

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

Konstantin V. Kudryavtsev<sup>a,b\*</sup> and Andrei V. Churakov<sup>c</sup>

<sup>a</sup>Department of Chemistry, M.V. Lomonosov Moscow State University, Leninskie Gory 1/3, Moscow 119991, Russian Federation, <sup>b</sup>Institute of Physiologically Active Compounds, Russian Academy of Sciences, Chernogolovka 142432, Moscow region, Russian Federation, and <sup>c</sup>Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii prosp. 31, Moscow 119991, Russian Federation

Correspondence e-mail: kudr@org.chem.msu.ru

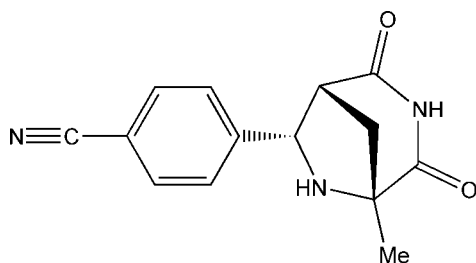
Received 28 April 2012; accepted 4 May 2012

Key indicators: single-crystal X-ray study;  $T = 150$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.040;  $wR$  factor = 0.110; data-to-parameter ratio = 13.1.

In the title compound,  $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2$ , the relative stereochemistry of the three stereogenic C atoms has been determined. In the crystal,  $\text{N}-\text{H}\cdots\text{O}$  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

$\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2$   
 $M_r = 255.27$   
 Monoclinic,  $P2_1/c$   
 $a = 14.8572$  (13) Å  
 $b = 6.2269$  (6) Å  
 $c = 13.1215$  (12) Å  
 $\beta = 95.568$  (1)°  
 $V = 1208.20$  (19) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.10$  mm<sup>-1</sup>  
 $T = 150$  K  
 $0.40 \times 0.15 \times 0.10$  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  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.019$

### 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<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.21$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N2}-\text{H2}\cdots\text{O2}^{\text{i}}$	0.899 (18)	2.368 (19)	3.2377 (14)	162.8 (15)
$\text{N1}-\text{H1}\cdots\text{O1}^{\text{ii}}$	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.* **A64**, 112–122.

## supporting information

*Acta Cryst.* (2012). E68, 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]benzotrile

Konstantin V. Kudryavtsev and Andrei V. Churakov

### S1. Comment

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

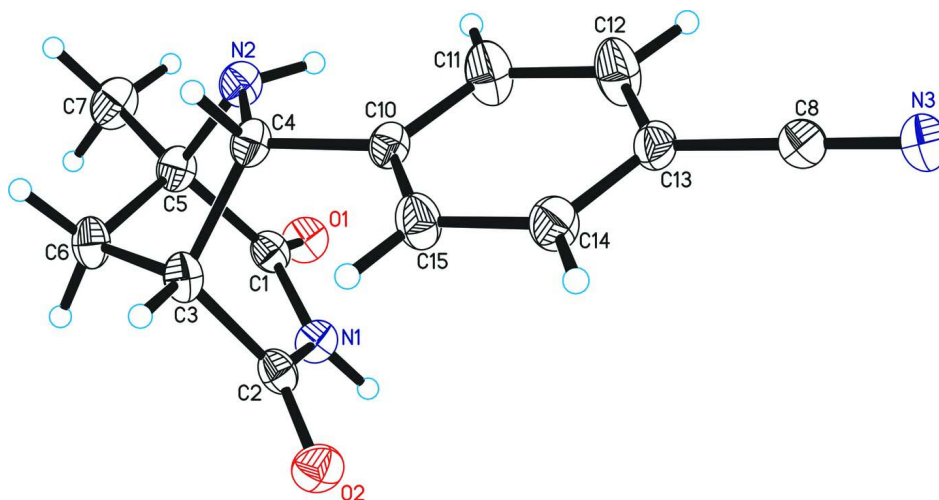
3,6-Diazabicyclo[3.2.1]octanes are of interest as a structural motif for enzymes inhibitors. Synthesis of substituted 3,6-diazabicyclo[3.2.1]octane is based on copper(I) catalyzed intramolecular imide formation (Kudryavtsev (2010), Fig. 3).

