



# Crystal structure and Hirshfeld surface analysis of two 5,11-methanobenzo[g][1,2,4]triazolo[1,5-c]-[1,3,5]oxadiazocine derivatives

Mustafa Kemal Gumus,<sup>a</sup> Sevgi Kansiz,<sup>b\*</sup> Cigdem Yuksektepe Ataol,<sup>c</sup> Necmi Dege<sup>b</sup> and Igor O. Fritsky<sup>d\*</sup>

Received 11 March 2019

Accepted 16 March 2019

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

**Keywords:** crystal structure; Biginelli condensation; benzoxadiazocine; hydrogen bonding; C—H··· $\pi$  interactions; C—Br··· $\pi$  interactions; Hirshfeld surface analysis.

**CCDC references:** 1903781; 1882558

**Supporting information:** this article has supporting information at journals.iucr.org/e

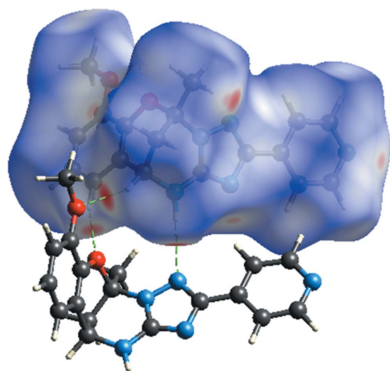
<sup>a</sup>Artvin Coruh University, Science-Technology Research and Application Center, Artvin 08000, Turkey, <sup>b</sup>Ondokuz Mayıs University, Faculty of Arts and Sciences, Department of Physics, 55139 Kurupelit, Samsun, Turkey, <sup>c</sup>Cankiri Karatekin University, Faculty of Science, Department of Physics, 18100 Cankiri, Turkey, and <sup>d</sup>Taras Shevchenko National University of Kyiv, Department of Chemistry, 64 Vladimirska Str., Kiev 01601, Ukraine. \*Correspondence e-mail: sevgi.kansiz85@gmail.com, ifritsky@univ.kiev.ua

In the title compounds, 9-bromo-2,5-dimethyl-11,12-dihydro-5*H*-5,11-methanobenzo[g][1,2,4]triazolo[1,5-*c*][1,3,5]oxadiazocine, C<sub>13</sub>H<sub>13</sub>BrN<sub>4</sub>O (**I**), and 7-methoxy-5-methyl-2-(pyridin-4-yl)-11,12-dihydro-5*H*-5,11-methanobenzo[g][1,2,4]triazolo[1,5-*c*][1,3,5]oxadiazocine, C<sub>18</sub>H<sub>17</sub>N<sub>5</sub>O<sub>2</sub> (**II**), the triazole ring is inclined to the benzene ring by 85.15 (9) and 76.98 (5)° in compounds **I** and **II**, respectively. In **II**, the pyridine ring is almost coplanar with the triazole ring, having a dihedral angle of 4.19 (8)°. In the crystal of **I**, pairs of N—H···N hydrogen bonds link the molecules to form inversion dimers with an *R*<sub>2</sub><sup>2</sup>(8) ring motif. The dimers are linked by C—H··· $\pi$  and C—Br··· $\pi$  interactions forming layers parallel to the *bc* plane. In the crystal of **II**, molecules are linked by N—H···N and C—H···O hydrogen bonds forming chains propagating along the *b*-axis direction. The intermolecular interactions were investigated using Hirshfeld surface analysis and two-dimensional fingerprint plots, and the molecular electrostatic potential surface was also analysed. The Hirshfeld surface analysis of **I** suggests that the most significant contributions to the crystal packing are H···H (42.4%) and O···H/H···O (17.9%) contacts. For compound **II**, the H···H (48.5%), C···H/H···C (19.6%) and N···H/H···N (16.9%) interactions are the most important contributions.

## 1. Chemical context

In organic synthesis, a useful method to develop a chemical complexity from simple starting building blocks is the application of multicomponent reactions (MCRs) (Dömling *et al.*, 2012; Van der Heijden *et al.*, 2013). When aminoazoles having at least two non-equivalent reaction centres are used as building blocks, the method is generally characterized by ambiguous selectivity and different reaction outcomes (Murlykina *et al.*, 2018). According to Sedash *et al.*, Biginelli-like MCRs of 3-amino-1,2,4-triazole with aldehydes and  $\alpha$ -carbonyl CH-acids may generate several types of heterocyclic products (Sedash *et al.*, 2012). The same starting compound with acetone and a 2-hydroxybenzaldehyde derivative under acidic conditions leads to the formation of different products (Gorobets *et al.*, 2010; Kondratiuk *et al.*, 2016; Gümüş *et al.*, 2017; Komykhov *et al.*, 2017).

Continuing our studies on the synthesis and crystal structure analyses of derivatives of a new type of oxygen-bridged Biginelli compound (Aydemir *et al.*, 2018; Gümüş *et al.*, 2017, 2018*a,b*), two new novel Biginelli-like assemblies of 3-amino-5-methyl-1,2,4-triazole/5-amino-3-(pyridin-4-yl)-1,2,4-triazole



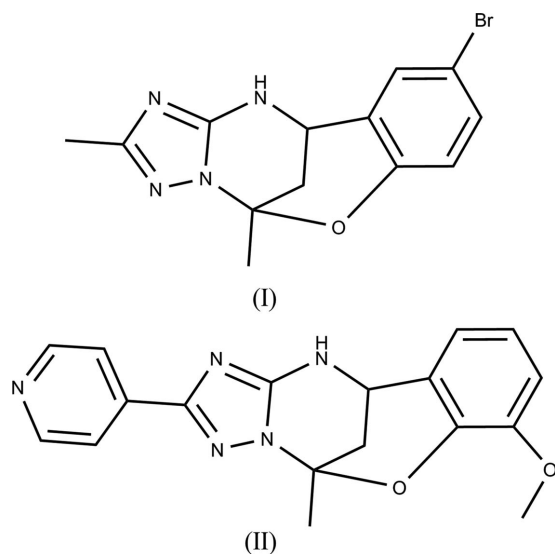
**Table 1**  
Hydrogen-bond geometry (Å, °) for (I).

Cg1 and Cg4 are the centroids of rings N2–N4/C11/C12 and C1–C6.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1A\cdots N2^i$	0.83 (2)	2.13 (2)	2.949 (3)	174 (2)
$C8-H8A\cdots Cg4^{ii}$	0.97	2.86	3.823 (3)	175
$C2-Br1\cdots Cg1^{iii}$	1.89 (1)	3.40 (1)	4.724 (3)	124 (1)

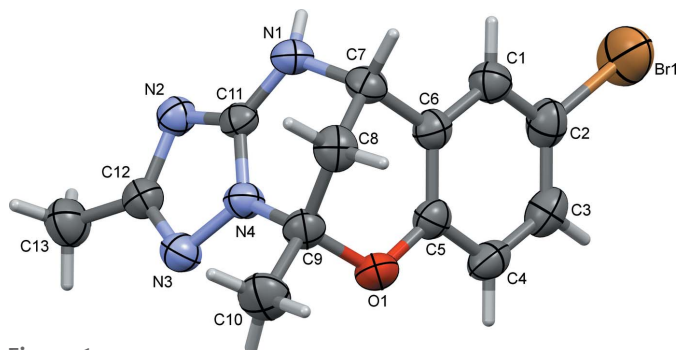
Symmetry codes: (i)  $-x+1, -y+1, -z+1$ ; (ii)  $-x+1, -y+1, -z+2$ ; (iii)  $x, y-1, z$ .

with acetone and 5-bromosalicylaldehyde/*o*-vanillin have been developed to offer easy access to the title compounds, **I** and **II**, examples of this new class of heterocycles.



