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## Structure Reports

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1-[1-(2,1,3-Benzoxadiazol-5-ylmethyl)-1*H*-1,2,3-triazol-4-yl]hexan-1-oneJessie A. Key,<sup>a</sup> Christopher W. Cairo<sup>a</sup> and Robert McDonald<sup>b\*</sup>

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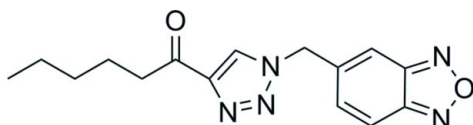
Received 21 August 2012; accepted 5 October 2012

Key indicators: single-crystal X-ray study;  $T = 173$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.040;  $wR$  factor = 0.091; data-to-parameter ratio = 15.3.

The title compound,  $\text{C}_{15}\text{H}_{17}\text{N}_5\text{O}_2$ , was synthesized as part of a series of benzoxadiazole analogs which were examined for fluorescent properties by Cu-catalysed azide-alkyne cycloaddition (CuAAC) of a 4-azidomethyl-benzoxadiazole substrate. The structure shows a nearly coplanar orientation of the hexanone keto group and the 1,2,3-triazole ring [dihedral angle =  $4.3(3)^\circ$ ], while the benzoxadiazole and triazole groups are much more severely inclined [dihedral angle =  $70.87(4)^\circ$ ]. In the crystal, weak  $\text{C}-\text{H}\cdots\text{N}$  interactions connect translationally-related triazole rings, while another set of  $\text{C}-\text{H}\cdots\text{N}$  interactions is formed between inversion-related benzoxadiazole units, forming a three-dimensional network. The crystal studied was a non-merohedral twin with refined value of the twin fraction of 0.2289 (16).

## Related literature

For the synthesis of similar benzoxadiazole compounds, see: Key & Cairo (2011); Li *et al.* (2010). For two related benzoxadiazole-triazole structures, see: Key, Cairo & Ferguson (2012); Key, Cairo & McDonald (2012). For structures of 1-(aryl)methyl-1,2,3-triazole compounds with 4-carbonyl substituents [RC(O) or ROC(O)], see: Harju *et al.* (2003); Huang *et al.* (2010); Dong & Cheng (2011); Jia & Lu (2011); Menendez *et al.* (2012).



## Experimental

## Crystal data

 $\text{C}_{15}\text{H}_{17}\text{N}_5\text{O}_2$  $M_r = 299.34$ 

Monoclinic,  $P2_1/c$   
 $a = 16.5752(16)$  Å  
 $b = 5.5429(5)$  Å  
 $c = 16.2452(16)$  Å  
 $\beta = 91.3612(13)^\circ$   
 $V = 1492.1(2)$  Å<sup>3</sup>

$Z = 4$   
Mo  $K\alpha$  radiation  
 $\mu = 0.09$  mm<sup>-1</sup>  
 $T = 173$  K  
 $0.74 \times 0.14 \times 0.06$  mm

## Data collection

Bruker APEXII CCD diffractometer  
Absorption correction: multi-scan (TWINABS; Bruker, 2008)  
 $T_{\min} = 0.935$ ,  $T_{\max} = 0.995$

45733 measured reflections  
3079 independent reflections  
2413 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.051$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$   
 $wR(F^2) = 0.091$   
 $S = 1.03$   
3079 reflections

201 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.19$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.17$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$                      | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|---|--------------|--------------------|-------------|----------------------|
| $\text{C3}-\text{H3}\cdots\text{N2}^i$    | 0.95         | 2.58               | 3.475 (2)   | 158                  |
| $\text{C8}-\text{H8}\cdots\text{N5}^{ii}$ | 0.95         | 2.41               | 3.350 (2)   | 171                  |

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

Data collection: APEX2 (Bruker, 2008); cell refinement: SAINT (Bruker, 2008); data reduction: SAINT; program(s) used to solve structure: SHELXD (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: publCIF (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: MW2084).