### S2. Experimental

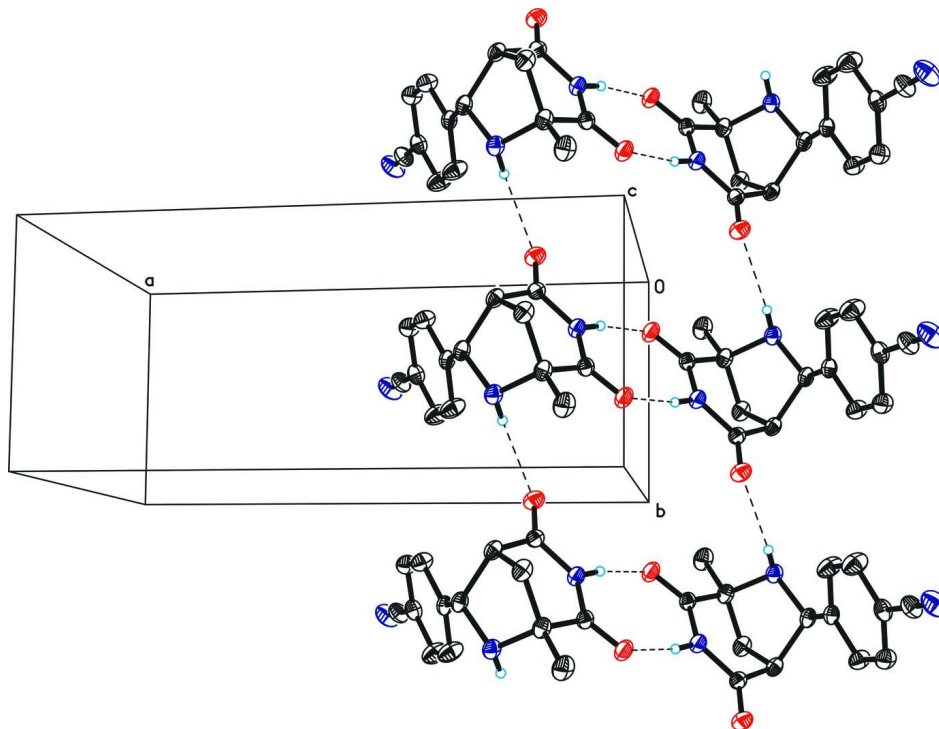
(2*SR*,4*SR*,5*RS*)-Methyl 4-carbamoyl-5-(4-cyanophenyl)-2-methylpyrrolidine-2-carboxylate (0.862 g, 3.0 mmol) was dissolved in 30 ml of DMF, 0.054 g (0.6 mmol) of CuCN were added, and the mixture was stirred under argon at 413 K during 6 h. The solvent was distilled off under reduced pressure, and the residue was dissolved in 20 ml of AcOEt, washed with saturated solution of NaHCO<sub>3</sub> (2 x 7 ml). Organic phase was dried under Na<sub>2</sub>SO<sub>4</sub>, 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)benzotrile. Yield 0.490 g (64%), colourless crystals, m.p. 497–499 K. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 1.38 (s, 3H, CH<sub>3</sub>), 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). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): 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<sub>14</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>: 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.

### S3. Refinement

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

**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.

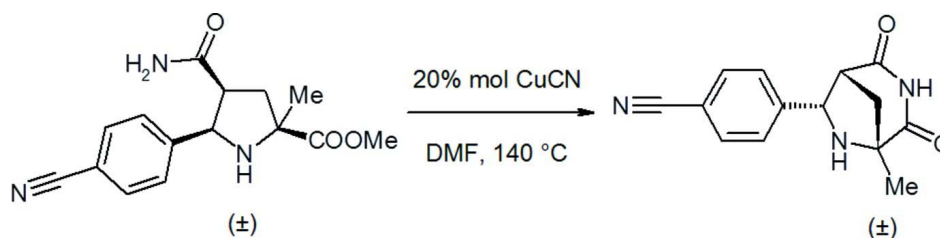


Figure 3

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*C<sub>14</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub> $M_r = 255.27$ Monoclinic, *P*2<sub>1</sub>/*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<sup>3</sup> $Z = 4$  $F(000) = 536$  $D_x = 1.403$  Mg m<sup>-3</sup>Mo *K*α radiation,  $\lambda = 0.71073$  Å

Cell parameters from 5466 reflections

 $\theta = 2.3$ – $31.0$ ° $\mu = 0.10$  mm<sup>-1</sup> $T = 150$  K

Block, colourless

 $0.40 \times 0.15 \times 0.10$  mm*Data collection*Bruker SMART APEXII  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 $\omega$  scansAbsorption correction: multi-scan  
(*SADABS*; Bruker, 2008) $T_{\min} = 0.962$ ,  $T_{\max} = 0.990$ 

11909 measured reflections

2924 independent reflections

2601 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.019$  $\theta_{\max} = 28.0$ °,  $\theta_{\min} = 2.8$ ° $h = -19 \rightarrow 19$  $k = -8 \rightarrow 8$  $l = -17 \rightarrow 17$ *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 methodsSecondary 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<sup>-3</sup> $\Delta\rho_{\min} = -0.21$  e Å<sup>-3</sup>*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 ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
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 ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
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, °)*

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, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2...O2 <sup>i</sup>	0.899 (18)	2.368 (19)	3.2377 (14)	162.8 (15)
N1—H1...O1 <sup>ii</sup>	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.