## 2. Structural commentary

The molecular structures of compounds **I** and **II** are illustrated in Figs. 1 and 2, respectively. The conformations of the two compounds are very similar, as shown by the structural overlap of the two compounds [r.m.s. deviation = 0.005 Å (Mercury; Macrae *et al.*, 2008)], illustrated in Fig. 3. In **I**, the triazole ring (N2–N4/C11/C12) is inclined to the benzene ring (C1–C6) by 85.12 (12)°, compared to 76.96 (8)° in **II**. In the central 6-oxa-2,4λ²-diazabicyclo[3.3.1]nonane moiety, ring (N1/N4/C7–C9/C11) has a half-chair conformation in both



**Figure 1**  
The molecular structure of compound **I**, with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

**Table 2**  
Hydrogen-bond geometry (Å, °) for (II).

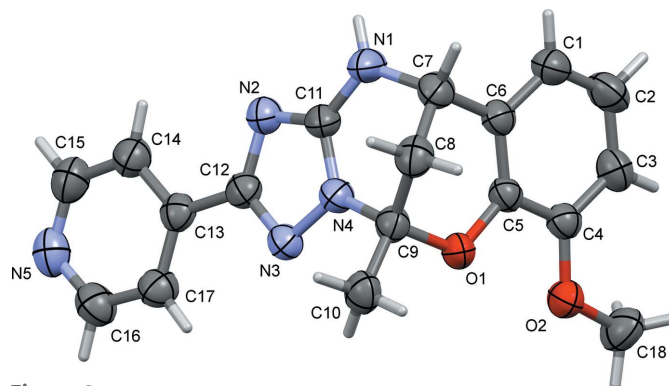
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1A\cdots N3^i$	0.83 (2)	2.53 (2)	3.356 (2)	169 (2)
$C1-H1\cdots O1^i$	0.93	2.53	3.426 (2)	163
$C7-H7\cdots O2^i$	0.98	2.35	3.264 (2)	155

Symmetry code: (i)  $-x+\frac{1}{2}, y+\frac{1}{2}, z$ .

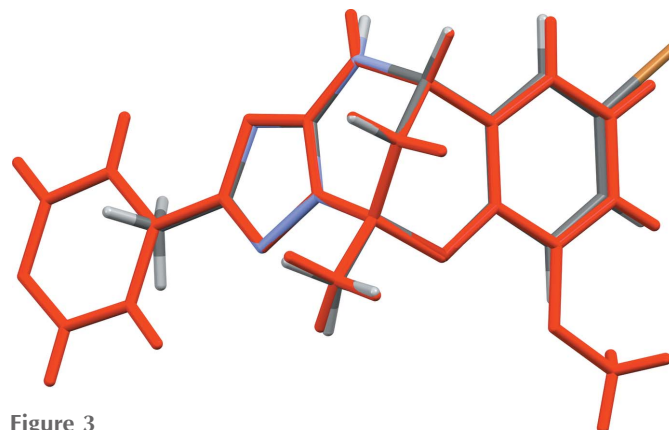
compounds, while ring O1/C5–C9 has an envelope conformation, with atom C8 as the flap, in both compounds. The mean planes of these two rings are almost normal to each other, with a dihedral angle of 86.94 (11)° in **I** and 88.69 (8)° in **II**. In compound **II**, the pyridine ring (N5/C13–C17) is almost coplanar with the triazole ring, having a dihedral angle of 4.19 (8)°. The bond lengths and angles in the title compounds are very close to those observed for similar compounds, for example, the pyridin-3-yl analogue of compound **II** (Gümüş *et al.*, 2018); see also section *Database survey*.

## 3. Supramolecular features

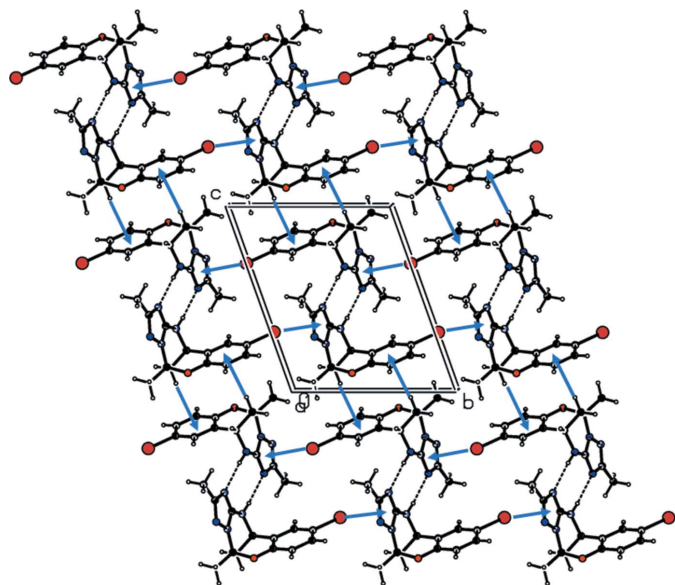
In the crystal of **I**, molecules are linked by a pair of  $N-H\cdots N$  hydrogen bonds, forming inversion dimers with an  $R_2^2(8)$  ring motif (Table 1 and Fig. 4). The dimers are linked by  $C-H\cdots\pi$



**Figure 2**  
The molecular structure of compound **II**, with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.



**Figure 3**  
A view of the structural overlap of molecules **I** and **II** (in red), having an r.m.s. deviation of 0.005 Å (Mercury; Macrae *et al.*, 2008).


**Figure 4**

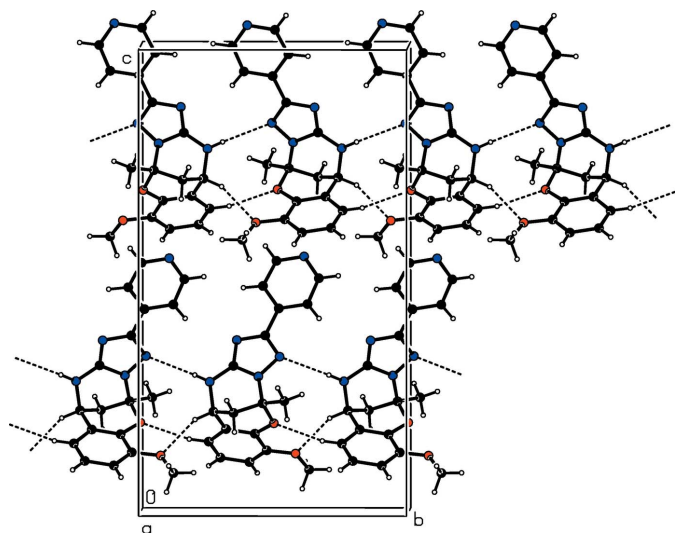
A view along the *a* axis of the crystal packing of compound **I**. Dashed lines denote the intermolecular N—H...N hydrogen bonds, forming an inversion dimer with an  $R_2^2(8)$  ring motif (Table 1). C—H... $\pi$  and C—Br... $\pi$  interactions are shown as blue arrows (Table 1).

and C—Br... $\pi$  interactions forming layers parallel to the *bc* plane (Table 1 and Fig. 4).

In the crystal of **II**, molecules are connected *via* intermolecular N—H...N and C—H...O hydrogen bonds, forming chains propagating along the *b*-axis direction (Table 2 and Fig. 5). Within the chains there are  $R_2^2(10)$ ,  $R_2^2(11)$  and  $R_2^2(9)$  ring motifs present (Table 2 and Fig. 5).

#### 4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.40, update of November 2018; Groom *et al.*, 2016)

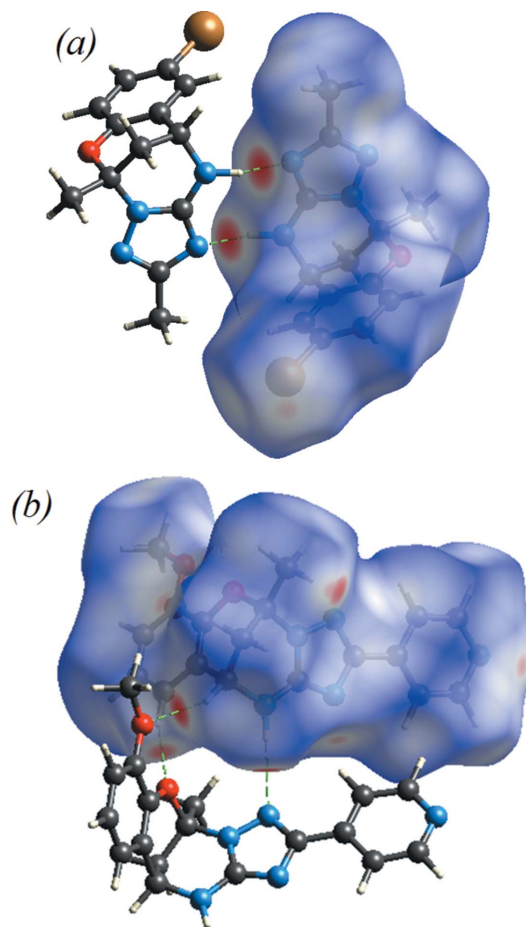

**Figure 5**

A view along the *a* axis of the crystal packing of compound **II**. Dashed lines denote intermolecular hydrogen bonds (Table 2).

for the triazolo-benzoxadiazocine skeleton yielded 4 hits, namely 7-ethoxy-5-methyl-11,12-dihydro-5,11-methano[1,2,4]-triazolo[1,5-*c*][1,3,5]benzoxadiazocine (HUVCEH; Gorobets *et al.*, 2010), 7-ethoxy-5-methyl-2-(pyridin-3-yl)-11,12-dihydro-5*H*-5,11-methano[1,2,4]triazolo[1,5-*c*][1,3,5]benzoxadiazocine (RETCAX; Aydemir *et al.*, 2018), 7-methoxy-5-methyl-2-phenyl-11,12-dihydro-5*H*-5,11-methano[1,2,4]triazolo[1,5-*c*][1,3,5]benzoxadiazocine (SILBEX; Gümüş *et al.*, 2018*b*), with two independent molecules in the asymmetric unit, and 7-methoxy-5-methyl-2-(pyridin-3-yl)-11,12-dihydro-5*H*-5,11-methano[1,2,4]triazolo[1,5-*c*][1,3,5]benzoxadiazocine (WEXYUM; Gümüş *et al.*, 2018*a*), also with two independent molecules per asymmetric unit.