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## supporting information

*Acta Cryst.* (2012). E68, o3132 [doi:10.1107/S1600536812041839]

**1-[1-(2,1,3-Benzoxadiazol-5-ylmethyl)-1H-1,2,3-triazol-4-yl]hexan-1-one**

Jessie A. Key, Christopher W. Cairo and Robert McDonald

**S1. Comment**

In an effort to explore benzoxadiazole derivatives with interesting spectroscopic properties, we generated the title compound, I, for comparison to its parent 4-azidomethyl-benzoxadiazole (II). Although we observed large changes in the spectra of substrates with an azido group conjugated to the chromophore, derivatives with an intervening methylene group tended to have only small changes upon triazole formation (Key & Cairo, 2011). Compound I was synthesized unintentionally through the use of an oxidized sample of *n*-octyne which also contained oct-1-yn-3-one as an impurity. The hexanone product was isolated by column chromatography and used for structural studies. ( $\lambda_{\max,ABS}$  EtOH: 278, 289 nm, Absorption coefficient: 12,300  $M^{-1}cm^{-1}$ )

In the crystal the 1,2,3-triazole ring and hexan-1-on-1-yl groups are nearly coplanar; the angle between the ketonic fragment (O2-C10-C11) and the 1,2,3-triazole ring is 4.3 (3)°. The rings of the benzoxadiazole and triazole groups are much more severely inclined (70.87 (4)°). Weak C-H $\cdots$ N interactions are observed between triazole moieties related via translation parallel to the *b* axis (2.41 Å for H8 $\cdots$ N5[x, -1+y, z]). A further set of weak C-H $\cdots$ N interactions is seen between benzoxadiazole groups related by the inversion center (0, 1/2, 0) (2.58 Å for H3 $\cdots$ N2[-x, 1-y, -z]). A parallel-stacking interaction is observed between benzoxadiazole rings related by inversion through the origin (interplanar spacing = 3.328 Å).

