7—H71	1.002 (19)
N2—C5	1.4831 (15)	C8—C13	1.4426 (16)
N2—H2	0.899 (18)	C10—C15	1.3944 (16)
N3—C8	1.1457 (17)	C10—C11	1.3960 (17)
C1—C5	1.5331 (16)	C11—C12	1.3890 (18)
C2—C3	1.5080 (16)	C11—H11	0.971 (19)
C3—C6	1.5327 (15)	C12—C13	1.3879 (19)
C3—C4	1.5620 (17)	C12—H12	1.01 (2)
C3—H3	0.998 (16)	C13—C14	1.3919 (18)
C4—C10	1.5161 (15)	C14—C15	1.3843 (17)
C4—H4	0.997 (15)	C14—H14	0.931 (17)
C5—C7	1.5155 (16)	C15—H15	0.944 (18)
C1—N1—C2	124.90 (10)	C5—C6—H62	110.7 (9)
C1—N1—H1	116.8 (11)	C3—C6—H62	109.9 (9)
C2—N1—H1	118.0 (11)	C5—C6—H61	113.2 (9)
C4—N2—C5	108.84 (9)	C3—C6—H61	110.9 (9)
C4—N2—H2	113.2 (11)	H62—C6—H61	111.2 (12)
C5—N2—H2	111.3 (11)	C5—C7—H73	107.1 (11)
O1—C1—N1	120.48 (11)	C5—C7—H72	110.8 (10)
O1—C1—C5	123.50 (11)	H73—C7—H72	110.3 (14)
N1—C1—C5	115.97 (10)	C5—C7—H71	108.5 (11)
O2—C2—N1	120.71 (11)	H73—C7—H71	107.9 (15)
O2—C2—C3	124.53 (11)	H72—C7—H71	112.1 (15)
N1—C2—C3	114.76 (10)	N3—C8—C13	179.09 (15)
C2—C3—C6	108.91 (9)	C15—C10—C11	118.62 (11)
C2—C3—C4	110.75 (9)	C15—C10—C4	119.08 (10)
C6—C3—C4	101.02 (9)	C11—C10—C4	122.20 (11)
C2—C3—H3	108.4 (9)	C12—C11—C10	120.64 (12)

C6—C3—H3	114.4 (9)	C12—C11—H11	118.1 (11)
C4—C3—H3	113.1 (9)	C10—C11—H11	121.3 (11)
N2—C4—C10	115.62 (10)	C13—C12—C11	119.78 (12)
N2—C4—C3	104.39 (9)	C13—C12—H12	119.5 (12)
C10—C4—C3	116.00 (9)	C11—C12—H12	120.7 (12)
N2—C4—H4	108.7 (9)	C12—C13—C14	120.37 (11)
C10—C4—H4	106.4 (9)	C12—C13—C8	119.00 (12)
C3—C4—H4	105.1 (9)	C14—C13—C8	120.62 (11)
N2—C5—C7	112.09 (11)	C15—C14—C13	119.33 (11)
N2—C5—C6	102.15 (9)	C15—C14—H14	119.0 (10)
C7—C5—C6	115.05 (10)	C13—C14—H14	121.7 (10)
N2—C5—C1	107.06 (9)	C14—C15—C10	121.25 (12)
C7—C5—C1	111.09 (10)	C14—C15—H15	118.2 (11)
C6—C5—C1	108.79 (10)	C10—C15—H15	120.5 (11)
C5—C6—C3	100.36 (9)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O2^{i}	0.899 (18)	2.368 (19)	3.2377 (14)	162.8 (15)
N1—H1···O1^{ii}	0.877 (17)	2.032 (17)	2.9019 (14)	171.3 (15)

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