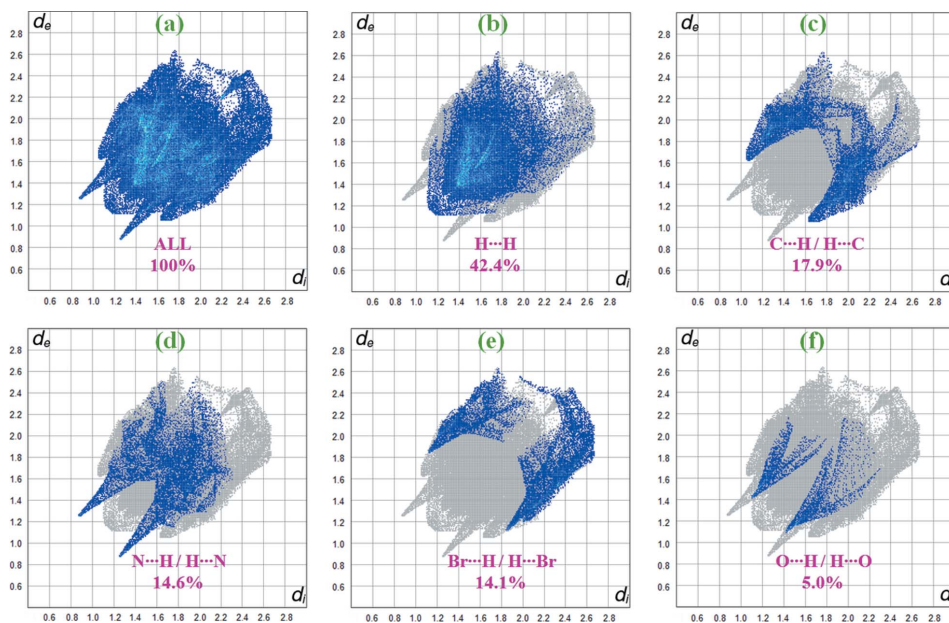
The conformations of all four compounds resemble those of compounds **I** and **II**, with the dihedral angle between the triazole and benzene rings varying from *ca* 71.20 to 87.37°, compared to 85.12 (12) and 76.96 (8)° in compounds **I** and **II**, respectively.

The geometrical parameters of the four compounds are very similar to each other and to those of compounds **I** and **II**. The C9—O1 and C5—O1 bond lengths are 1.456 (3) and 1.375 (3) Å, respectively, in **I** and 1.441 (2) and 1.385 (2) Å in **II**, compared to *ca* 1.445 and 1.374 Å in HUVCEH, 1.444 and


**Figure 6**

$d_{\text{norm}}$  mapped on Hirshfeld surfaces for visualizing the intermolecular interactions of (a) compound **I** and (b) compound **II**.





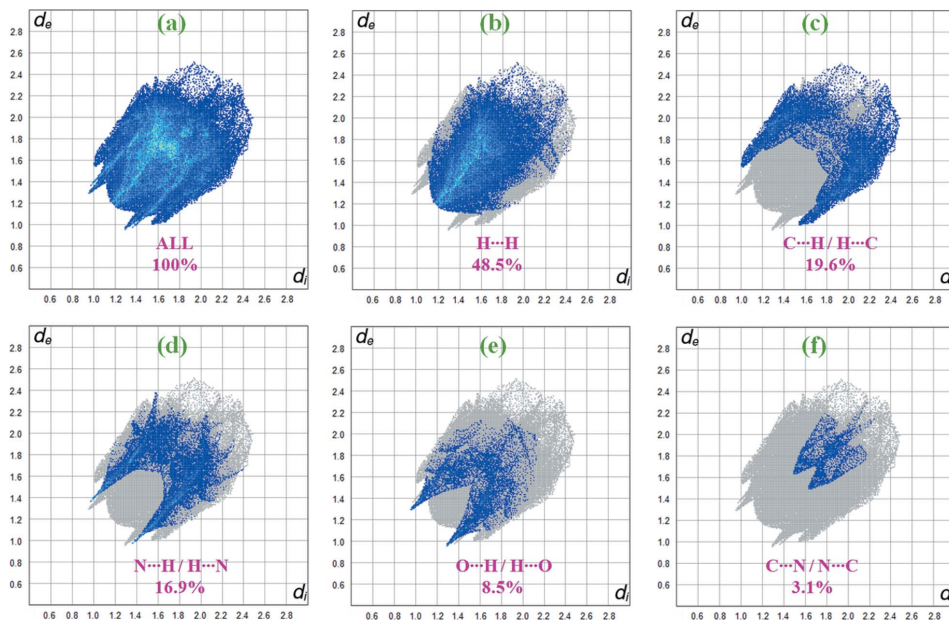
**Figure 7**  
2D fingerprint plots for compound **I**, with a  $d_{\text{norm}}$  view and the relative contributions of the atom pairs to the Hirshfeld surface.

1.390 Å in RETCAX, 1.343/1.436 and 1.381/1.381 Å in SILBEX, and 1.429/1.444 and 1.377/1.380 Å in WEXYUW. In addition, the N3–N4 bond length is 1.388 (3) Å in **I** and 1.381 (2) Å in **II**, compared to *ca* 1.385, 1.389, 1.376/1.382 and 1.379/1.381 Å in HUVCEH, RETCAX, SILBEX and WEXYUW, respectively.

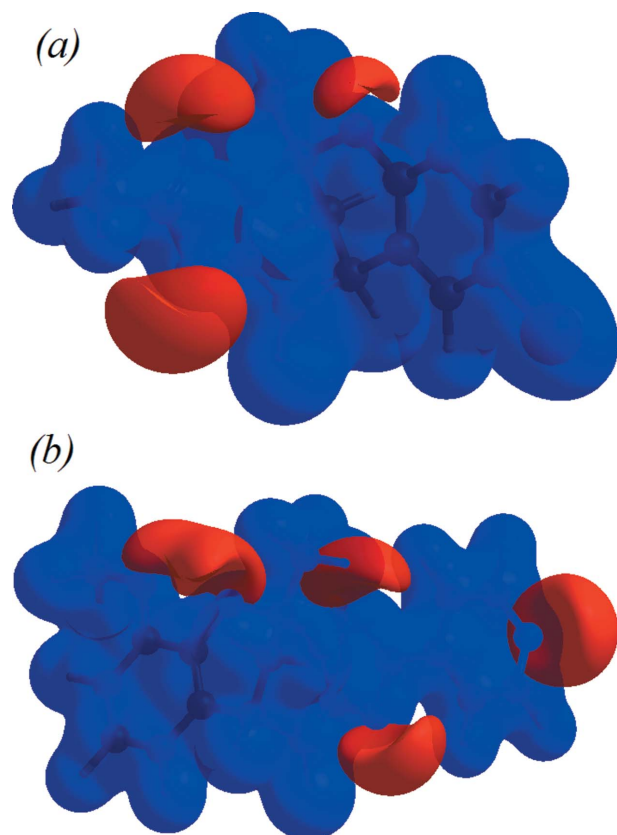
## 5. Hirshfeld surface analysis

The Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) and the associated two-dimensional (2D) fingerprint plots

(McKinnon *et al.*, 2007) were performed with *Crystal-Explorer17* (Turner *et al.*, 2017). The Hirshfeld surfaces were generated using a standard (high) surface resolution with the three-dimensional (3D)  $d_{\text{norm}}$  surfaces mapped over a fixed colour scale of  $-0.378$  (red) to  $1.282$  Å (blue) for compound **I** and from  $-0.259$  (red) to  $1.216$  Å (blue) for compound **II**. The red spots on the surface indicate the intermolecular contacts involved in the hydrogen bonds. In Fig. 6(a), the identified red spot is attributed to the  $\text{H}\cdots\text{N}$  close contacts. Also in Fig. 6(a), the  $\text{N}-\text{H}\cdots\text{N}$  contacts are shown in the  $d_{\text{norm}}$  mapped surface as deep-red depression areas showing the interaction between



**Figure 8**  
2D fingerprint plots for compound **II**, with a  $d_{\text{norm}}$  view and the relative contributions of the atom pairs to the Hirshfeld surface.