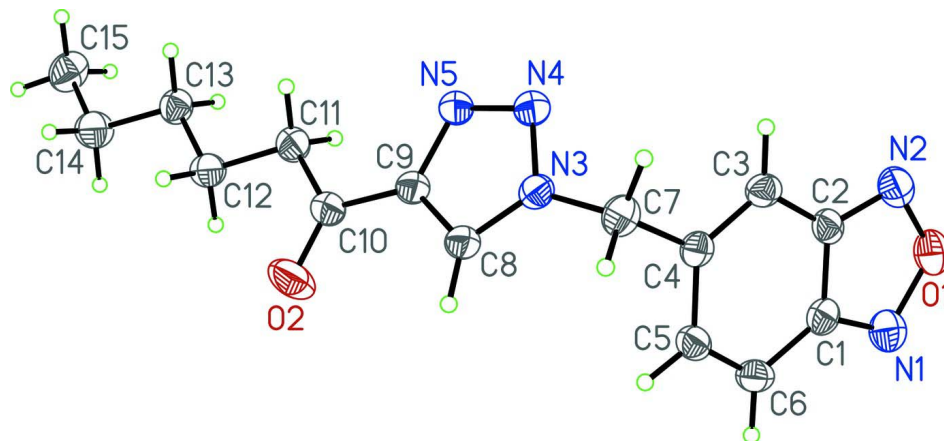
**S2. Experimental**

4-(Azidomethyl)benz-[2,1,3-*d*]-oxadiazole (II) (40 mg, 0.23 mmol, 1 equiv) was dissolved in 1:1 water/methanol (5 mL). To this solution was added *n*-octyne (0.17 mL, 1.14 mmol, 5 equiv), which also contained oct-1-yn-3-one as an impurity. Copper sulfate (7 mg, 0.046 mmol, 0.2 equiv) and ascorbic acid (12 mg, 0.068 mmol, 0.3 equiv) were then added to the solution. The reaction mixture was allowed to stir at room temperature for approximately 1 h, forming a red precipitate. The precipitate was filtered off and the product was obtained after purification by column chromatography (EtOAc/hexanes) (35 mg, 51% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.16 (s, 1H), 7.89 (d, 1H, <sup>3</sup>*J* = 9.2 Hz), 7.51 (s, 1H), 7.32 (dd, 1H, <sup>4</sup>*J* = 1.2 Hz, <sup>3</sup>*J* = 9.2 Hz), 5.70 (s, 2H), 3.11 (t, 2H, <sup>3</sup>*J* = 7.2 Hz), 1.74 (m, 2H), 1.36 (m, 4H), 0.89 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  195.5, 149.1, 148.9, 148.8, 138.1, 131.1, 126.0, 118.5, 116.0, 54.1, 39.8, 31.6, 23.8, 22.7, 14.2; IR (microscope):  $\nu$  = 3098, 2954, 2930, 1691, 1531  $cm^{-1}$ ; ES-HRMS calculated for C<sub>15</sub>H<sub>17</sub>N<sub>5</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup>: 322.1279; observed: 322.1279. *R*<sub>f</sub> = 0.45 (1:1 EtOAc/hexanes).

**S3. Refinement**

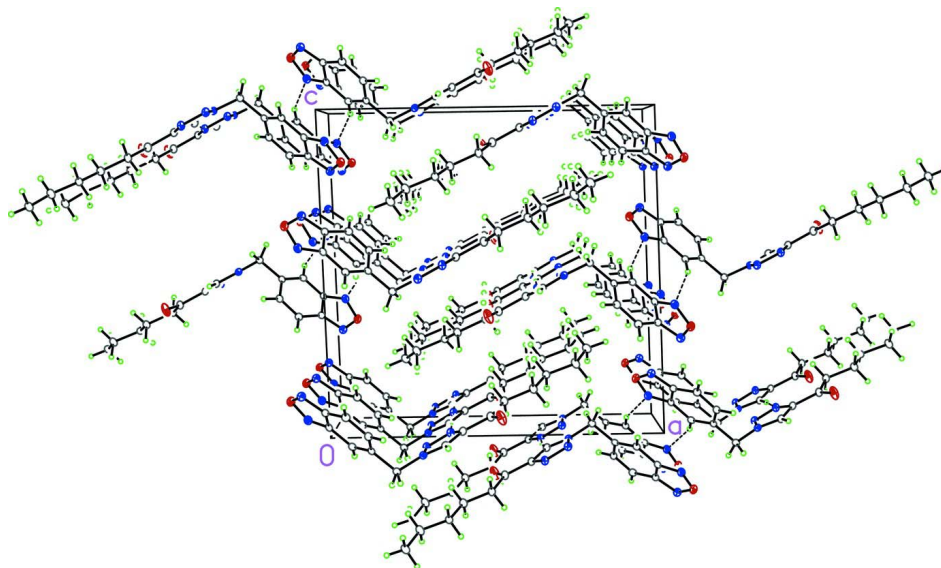
The crystal used for data collection was found to display non-merohedral twinning. Both components of the twin were indexed with the program *CELL\_NOW* (Bruker, 2008). The second twin component can be related to the first component by 180° rotation about the [-1 0 2] axis in both real and reciprocal space. A raw data file was produced by the data integration program *SAINTE* (Bruker, 2008), using the two-component orientation matrix file that had been produced by

*CELL\_NOW*. Integrated intensities for the reflections from the two components were written into a *SHELXL-97* HKL5 reflection file with the program *TWINABS* (Bruker, 2008), using all reflection data (exactly overlapped, partially overlapped and non-overlapped). The reflection (1 0 0) was found to have an excessively high disagreement between  $F_o$  and  $F_c$ , and was omitted from the refinement. The refined value of the twin fraction (*SHELXL-97* BASF parameter) was 0.2289 (16). All H atoms were generated in idealized positions and refined using a riding model with fixed C-H distances ( $C-H_{\text{aromatic}} = 0.95 \text{ \AA}$ ,  $C-H_{\text{methylene}} = 0.99 \text{ \AA}$ ,  $C-H_{\text{methyl}} = 0.98 \text{ \AA}$ ) and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .



**Figure 1**

View of I. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 50% probability level. Hydrogen atoms are represented with artificially small thermal parameters.



**Figure 2**

Illustration of crystal packing as viewed parallel to the crystal *b* axis. Nonbonded C-H...N interactions are shown with dashed lines (see Table 1).

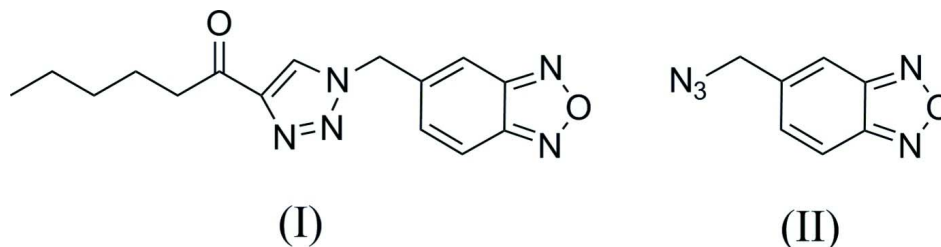


Figure 3

Compounds used in this study.

**1-[1-(2,1,3-Benzoxadiazol-5-ylmethyl)-1H-1,2,3-triazol-4-yl]hexan-1-one***Crystal data* $C_{15}H_{17}N_5O_2$  $M_r = 299.34$ Monoclinic,  $P2_1/c$ 

Hall symbol: -P 2ybc

 $a = 16.5752$  (16) Å $b = 5.5429$  (5) Å $c = 16.2452$  (16) Å $\beta = 91.3612$  (13)° $V = 1492.1$  (2) Å<sup>3</sup> $Z = 4$  $F(000) = 632$  $D_x = 1.333$  Mg m<sup>-3</sup>Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 5974 reflections

 $\theta = 2.5$ – $24.3$ ° $\mu = 0.09$  mm<sup>-1</sup> $T = 173$  K

Rod, colourless

 $0.74 \times 0.14 \times 0.06$  mm*Data collection*Bruker APEXII CCD  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.26 pixels mm<sup>-1</sup> $\omega$  scansAbsorption correction: multi-scan  
(TWINABS; Bruker, 2008) $T_{\min} = 0.935$ ,  $T_{\max} = 0.995$ 

45733 measured reflections

3079 independent reflections

2413 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.051$  $\theta_{\max} = 26.5$ °,  $\theta_{\min} = 1.2$ ° $h = -20 \rightarrow 20$  $k = -6 \rightarrow 6$  $l = -20 \rightarrow 20$ *Refinement*Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.040$  $wR(F^2) = 0.091$  $S = 1.03$ 

3079 reflections

201 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methodsSecondary atom site location: difference Fourier  
mapHydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0331P)^2 + 0.4646P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} < 0.001$  $\Delta\rho_{\max} = 0.19$  e Å<sup>-3</sup> $\Delta\rho_{\min} = -0.17$  e Å<sup>-3</sup>Extinction correction: *SHELXL*, $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$ 

Extinction coefficient: 0.0114 (15)