**Figure 9**  
The view of the three-dimensional Hirshfeld surface of (a) compound **I** and (b) compound **II**, plotted over the electrostatic potential surface.

the neighbouring molecules for compound **I**. Similarly, the red spots on the surface correspond to C—H···O and N—H···N hydrogen bonds in compound **II** (Fig. 6b).

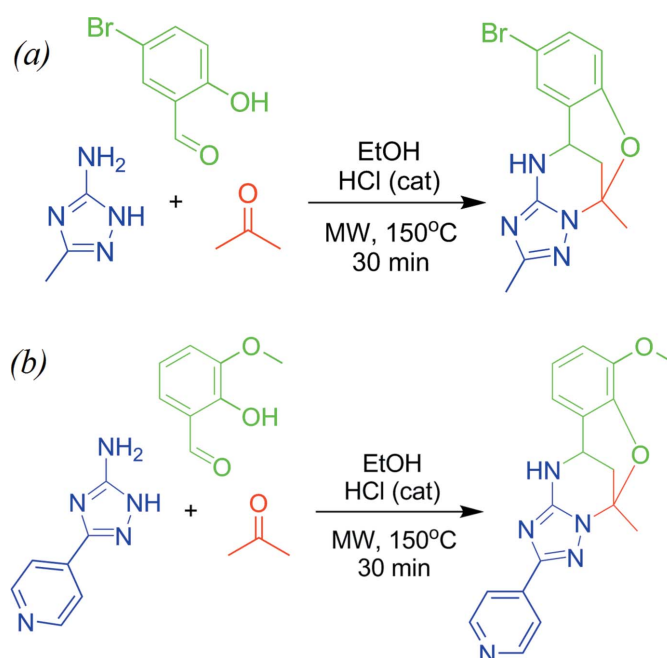
Fig. 7(a) shows the 2D fingerprint plot of the sum of the contacts contributing to the Hirshfeld surface of compound **I** represented in normal mode. 2D fingerprint plots provide information about the major and minor percentage contribution of the interatomic contacts in compound **I**. The blue colour refers to the frequency of occurrence of the ( $d_i$ ,  $d_e$ ) pair and the grey colour is the outline of the full fingerprint (Zaini *et al.*, 2019). The fingerprint plots (Fig. 7b) show that the H···H contacts clearly make the most significant contribution to the Hirshfeld surface (42.4%). In addition, C···H/H···C, N···H/H···N and Br···H/H···Br contacts contribute 17.9, 14.6 and 14.1%, respectively, to the Hirshfeld surface. Much weaker O···H/H···O (5.0%), Br···N/N···Br (2.7%), Br···C/C···Br (1.8%) and Br···Br (1.0%) contacts also occur. In particular, the O···H/H···O contacts indicate the presence of intermolecular C—H···O interactions.

Similarly, for compound **II**, the H···H interactions appear in the middle of the scattered points in the 2D fingerprint plots with a contribution to the overall Hirshfeld surface of 48.5% (Fig. 8b). The contribution from the N···H/H···N contacts, corresponding to the N—H···N interactions, is represented by a pair of sharp spikes characteristic of a strong hydrogen-bond interaction (16.9%) (Fig. 8d). The whole fingerprint region and all other interactions are displayed in Fig. 8.

Views of the molecular electrostatic potential, in the range  $-0.0500$  to  $0.0500$  a.u. using the STO-3G basis set at the Hartree–Fock level of theory, for compounds **I** and **II** are shown in Figs. 9(a) and 9(b), respectively. In Fig. 9(a), the N—H···N hydrogen-bond donors and acceptors are shown as blue and red areas around the atoms related with positive (hydrogen-bond donors) and negative (hydrogen-bond acceptors) electrostatic potentials, respectively. Also, in Figs. 9(a) and 9(b), the N—H···N and C—H···O contacts in compounds **I** and **II** are given in the molecular electrostatic potential mapped surface showing the interaction between neighbouring molecules.

## 6. Synthesis and crystallization

The synthesis of the title compounds (Fig. 10) has been described by Gümüş *et al.* (2017). 3-Amino-5-methyl-1,2,4-triazole/3-amino-5-(pyridin-4-yl)-1,2,4-triazole (1.0 mmol), 5-bromosalicylaldehyde (1.0 mmol) for compound **I** [*o*-vanillin (1.0 mmol) for compound **II**], acetone (0.22 ml, 3.0 mmol), and absolute EtOH (2.0 ml) were mixed in a microwave process vial, then a 4 N solution of HCl in dioxane (0.07 ml, 0.3 mmol) was added. The mixtures were irradiated at 423 K for 30 min. The reaction mixtures were cooled by an air flow and stirred for 24 h at room temperature for complete precipitation of the products. The precipitates were filtered off, washed with EtOH (1.0 ml) and Et<sub>2</sub>O (3 × 1.0 ml), and then dried. The compounds were obtained in the form of white solids. They were recrystallized from ethanol yielding colourless prismatic crystals for both compounds **I** and **II**.



**Figure 10**  
The synthesis of (a) compound **I** and (b) compound **II**.

**Table 3**  
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	C <sub>13</sub> H <sub>13</sub> BrN <sub>4</sub> O	C <sub>18</sub> H <sub>17</sub> N <sub>5</sub> O <sub>2</sub>
<i>M<sub>r</sub></i>	321.18	335.36
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Orthorhombic, <i>Pbca</i>
Temperature (K)	296	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.1446 (6), 9.7407 (8), 11.6801 (11)	11.2814 (6), 12.6299 (6), 22.0008 (15)
$\alpha$ , $\beta$ , $\gamma$ (°)	109.657 (7), 92.325 (8), 91.664 (7)	90, 90, 90
<i>V</i> (Å <sup>3</sup> )	657.13 (11)	3134.7 (3)
<i>Z</i>	2	8
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	3.13	0.10
Crystal size (mm)	0.34 × 0.19 × 0.11	0.31 × 0.22 × 0.15
Data collection		
Diffractometer	Stoe IPDS 2	Stoe IPDS 2
Absorption correction	Integration ( <i>X-RED32</i> ; Stoe & Cie, 2002)	Integration ( <i>X-RED32</i> ; Stoe & Cie, 2002)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.477, 0.748	0.975, 0.986
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	12939, 4242, 2223	23575, 4432, 1789
<i>R<sub>int</sub></i>	0.051	0.086
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.729	0.698
Refinement		
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.045, 0.115, 0.98	0.039, 0.073, 0.80
No. of reflections	4242	4432
No. of parameters	178	231
No. of restraints	1	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.28, -0.70	0.16, -0.14

Computer programs: *X-AREA* and *X-RED32* (Stoe & Cie, 2002), *SHELXT2017* (Sheldrick, 2015a), *Mercury* (Macrae *et al.*, 2008), *WinGX* (Farrugia, 2012), *SHELXL2018* (Sheldrick, 2015b), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. For compound **I**, the nitrogen-bound H atom was located in a difference Fourier map and refined subject to a restraint of N–H = 0.86 (2) Å, while for compound **II**, the nitrogen-bound H atom was also located in a difference Fourier map and was freely refined. For both compounds, the C-bound H atoms were positioned geometrically and refined using a riding model, with C–H = 0.93–0.97 Å and *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(C) for methyl H atoms and 1.2*U*<sub>eq</sub>(C) otherwise.

## Acknowledgements

The authors acknowledge the Faculty of Arts and Sciences, Ondokuz Mayıs University, Turkey, for the use of the Stoe IPDS 2 diffractometer (purchased under grant F.279 of the University Research Fund) and the Council of Higher Education of Turkey, Mevlana Exchange Program (MEV-2016-027).

## References

Aydemir, E., Kansız, S., Gumus, M. K., Gorobets, N. Y. & Dege, N. (2018). *Acta Cryst.* **E74**, 367–370.  
 Dömling, A., Wang, W. & Wang, K. (2012). *Chem. Rev.* **112**, 3083–3135.  
 Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Gorobets, N. Y., Sedash, Y. V., Ostras, K. S., Zaremba, O. V., Shishkina, S. V., Baumer, V. N., Shishkin, O. V., Kovalenko, S. M., Desenko, S. M. & Van der Eycken, E. V. (2010). *Tetrahedron Lett.* **51**, 2095–2098.  
 Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.  
 Gümüş, M. K., Gorobets, N. Y., Sedash, Y. V., Chebanov, V. A. & Desenko, S. M. (2017). *Chem. Heterocycl. Compd.* **53**, 1261–1267.  
 Gümüş, M. K., Kansız, S., Aydemir, E., Gorobets, N. Y. & Dege, N. (2018a). *J. Mol. Struct.* **1168**, 280–290.  
 Gümüş, M. K., Kansız, S., Dege, N. & Kalibabchuk, V. A. (2018b). *Acta Cryst.* **E74**, 1211–1214.  
 Heijden, G. van der, Ruijter, E. & Orru, R. V. A. (2013). *Synlett*, **24**, 666–685.  
 Komykhov, S. A., Bondarenko, A. A., Musatov, V. I., Diachkov, M. V., Gorobets, N. Y. & Desenko, S. M. (2017). *Chem. Heterocycl. Compd.* **53**, 378–380.  
 Kondratiuk, M., Gorobets, N. Y., Sedash, Y. V., Gümüş, M. K. & Desenko, S. M. (2016). *Molbank*, **2016**, M898.  
 Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.  
 McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814–3816.  
 Murlykina, M. V., Morozova, A. D., Zviagin, I. M., Sakhno, Y. I., Desenko, S. M. & Chebanov, V. A. (2018). *Frontiers Chem.* **6**, article 527.  
 Sedash, Y. V., Gorobets, N. Y., Chebanov, V. A., Konovalova, I. S., Shishkin, O. V. & Desenko, S. M. (2012). *RSC Adv.* **2**, 6719–6728.  
 Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.  
 Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.  
 Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.

- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Stoe & Cie (2002). *X-AREA* and *X-RED32*. Stoe & Cie GmbH, Darmstadt, Germany.
- Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *CrystalExplorer17*. University of Western Australia. <http://hirshfeldsurface.net>
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Zaini, M. F., Razak, I. A., Anis, M. Z. & Arshad, S. (2019). *Acta Cryst.* **E75**, 58–63.

## supporting information

*Acta Cryst.* (2019). E75, 492-498 [https://doi.org/10.1107/S2056989019003700]

## Crystal structure and Hirshfeld surface analysis of two 5,11-methanobenzo[g][1,2,4]triazolo[1,5-c][1,3,5]oxadiazocine derivatives

Mustafa Kemal Gumus, Sevgi Kansiz, Cigdem Yuksektepe Ataoğlu, Necmi Dege and Igor O. Fritsky

### Computing details

For both structures, data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXT2017* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2008) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 2012), *SHELXL2018* (Sheldrick, 2015b), *PLATON* (Spek, 2009) and *pubCIF* (Westrip, 2010).

### 9-Bromo-2,5-dimethyl-11,12-dihydro-5H-5,11-methanobenzo[g][1,2,4]triazolo[1,5-c][1,3,5]oxadiazocine (I)

#### Crystal data

C<sub>13</sub>H<sub>13</sub>BrN<sub>4</sub>O

*M<sub>r</sub>* = 321.18

Triclinic, *P* $\bar{1}$

*a* = 6.1446 (6) Å

*b* = 9.7407 (8) Å

*c* = 11.6801 (11) Å

$\alpha$  = 109.657 (7)°

$\beta$  = 92.325 (8)°

$\gamma$  = 91.664 (7)°

*V* = 657.13 (11) Å<sup>3</sup>

*Z* = 2

*F*(000) = 324

*D<sub>x</sub>* = 1.623 Mg m<sup>-3</sup>

Mo *K* $\alpha$  radiation,  $\lambda$  = 0.71073 Å

Cell parameters from 9169 reflections

$\theta$  = 2.4–31.5°

$\mu$  = 3.13 mm<sup>-1</sup>

*T* = 296 K

Prism, colourless

0.34 × 0.19 × 0.11 mm

#### Data collection

Stoe IPDS 2

diffractometer

Radiation source: sealed X-ray tube, 12 x 0.4

mm long-fine focus

Detector resolution: 6.67 pixels mm<sup>-1</sup>

rotation method scans

Absorption correction: integration

(*X-RED32*; Stoe & Cie, 2002)

*T<sub>min</sub>* = 0.477, *T<sub>max</sub>* = 0.748

12939 measured reflections

4242 independent reflections

2223 reflections with *I* > 2 $\sigma$ (*I*)

*R<sub>int</sub>* = 0.051

$\theta_{\max}$  = 31.2°,  $\theta_{\min}$  = 2.4°

*h* = -8→8

*k* = -14→13

*l* = -16→16

#### Refinement

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.045

*wR*(*F*<sup>2</sup>) = 0.115

*S* = 0.98

4242 reflections

178 parameters

1 restraint



Primary atom site location: structure-invariant direct methods  
 Secondary atom site location: difference Fourier map  
 Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0513P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.28 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.70 \text{ e } \text{\AA}^{-3}$

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.50800 (8)	-0.00902 (3)	0.68588 (4)	0.09386 (19)
O1	0.1825 (3)	0.59496 (18)	0.89977 (14)	0.0477 (4)
N1	0.5602 (3)	0.5822 (2)	0.66868 (17)	0.0408 (4)
H1A	0.613 (4)	0.519 (2)	0.6116 (19)	0.041 (7)*
N2	0.2699 (3)	0.63495 (19)	0.54765 (16)	0.0406 (4)
N3	0.0498 (3)	0.7412 (2)	0.70145 (17)	0.0452 (4)
N4	0.2379 (3)	0.69449 (19)	0.74411 (16)	0.0392 (4)
C1	0.5355 (4)	0.2973 (3)	0.7486 (2)	0.0473 (5)
H1	0.669578	0.280839	0.713372	0.057*
C2	0.4059 (5)	0.1815 (3)	0.7523 (2)	0.0532 (6)
C3	0.2065 (5)	0.2025 (3)	0.8038 (2)	0.0541 (6)
H3	0.120166	0.123167	0.805244	0.065*
C4	0.1360 (4)	0.3423 (3)	0.8533 (2)	0.0483 (6)
H4	0.002492	0.357929	0.889189	0.058*
C5	0.2649 (4)	0.4592 (2)	0.84915 (19)	0.0414 (5)
C6	0.4666 (4)	0.4381 (2)	0.79711 (19)	0.0402 (5)
C7	0.6010 (4)	0.5663 (2)	0.7867 (2)	0.0415 (5)
H7	0.756370	0.552230	0.799071	0.050*
C8	0.5347 (4)	0.7044 (3)	0.8840 (2)	0.0465 (5)
H8A	0.576019	0.701721	0.964269	0.056*
H8B	0.607448	0.789210	0.874330	0.056*
C9	0.2895 (4)	0.7133 (2)	0.87046 (19)	0.0433 (5)
C10	0.1984 (5)	0.8514 (3)	0.9542 (2)	0.0613 (7)
H10A	0.042029	0.844207	0.945156	0.092*
H10B	0.251676	0.933353	0.933786	0.092*
H10C	0.243425	0.864266	1.037001	0.092*
C11	0.3650 (4)	0.6328 (2)	0.65048 (19)	0.0355 (4)
C12	0.0793 (4)	0.7029 (2)	0.5845 (2)	0.0437 (5)
C13	-0.0777 (5)	0.7335 (3)	0.4974 (3)	0.0612 (7)
H13A	-0.030509	0.821212	0.483641	0.092*
H13B	-0.219248	0.745678	0.530443	0.092*
H13C	-0.085106	0.653506	0.421778	0.092*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.1300 (4)	0.04262 (16)	0.1075 (3)	0.01035 (16)	0.0421 (2)	0.01877 (15)
O1	0.0489 (10)	0.0537 (9)	0.0436 (9)	0.0088 (7)	0.0140 (7)	0.0188 (7)
N1	0.0360 (10)	0.0454 (9)	0.0406 (10)	0.0051 (8)	0.0096 (8)	0.0129 (8)
N2	0.0446 (11)	0.0401 (9)	0.0375 (9)	0.0031 (8)	0.0050 (8)	0.0134 (7)
N3	0.0408 (11)	0.0513 (10)	0.0448 (11)	0.0092 (8)	0.0046 (9)	0.0170 (8)
N4	0.0369 (10)	0.0436 (9)	0.0364 (9)	0.0062 (8)	0.0065 (8)	0.0118 (7)
C1	0.0491 (14)	0.0480 (12)	0.0449 (13)	0.0068 (10)	0.0054 (10)	0.0152 (10)
C2	0.0699 (18)	0.0412 (11)	0.0495 (14)	0.0020 (11)	0.0044 (13)	0.0163 (10)
C3	0.0623 (17)	0.0528 (13)	0.0510 (14)	-0.0091 (12)	0.0021 (12)	0.0237 (11)
C4	0.0442 (14)	0.0637 (14)	0.0422 (12)	-0.0030 (11)	0.0054 (10)	0.0249 (11)
C5	0.0450 (13)	0.0485 (11)	0.0329 (10)	0.0042 (10)	0.0029 (9)	0.0164 (9)
C6	0.0393 (13)	0.0452 (11)	0.0363 (11)	0.0010 (9)	-0.0012 (9)	0.0145 (9)
C7	0.0326 (12)	0.0454 (11)	0.0458 (12)	0.0020 (9)	0.0009 (9)	0.0147 (9)
C8	0.0479 (14)	0.0454 (11)	0.0423 (12)	-0.0034 (10)	-0.0057 (10)	0.0111 (9)
C9	0.0495 (14)	0.0434 (11)	0.0350 (11)	0.0058 (10)	0.0063 (10)	0.0098 (9)
C10	0.0732 (19)	0.0571 (14)	0.0457 (14)	0.0131 (13)	0.0099 (13)	0.0051 (11)
C11	0.0351 (12)	0.0344 (9)	0.0367 (11)	-0.0019 (8)	0.0059 (9)	0.0114 (8)
C12	0.0441 (13)	0.0452 (11)	0.0433 (13)	0.0040 (10)	0.0045 (10)	0.0163 (9)
C13	0.0602 (18)	0.0716 (17)	0.0561 (15)	0.0146 (14)	0.0005 (13)	0.0267 (13)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Br1—C2	1.892 (2)	C4—C5	1.383 (3)
O1—C5	1.375 (3)	C4—H4	0.9300
O1—C9	1.456 (3)	C5—C6	1.393 (3)
N1—C11	1.346 (3)	C6—C7	1.518 (3)
N1—C7	1.451 (3)	C7—C8	1.519 (3)
N1—H1A	0.825 (16)	C7—H7	0.9800
N2—C11	1.321 (3)	C8—C9	1.517 (4)
N2—C12	1.374 (3)	C8—H8A	0.9700
N3—C12	1.311 (3)	C8—H8B	0.9700
N3—N4	1.388 (3)	C9—C10	1.511 (3)
N4—C11	1.350 (3)	C10—H10A	0.9600
N4—C9	1.445 (3)	C10—H10B	0.9600
C1—C2	1.375 (4)	C10—H10C	0.9600
C1—C6	1.383 (3)	C12—C13	1.482 (4)
C1—H1	0.9300	C13—H13A	0.9600
C2—C3	1.377 (4)	C13—H13B	0.9600
C3—C4	1.378 (4)	C13—H13C	0.9600
C3—H3	0.9300		
C5—O1—C9	116.13 (17)	C8—C7—H7	109.7
C11—N1—C7	115.79 (18)	C9—C8—C7	108.11 (18)
C11—N1—H1A	119.1 (17)	C9—C8—H8A	110.1
C7—N1—H1A	114.7 (17)	C7—C8—H8A	110.1