*Special details*

**Geometry.** All standard uncertainties (s.u.'s) (except the s.u. in the dihedral angle between two least-squares planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving least-squares 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   | -0.07380 (7) | 0.1919 (2)  | 0.16041 (7)   | 0.0409 (3)                       |
| O2   | 0.51268 (8)  | 0.0088 (2)  | 0.11538 (10)  | 0.0593 (4)                       |
| N1   | -0.03444 (8) | -0.0165 (3) | 0.18558 (9)   | 0.0382 (4)                       |
| N2   | -0.03404 (8) | 0.3110 (3)  | 0.09850 (9)   | 0.0363 (3)                       |
| N3   | 0.29027 (7)  | 0.1559 (2)  | 0.00229 (8)   | 0.0272 (3)                       |
| N4   | 0.29675 (8)  | 0.3994 (2)  | 0.00904 (9)   | 0.0317 (3)                       |
| N5   | 0.36597 (7)  | 0.4428 (2)  | 0.04758 (9)   | 0.0309 (3)                       |
| C1   | 0.02958 (9)  | -0.0270 (3) | 0.13892 (9)   | 0.0287 (4)                       |
| C2   | 0.02964 (8)  | 0.1752 (3)  | 0.08476 (9)   | 0.0272 (3)                       |
| C3   | 0.09143 (9)  | 0.2061 (3)  | 0.02610 (9)   | 0.0278 (3)                       |
| H3   | 0.0918       | 0.3406      | -0.0101       | 0.033*                           |
| C4   | 0.14968 (9)  | 0.0339 (3)  | 0.02451 (9)   | 0.0256 (3)                       |
| C5   | 0.14964 (9)  | -0.1700 (3) | 0.07982 (10)  | 0.0289 (3)                       |
| H5   | 0.1919       | -0.2850     | 0.0766        | 0.035*                           |
| C6   | 0.09180 (9)  | -0.2039 (3) | 0.13617 (10)  | 0.0311 (4)                       |
| H6   | 0.0927       | -0.3392     | 0.1721        | 0.037*                           |
| C7   | 0.21712 (9)  | 0.0526 (3)  | -0.03636 (10) | 0.0314 (4)                       |
| H7A  | 0.2294       | -0.1098     | -0.0580       | 0.038*                           |
| H7B  | 0.1994       | 0.1553      | -0.0833       | 0.038*                           |
| C8   | 0.35461 (9)  | 0.0453 (3)  | 0.03618 (10)  | 0.0293 (4)                       |
| H8   | 0.3646       | -0.1233     | 0.0395        | 0.035*                           |
| C9   | 0.40295 (9)  | 0.2287 (3)  | 0.06506 (10)  | 0.0288 (4)                       |
| C10  | 0.48268 (9)  | 0.2074 (3)  | 0.10742 (10)  | 0.0330 (4)                       |
| C11  | 0.52284 (9)  | 0.4320 (3)  | 0.13876 (11)  | 0.0331 (4)                       |
| H11A | 0.4886       | 0.5057      | 0.1811        | 0.040*                           |
| H11B | 0.5268       | 0.5484      | 0.0928        | 0.040*                           |
| C12  | 0.60693 (9)  | 0.3892 (3)  | 0.17585 (11)  | 0.0349 (4)                       |
| H12A | 0.6029       | 0.2767      | 0.2229        | 0.042*                           |
| H12B | 0.6409       | 0.3117      | 0.1341        | 0.042*                           |
| C13  | 0.64772 (9)  | 0.6203 (3)  | 0.20530 (10)  | 0.0320 (4)                       |
| H13A | 0.6496       | 0.7355      | 0.1588        | 0.038*                           |
| H13B | 0.6149       | 0.6941      | 0.2488        | 0.038*                           |
| C14  | 0.73289 (10) | 0.5801 (3)  | 0.23904 (12)  | 0.0422 (4)                       |
| H14A | 0.7665       | 0.5154      | 0.1946        | 0.051*                           |

|      |              |            |              |            |
|------|--------------|------------|--------------|------------|
| H14B | 0.7315       | 0.4576     | 0.2833       | 0.051*     |
| C15  | 0.77195 (11) | 0.8090 (4) | 0.27312 (11) | 0.0450 (5) |
| H15A | 0.8265       | 0.7723     | 0.2939       | 0.054*     |
| H15B | 0.7397       | 0.8722     | 0.3180       | 0.054*     |
| H15C | 0.7748       | 0.9300     | 0.2293       | 0.054*     |