C11—N2—C12	103.07 (18)	C9—C8—H8B	110.1
C12—N3—N4	101.80 (18)	C7—C8—H8B	110.1
C11—N4—N3	109.66 (17)	H8A—C8—H8B	108.4
C11—N4—C9	125.84 (19)	N4—C9—O1	109.02 (17)
N3—N4—C9	124.48 (18)	N4—C9—C10	111.4 (2)
C2—C1—C6	120.1 (2)	O1—C9—C10	105.3 (2)
C2—C1—H1	119.9	N4—C9—C8	106.70 (19)
C6—C1—H1	119.9	O1—C9—C8	109.36 (18)
C1—C2—C3	121.2 (2)	C10—C9—C8	114.9 (2)
C1—C2—Br1	118.6 (2)	C9—C10—H10A	109.5
C3—C2—Br1	120.20 (19)	C9—C10—H10B	109.5
C2—C3—C4	119.4 (2)	H10A—C10—H10B	109.5
C2—C3—H3	120.3	C9—C10—H10C	109.5
C4—C3—H3	120.3	H10A—C10—H10C	109.5
C3—C4—C5	119.7 (2)	H10B—C10—H10C	109.5
C3—C4—H4	120.2	N2—C11—N1	128.76 (19)
C5—C4—H4	120.2	N2—C11—N4	110.04 (19)
O1—C5—C4	116.1 (2)	N1—C11—N4	121.19 (19)
O1—C5—C6	122.9 (2)	N3—C12—N2	115.4 (2)
C4—C5—C6	121.0 (2)	N3—C12—C13	122.9 (2)
C1—C6—C5	118.6 (2)	N2—C12—C13	121.7 (2)
C1—C6—C7	120.8 (2)	C12—C13—H13A	109.5
C5—C6—C7	120.5 (2)	C12—C13—H13B	109.5
N1—C7—C6	110.99 (18)	H13A—C13—H13B	109.5
N1—C7—C8	108.26 (18)	C12—C13—H13C	109.5
C6—C7—C8	108.33 (19)	H13A—C13—H13C	109.5
N1—C7—H7	109.7	H13B—C13—H13C	109.5
C6—C7—H7	109.7		
C12—N3—N4—C11	0.2 (2)	C11—N4—C9—O1	-97.7 (2)
C12—N3—N4—C9	178.8 (2)	N3—N4—C9—O1	84.0 (2)
C6—C1—C2—C3	0.0 (4)	C11—N4—C9—C10	146.5 (2)
C6—C1—C2—Br1	-179.53 (18)	N3—N4—C9—C10	-31.8 (3)
C1—C2—C3—C4	-0.4 (4)	C11—N4—C9—C8	20.3 (3)
Br1—C2—C3—C4	179.14 (19)	N3—N4—C9—C8	-158.00 (19)
C2—C3—C4—C5	0.8 (4)	C5—O1—C9—N4	70.6 (2)
C9—O1—C5—C4	-165.8 (2)	C5—O1—C9—C10	-169.73 (19)
C9—O1—C5—C6	14.7 (3)	C5—O1—C9—C8	-45.7 (2)
C3—C4—C5—O1	179.6 (2)	C7—C8—C9—N4	-51.2 (2)
C3—C4—C5—C6	-0.8 (3)	C7—C8—C9—O1	66.6 (2)
C2—C1—C6—C5	0.0 (3)	C7—C8—C9—C10	-175.2 (2)
C2—C1—C6—C7	-176.2 (2)	C12—N2—C11—N1	-178.0 (2)
O1—C5—C6—C1	179.9 (2)	C12—N2—C11—N4	0.7 (2)
C4—C5—C6—C1	0.4 (3)	C7—N1—C11—N2	-167.4 (2)
O1—C5—C6—C7	-3.9 (3)	C7—N1—C11—N4	14.1 (3)
C4—C5—C6—C7	176.6 (2)	N3—N4—C11—N2	-0.6 (2)
C11—N1—C7—C6	72.2 (2)	C9—N4—C11—N2	-179.14 (19)
C11—N1—C7—C8	-46.6 (2)	N3—N4—C11—N1	178.19 (18)

C1—C6—C7—N1	81.8 (3)	C9—N4—C11—N1	-0.4 (3)
C5—C6—C7—N1	-94.2 (2)	N4—N3—C12—N2	0.3 (3)
C1—C6—C7—C8	-159.5 (2)	N4—N3—C12—C13	-178.2 (2)
C5—C6—C7—C8	24.5 (3)	C11—N2—C12—N3	-0.6 (3)
N1—C7—C8—C9	66.4 (2)	C11—N2—C12—C13	177.9 (2)
C6—C7—C8—C9	-54.0 (2)		

*Hydrogen-bond geometry* (Å, °)

Cg1 and Cg4 are the centroids of rings N2-N4/C11/C12 and C1-C6.

<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>
N1—H1 <i>A</i> ...N2 <sup>i</sup>	0.83 (2)	2.13 (2)	2.949 (3)	174 (2)
C8—H8 <i>A</i> ...Cg4 <sup>ii</sup>	0.97	2.86	3.823 (3)	175
C2—Br1...Cg1 <sup>iii</sup>	1.89 (1)	3.40 (1)	4.724 (3)	124 (1)

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

### 7-Methoxy-5-methyl-2-(pyridin-4-yl)-11,12-dihydro-5*H*-5,11-methanobenzo[*g*][1,2,4]triazolo[1,5-*c*][1,3,5]oxadiazocine (II)

*Crystal data*

C<sub>18</sub>H<sub>17</sub>N<sub>5</sub>O<sub>2</sub>  
*M<sub>r</sub>* = 335.36  
 Orthorhombic, *Pbca*  
*a* = 11.2814 (6) Å  
*b* = 12.6299 (6) Å  
*c* = 22.0008 (15) Å  
*V* = 3134.7 (3) Å<sup>3</sup>  
*Z* = 8  
*F*(000) = 1408

*D<sub>x</sub>* = 1.421 Mg m<sup>-3</sup>  
 Mo *Kα* radiation,  $\lambda$  = 0.71073 Å  
 Cell parameters from 10886 reflections  
 $\theta$  = 1.6–30.1°  
 $\mu$  = 0.10 mm<sup>-1</sup>  
*T* = 296 K  
 Prism, colorless  
 0.31 × 0.22 × 0.15 mm

*Data collection*

Stoe IPDS 2  
 diffractometer  
 Radiation source: sealed X-ray tube, 12 x 0.4  
 mm long-fine focus  
 Detector resolution: 6.67 pixels mm<sup>-1</sup>  
 rotation method scans  
 Absorption correction: integration  
 (X-RED32; Stoe & Cie, 2002)  
*T<sub>min</sub>* = 0.975, *T<sub>max</sub>* = 0.986

23575 measured reflections  
 4432 independent reflections  
 1789 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.086  
 $\theta_{\max}$  = 29.7°,  $\theta_{\min}$  = 1.9°  
*h* = -15→15  
*k* = -15→17  
*l* = -30→29

*Refinement*

Refinement on *F*<sup>2</sup>  
 Least-squares matrix: full  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.039  
*wR*(*F*<sup>2</sup>) = 0.073  
*S* = 0.80  
 4432 reflections  
 231 parameters  
 0 restraints  
 Primary atom site location: structure-invariant  
 direct methods

Secondary atom site location: difference Fourier  
 map  
 Hydrogen site location: mixed  
 H atoms treated by a mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0216P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.16 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.14 \text{ e \AA}^{-3}$



*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.29552 (8)	1.00618 (8)	0.68647 (4)	0.0441 (3)
O2	0.13197 (9)	0.92768 (9)	0.61850 (5)	0.0507 (3)
N1	0.28301 (15)	1.24578 (13)	0.77525 (6)	0.0595 (4)
H1A	0.2548 (17)	1.3017 (16)	0.7892 (9)	0.081 (7)*
N2	0.22677 (12)	1.14540 (11)	0.86379 (6)	0.0491 (3)
N3	0.29188 (11)	0.98503 (10)	0.82932 (5)	0.0453 (3)
N4	0.31364 (11)	1.06389 (11)	0.78728 (6)	0.0455 (3)
N5	0.13813 (13)	0.89571 (14)	1.04161 (7)	0.0604 (4)
C1	0.13984 (16)	1.25155 (14)	0.64423 (8)	0.0553 (5)
H1	0.144023	1.324469	0.649710	0.066*
C2	0.05311 (15)	1.20940 (16)	0.60829 (9)	0.0625 (5)
H2	-0.001899	1.253997	0.589972	0.075*
C3	0.04590 (14)	1.10106 (15)	0.59873 (8)	0.0531 (5)
H3	-0.013911	1.073106	0.574462	0.064*
C4	0.12779 (13)	1.03541 (13)	0.62538 (7)	0.0425 (4)
C5	0.21547 (13)	1.07829 (12)	0.66266 (6)	0.0403 (4)
C6	0.22189 (14)	1.18600 (12)	0.67265 (7)	0.0437 (4)
C7	0.31960 (15)	1.23155 (13)	0.71187 (7)	0.0518 (5)
H7	0.345007	1.299766	0.695115	0.062*
C8	0.42279 (14)	1.15486 (13)	0.71098 (8)	0.0528 (4)
H8A	0.455901	1.150691	0.670365	0.063*
H8B	0.484397	1.178879	0.738475	0.063*
C9	0.37794 (13)	1.04721 (13)	0.73060 (7)	0.0436 (4)
C10	0.47358 (13)	0.96458 (14)	0.73722 (7)	0.0548 (5)
H10A	0.531162	0.988226	0.766340	0.082*
H10B	0.438977	0.899338	0.750878	0.082*
H10C	0.511468	0.953579	0.698666	0.082*
C11	0.27338 (14)	1.15751 (13)	0.80925 (7)	0.0465 (4)
C12	0.24111 (13)	1.03928 (13)	0.87389 (7)	0.0439 (4)
C13	0.20625 (13)	0.98919 (13)	0.93123 (7)	0.0441 (4)
C14	0.16193 (14)	1.04894 (15)	0.97868 (7)	0.0545 (5)
H14	0.153807	1.121901	0.974754	0.065*
C15	0.12990 (15)	0.99893 (17)	1.03192 (8)	0.0610 (5)
H15	0.100395	1.040698	1.063278	0.073*
C16	0.18286 (15)	0.84001 (17)	0.99569 (8)	0.0589 (5)
H16	0.191250	0.767376	1.001142	0.071*
C17	0.21758 (14)	0.88170 (13)	0.94085 (8)	0.0527 (4)
H17	0.248277	0.838119	0.910630	0.063*
C18	0.04328 (16)	0.87855 (15)	0.58270 (9)	0.0687 (6)

H18A	0.054849	0.803252	0.583059	0.103*
H18B	0.048312	0.904149	0.541693	0.103*
H18C	-0.033421	0.894966	0.599078	0.103*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0497 (6)	0.0416 (7)	0.0411 (6)	0.0029 (5)	-0.0089 (5)	-0.0003 (5)
O2	0.0551 (7)	0.0467 (8)	0.0502 (7)	-0.0023 (6)	-0.0106 (6)	-0.0008 (6)
N1	0.0996 (13)	0.0358 (10)	0.0432 (8)	0.0024 (9)	0.0045 (8)	-0.0013 (8)
N2	0.0637 (9)	0.0436 (9)	0.0399 (8)	-0.0009 (7)	0.0013 (7)	0.0009 (7)
N3	0.0543 (8)	0.0409 (8)	0.0407 (7)	-0.0029 (7)	-0.0002 (7)	0.0032 (7)
N4	0.0598 (8)	0.0372 (8)	0.0395 (7)	-0.0011 (6)	0.0015 (6)	0.0025 (7)
N5	0.0608 (10)	0.0736 (12)	0.0466 (9)	-0.0055 (8)	-0.0015 (8)	0.0085 (9)
C1	0.0714 (11)	0.0424 (11)	0.0521 (10)	0.0062 (10)	0.0014 (10)	0.0024 (9)
C2	0.0645 (12)	0.0555 (13)	0.0674 (13)	0.0164 (10)	-0.0051 (11)	0.0123 (11)
C3	0.0497 (10)	0.0591 (13)	0.0506 (11)	0.0030 (9)	-0.0065 (9)	0.0065 (10)
C4	0.0467 (9)	0.0406 (11)	0.0401 (9)	0.0008 (8)	0.0027 (8)	0.0030 (8)
C5	0.0440 (9)	0.0399 (10)	0.0368 (8)	0.0035 (8)	0.0021 (7)	0.0045 (8)
C6	0.0546 (10)	0.0398 (10)	0.0367 (9)	-0.0001 (8)	0.0040 (8)	0.0047 (8)
C7	0.0702 (11)	0.0413 (11)	0.0439 (10)	-0.0078 (9)	0.0021 (9)	0.0046 (9)
C8	0.0561 (10)	0.0547 (11)	0.0474 (10)	-0.0123 (9)	-0.0010 (8)	0.0012 (9)
C9	0.0470 (9)	0.0455 (10)	0.0383 (9)	-0.0034 (8)	-0.0031 (8)	-0.0013 (8)
C10	0.0514 (10)	0.0635 (12)	0.0495 (10)	0.0068 (9)	-0.0091 (8)	-0.0024 (9)
C11	0.0626 (11)	0.0357 (10)	0.0412 (9)	-0.0013 (8)	-0.0047 (8)	-0.0011 (9)
C12	0.0464 (9)	0.0420 (10)	0.0433 (9)	-0.0034 (7)	-0.0034 (7)	-0.0004 (8)
C13	0.0437 (8)	0.0465 (11)	0.0421 (9)	-0.0062 (8)	-0.0027 (7)	-0.0009 (8)
C14	0.0634 (11)	0.0524 (12)	0.0477 (10)	-0.0035 (9)	0.0001 (8)	-0.0016 (10)
C15	0.0673 (12)	0.0705 (15)	0.0451 (11)	-0.0039 (11)	0.0003 (9)	-0.0036 (11)
C16	0.0628 (11)	0.0551 (12)	0.0588 (12)	-0.0040 (10)	-0.0003 (10)	0.0117 (10)
C17	0.0587 (11)	0.0476 (11)	0.0518 (10)	-0.0046 (9)	0.0050 (9)	0.0004 (9)
C18	0.0694 (12)	0.0669 (14)	0.0697 (13)	-0.0007 (10)	-0.0176 (10)	-0.0199 (11)