*Atomic displacement parameters (Å<sup>2</sup>)*

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$    | $U^{13}$    | $U^{23}$    |
|-----|-------------|-------------|-------------|-------------|-------------|-------------|
| O1  | 0.0309 (6)  | 0.0481 (8)  | 0.0440 (7)  | 0.0059 (6)  | 0.0048 (5)  | -0.0042 (6) |
| O2  | 0.0466 (8)  | 0.0264 (7)  | 0.1034 (13) | 0.0055 (6)  | -0.0278 (8) | -0.0033 (7) |
| N1  | 0.0341 (7)  | 0.0428 (9)  | 0.0379 (8)  | 0.0016 (7)  | 0.0028 (6)  | -0.0012 (7) |
| N2  | 0.0316 (7)  | 0.0373 (8)  | 0.0400 (8)  | 0.0036 (6)  | -0.0019 (6) | -0.0019 (7) |
| N3  | 0.0270 (6)  | 0.0249 (7)  | 0.0297 (7)  | -0.0020 (5) | 0.0035 (5)  | -0.0010 (6) |
| N4  | 0.0301 (7)  | 0.0256 (7)  | 0.0395 (8)  | -0.0010 (6) | 0.0011 (6)  | 0.0004 (6)  |
| N5  | 0.0277 (7)  | 0.0242 (7)  | 0.0409 (8)  | -0.0001 (5) | 0.0004 (6)  | 0.0006 (6)  |
| C1  | 0.0264 (8)  | 0.0317 (9)  | 0.0279 (8)  | -0.0042 (7) | -0.0016 (6) | -0.0018 (7) |
| C2  | 0.0244 (7)  | 0.0258 (8)  | 0.0310 (8)  | -0.0003 (6) | -0.0061 (6) | -0.0037 (7) |
| C3  | 0.0304 (8)  | 0.0248 (8)  | 0.0281 (8)  | -0.0035 (7) | -0.0041 (6) | 0.0008 (7)  |
| C4  | 0.0254 (7)  | 0.0259 (8)  | 0.0254 (8)  | -0.0039 (6) | -0.0045 (6) | -0.0033 (6) |
| C5  | 0.0281 (8)  | 0.0250 (8)  | 0.0334 (8)  | 0.0024 (6)  | -0.0024 (6) | -0.0016 (7) |
| C6  | 0.0354 (8)  | 0.0256 (8)  | 0.0323 (9)  | -0.0004 (7) | -0.0019 (7) | 0.0037 (7)  |
| C7  | 0.0311 (8)  | 0.0339 (9)  | 0.0292 (9)  | -0.0043 (7) | -0.0012 (6) | -0.0042 (7) |
| C8  | 0.0288 (8)  | 0.0235 (8)  | 0.0359 (9)  | 0.0006 (6)  | 0.0040 (6)  | 0.0007 (7)  |
| C9  | 0.0277 (8)  | 0.0228 (8)  | 0.0359 (9)  | 0.0004 (6)  | 0.0036 (6)  | -0.0001 (7) |
| C10 | 0.0290 (8)  | 0.0258 (9)  | 0.0442 (10) | 0.0011 (7)  | -0.0009 (7) | 0.0014 (8)  |
| C11 | 0.0287 (8)  | 0.0285 (9)  | 0.0422 (10) | -0.0003 (7) | -0.0007 (7) | -0.0011 (7) |
| C12 | 0.0323 (8)  | 0.0312 (9)  | 0.0410 (10) | -0.0020 (7) | -0.0037 (7) | 0.0050 (8)  |
| C13 | 0.0295 (8)  | 0.0344 (9)  | 0.0321 (9)  | -0.0017 (7) | -0.0005 (7) | 0.0001 (7)  |
| C14 | 0.0370 (9)  | 0.0402 (11) | 0.0488 (11) | -0.0043 (8) | -0.0115 (8) | 0.0055 (9)  |
| C15 | 0.0410 (10) | 0.0518 (12) | 0.0418 (11) | -0.0113 (9) | -0.0077 (8) | 0.0025 (9)  |