*Geometric parameters (Å, °)*

O1—C5	1.3854 (16)	C5—C6	1.380 (2)
O1—C9	1.4408 (17)	C6—C7	1.513 (2)
O2—C4	1.3698 (18)	C7—C8	1.514 (2)
O2—C18	1.4165 (18)	C7—H7	0.9800
N1—C11	1.347 (2)	C8—C9	1.514 (2)
N1—C7	1.465 (2)	C8—H8A	0.9700
N1—H1A	0.83 (2)	C8—H8B	0.9700
N2—C11	1.3190 (19)	C9—C10	1.508 (2)
N2—C12	1.368 (2)	C10—H10A	0.9600
N3—C12	1.3263 (18)	C10—H10B	0.9600
N3—N4	1.3812 (17)	C10—H10C	0.9600
N4—C11	1.3557 (19)	C12—C13	1.465 (2)
N4—C9	1.4580 (19)	C13—C17	1.380 (2)

N5—C15	1.324 (2)	C13—C14	1.382 (2)
N5—C16	1.330 (2)	C14—C15	1.379 (2)
C1—C2	1.366 (2)	C14—H14	0.9300
C1—C6	1.390 (2)	C15—H15	0.9300
C1—H1	0.9300	C16—C17	1.374 (2)
C2—C3	1.387 (2)	C16—H16	0.9300
C2—H2	0.9300	C17—H17	0.9300
C3—C4	1.373 (2)	C18—H18A	0.9600
C3—H3	0.9300	C18—H18B	0.9600
C4—C5	1.395 (2)	C18—H18C	0.9600
C5—O1—C9	116.04 (12)	H8A—C8—H8B	108.4
C4—O2—C18	118.18 (13)	O1—C9—N4	107.90 (11)
C11—N1—C7	116.73 (15)	O1—C9—C10	106.13 (13)
C11—N1—H1A	117.7 (14)	N4—C9—C10	111.92 (13)
C7—N1—H1A	124.2 (14)	O1—C9—C8	110.29 (12)
C11—N2—C12	102.37 (14)	N4—C9—C8	106.29 (13)
C12—N3—N4	101.50 (12)	C10—C9—C8	114.20 (13)
C11—N4—N3	109.31 (12)	C9—C10—H10A	109.5
C11—N4—C9	126.70 (13)	C9—C10—H10B	109.5
N3—N4—C9	123.85 (13)	H10A—C10—H10B	109.5
C15—N5—C16	115.15 (16)	C9—C10—H10C	109.5
C2—C1—C6	120.34 (17)	H10A—C10—H10C	109.5
C2—C1—H1	119.8	H10B—C10—H10C	109.5
C6—C1—H1	119.8	N2—C11—N1	129.30 (16)
C1—C2—C3	120.96 (17)	N2—C11—N4	110.90 (14)
C1—C2—H2	119.5	N1—C11—N4	119.79 (15)
C3—C2—H2	119.5	N3—C12—N2	115.92 (14)
C4—C3—C2	119.44 (17)	N3—C12—C13	121.98 (15)
C4—C3—H3	120.3	N2—C12—C13	122.07 (15)
C2—C3—H3	120.3	C17—C13—C14	117.07 (15)
O2—C4—C3	125.16 (15)	C17—C13—C12	122.13 (15)
O2—C4—C5	115.23 (14)	C14—C13—C12	120.79 (15)
C3—C4—C5	119.61 (15)	C15—C14—C13	119.10 (17)
C6—C5—O1	123.62 (14)	C15—C14—H14	120.4
C6—C5—C4	120.92 (14)	C13—C14—H14	120.4
O1—C5—C4	115.43 (13)	N5—C15—C14	124.69 (18)
C5—C6—C1	118.71 (15)	N5—C15—H15	117.7
C5—C6—C7	120.25 (14)	C14—C15—H15	117.7
C1—C6—C7	121.00 (15)	N5—C16—C17	124.92 (19)
N1—C7—C6	112.58 (14)	N5—C16—H16	117.5
N1—C7—C8	107.90 (14)	C17—C16—H16	117.5
C6—C7—C8	108.02 (14)	C16—C17—C13	119.04 (17)
N1—C7—H7	109.4	C16—C17—H17	120.5
C6—C7—H7	109.4	C13—C17—H17	120.5
C8—C7—H7	109.4	O2—C18—H18A	109.5
C9—C8—C7	108.29 (13)	O2—C18—H18B	109.5
C9—C8—H8A	110.0	H18A—C18—H18B	109.5

C7—C8—H8A	110.0	O2—C18—H18C	109.5
C9—C8—H8B	110.0	H18A—C18—H18C	109.5
C7—C8—H8B	110.0	H18B—C18—H18C	109.5
C12—N3—N4—C11	-0.82 (15)	N3—N4—C9—O1	83.17 (16)
C12—N3—N4—C9	175.09 (13)	C11—N4—C9—C10	141.94 (15)
C6—C1—C2—C3	-0.9 (3)	N3—N4—C9—C10	-33.24 (19)
C1—C2—C3—C4	-0.6 (3)	C11—N4—C9—C8	16.63 (19)
C18—O2—C4—C3	-2.0 (2)	N3—N4—C9—C8	-158.54 (13)
C18—O2—C4—C5	178.11 (13)	C7—C8—C9—O1	65.73 (16)
C2—C3—C4—O2	-178.52 (15)	C7—C8—C9—N4	-50.97 (16)
C2—C3—C4—C5	1.3 (2)	C7—C8—C9—C10	-174.87 (13)
C9—O1—C5—C6	9.08 (19)	C12—N2—C11—N1	179.12 (17)
C9—O1—C5—C4	-172.98 (12)	C12—N2—C11—N4	0.13 (17)
O2—C4—C5—C6	179.17 (14)	C7—N1—C11—N2	-169.22 (16)
C3—C4—C5—C6	-0.7 (2)	C7—N1—C11—N4	9.7 (2)
O2—C4—C5—O1	1.17 (19)	N3—N4—C11—N2	0.44 (18)
C3—C4—C5—O1	-178.69 (13)	C9—N4—C11—N2	-175.31 (13)
O1—C5—C6—C1	177.12 (13)	N3—N4—C11—N1	-178.66 (14)
C4—C5—C6—C1	-0.7 (2)	C9—N4—C11—N1	5.6 (2)
O1—C5—C6—C7	-0.5 (2)	N4—N3—C12—N2	0.97 (17)
C4—C5—C6—C7	-178.34 (13)	N4—N3—C12—C13	-177.03 (13)
C2—C1—C6—C5	1.5 (2)	C11—N2—C12—N3	-0.73 (18)
C2—C1—C6—C7	179.10 (15)	C11—N2—C12—C13	177.26 (14)
C11—N1—C7—C6	73.9 (2)	N3—C12—C13—C17	-4.0 (2)
C11—N1—C7—C8	-45.3 (2)	N2—C12—C13—C17	178.14 (15)
C5—C6—C7—N1	-94.62 (18)	N3—C12—C13—C14	174.98 (14)
C1—C6—C7—N1	87.80 (19)	N2—C12—C13—C14	-2.9 (2)
C5—C6—C7—C8	24.4 (2)	C17—C13—C14—C15	-1.1 (2)
C1—C6—C7—C8	-153.16 (15)	C12—C13—C14—C15	179.90 (15)
N1—C7—C8—C9	67.08 (17)	C16—N5—C15—C14	1.2 (3)
C6—C7—C8—C9	-54.88 (16)	C13—C14—C15—N5	-0.1 (3)
C5—O1—C9—N4	74.33 (15)	C15—N5—C16—C17	-1.1 (3)
C5—O1—C9—C10	-165.55 (12)	N5—C16—C17—C13	0.0 (3)
C5—O1—C9—C8	-41.36 (16)	C14—C13—C17—C16	1.1 (2)
C11—N4—C9—O1	-101.66 (17)	C12—C13—C17—C16	-179.85 (14)

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A $\cdots$ N3 <sup>i</sup>	0.83 (2)	2.53 (2)	3.356 (2)	169 (2)
C1—H1 $\cdots$ O1 <sup>i</sup>	0.93	2.53	3.426 (2)	163
C7—H7 $\cdots$ O2 <sup>i</sup>	0.98	2.35	3.264 (2)	155

Symmetry code: (i)  $-x+1/2, y+1/2, z$ .