*Geometric parameters (Å, °)*

|        |             |          |           |
|--------|-------------|----------|-----------|
| O1—N2  | 1.3831 (18) | C7—H7B   | 0.9900    |
| O1—N1  | 1.3835 (18) | C8—C9    | 1.370 (2) |
| O2—C10 | 1.214 (2)   | C8—H8    | 0.9500    |
| N1—C1  | 1.320 (2)   | C9—C10   | 1.480 (2) |
| N2—C2  | 1.320 (2)   | C10—C11  | 1.495 (2) |
| N3—C8  | 1.3376 (19) | C11—C12  | 1.524 (2) |
| N3—N4  | 1.3581 (18) | C11—H11A | 0.9900    |
| N3—C7  | 1.4682 (19) | C11—H11B | 0.9900    |
| N4—N5  | 1.3160 (17) | C12—C13  | 1.520 (2) |
| N5—C9  | 1.3627 (19) | C12—H12A | 0.9900    |
| C1—C2  | 1.425 (2)   | C12—H12B | 0.9900    |
| C1—C6  | 1.425 (2)   | C13—C14  | 1.519 (2) |
| C2—C3  | 1.426 (2)   | C13—H13A | 0.9900    |
| C3—C4  | 1.358 (2)   | C13—H13B | 0.9900    |

|             |             |               |             |
|-------------|-------------|---------------|-------------|
| C3—H3       | 0.9500      | C14—C15       | 1.523 (2)   |
| C4—C5       | 1.444 (2)   | C14—H14A      | 0.9900      |
| C4—C7       | 1.513 (2)   | C14—H14B      | 0.9900      |
| C5—C6       | 1.354 (2)   | C15—H15A      | 0.9800      |
| C5—H5       | 0.9500      | C15—H15B      | 0.9800      |
| C6—H6       | 0.9500      | C15—H15C      | 0.9800      |
| C7—H7A      | 0.9900      |               |             |
|             |             |               |             |
| N2—O1—N1    | 112.57 (11) | N5—C9—C10     | 123.94 (14) |
| C1—N1—O1    | 104.30 (13) | C8—C9—C10     | 127.49 (14) |
| C2—N2—O1    | 104.33 (13) | O2—C10—C9     | 118.73 (15) |
| C8—N3—N4    | 111.20 (12) | O2—C10—C11    | 122.74 (14) |
| C8—N3—C7    | 129.75 (13) | C9—C10—C11    | 118.53 (14) |
| N4—N3—C7    | 119.02 (13) | C10—C11—C12   | 113.64 (14) |
| N5—N4—N3    | 106.65 (12) | C10—C11—H11A  | 108.8       |
| N4—N5—C9    | 108.83 (12) | C12—C11—H11A  | 108.8       |
| N1—C1—C2    | 109.40 (14) | C10—C11—H11B  | 108.8       |
| N1—C1—C6    | 129.85 (15) | C12—C11—H11B  | 108.8       |
| C2—C1—C6    | 120.73 (14) | H11A—C11—H11B | 107.7       |
| N2—C2—C1    | 109.39 (14) | C13—C12—C11   | 112.92 (14) |
| N2—C2—C3    | 129.38 (15) | C13—C12—H12A  | 109.0       |
| C1—C2—C3    | 121.22 (14) | C11—C12—H12A  | 109.0       |
| C4—C3—C2    | 116.78 (14) | C13—C12—H12B  | 109.0       |
| C4—C3—H3    | 121.6       | C11—C12—H12B  | 109.0       |
| C2—C3—H3    | 121.6       | H12A—C12—H12B | 107.8       |
| C3—C4—C5    | 121.82 (14) | C14—C13—C12   | 113.13 (14) |
| C3—C4—C7    | 120.05 (14) | C14—C13—H13A  | 109.0       |
| C5—C4—C7    | 118.13 (14) | C12—C13—H13A  | 109.0       |
| C6—C5—C4    | 122.70 (15) | C14—C13—H13B  | 109.0       |
| C6—C5—H5    | 118.6       | C12—C13—H13B  | 109.0       |
| C4—C5—H5    | 118.6       | H13A—C13—H13B | 107.8       |
| C5—C6—C1    | 116.74 (15) | C13—C14—C15   | 113.11 (15) |
| C5—C6—H6    | 121.6       | C13—C14—H14A  | 109.0       |
| C1—C6—H6    | 121.6       | C15—C14—H14A  | 109.0       |
| N3—C7—C4    | 111.25 (12) | C13—C14—H14B  | 109.0       |
| N3—C7—H7A   | 109.4       | C15—C14—H14B  | 109.0       |
| C4—C7—H7A   | 109.4       | H14A—C14—H14B | 107.8       |
| N3—C7—H7B   | 109.4       | C14—C15—H15A  | 109.5       |
| C4—C7—H7B   | 109.4       | C14—C15—H15B  | 109.5       |
| H7A—C7—H7B  | 108.0       | H15A—C15—H15B | 109.5       |
| N3—C8—C9    | 104.76 (14) | C14—C15—H15C  | 109.5       |
| N3—C8—H8    | 127.6       | H15A—C15—H15C | 109.5       |
| C9—C8—H8    | 127.6       | H15B—C15—H15C | 109.5       |
| N5—C9—C8    | 108.57 (13) |               |             |
|             |             |               |             |
| N2—O1—N1—C1 | -0.28 (17)  | C2—C1—C6—C5   | -0.3 (2)    |
| N1—O1—N2—C2 | 0.55 (16)   | C8—N3—C7—C4   | 94.95 (19)  |
| C8—N3—N4—N5 | 0.04 (18)   | N4—N3—C7—C4   | -82.78 (18) |

|             |              |                 |              |
|-------------|--------------|-----------------|--------------|
| C7—N3—N4—N5 | 178.17 (12)  | C3—C4—C7—N3     | 98.31 (16)   |
| N3—N4—N5—C9 | 0.00 (17)    | C5—C4—C7—N3     | -81.66 (17)  |
| O1—N1—C1—C2 | -0.09 (16)   | N4—N3—C8—C9     | -0.05 (17)   |
| O1—N1—C1—C6 | -178.92 (15) | C7—N3—C8—C9     | -177.93 (14) |
| O1—N2—C2—C1 | -0.58 (16)   | N4—N5—C9—C8     | -0.03 (18)   |
| O1—N2—C2—C3 | 178.43 (14)  | N4—N5—C9—C10    | 179.26 (15)  |
| N1—C1—C2—N2 | 0.45 (18)    | N3—C8—C9—N5     | 0.05 (17)    |
| C6—C1—C2—N2 | 179.40 (14)  | N3—C8—C9—C10    | -179.21 (15) |
| N1—C1—C2—C3 | -178.66 (14) | N5—C9—C10—O2    | -175.34 (17) |
| C6—C1—C2—C3 | 0.3 (2)      | C8—C9—C10—O2    | 3.8 (3)      |
| N2—C2—C3—C4 | -178.81 (15) | N5—C9—C10—C11   | 4.8 (2)      |
| C1—C2—C3—C4 | 0.1 (2)      | C8—C9—C10—C11   | -176.09 (16) |
| C2—C3—C4—C5 | -0.4 (2)     | O2—C10—C11—C12  | 4.1 (3)      |
| C2—C3—C4—C7 | 179.59 (13)  | C9—C10—C11—C12  | -176.03 (15) |
| C3—C4—C5—C6 | 0.4 (2)      | C10—C11—C12—C13 | 178.46 (14)  |
| C7—C4—C5—C6 | -179.61 (14) | C11—C12—C13—C14 | -177.59 (15) |
| C4—C5—C6—C1 | 0.0 (2)      | C12—C13—C14—C15 | -176.65 (15) |
| N1—C1—C6—C5 | 178.39 (16)  |                 |              |

*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> |
|--------------------------|-------------|---------------|-----------------------|-------------------------|
| C3—H3...N2 <sup>i</sup>  | 0.95        | 2.58          | 3.475 (2)             | 158                     |
| C8—H8...N5 <sup>ii</sup> | 0.95        | 2.41          | 3.350 (2)             | 171                     |

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