

# (1-[[2-(6-Methoxynaphthalen-1-yl)-ethyl]amino]ethylidene)oxidanium bromide monohydrate

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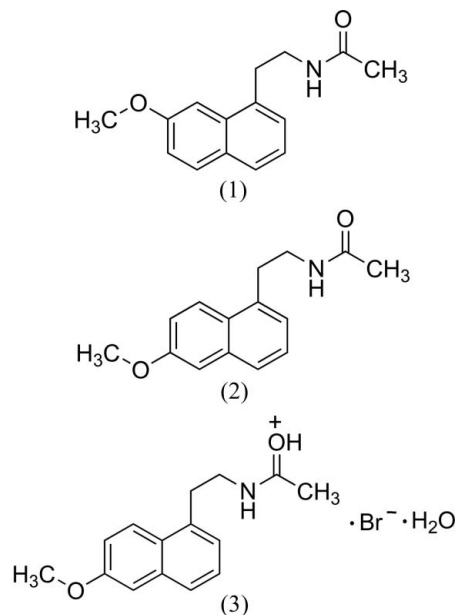
The title salt,  $C_{15}H_{18}NO_2^+ \cdot Br^- \cdot H_2O$ , is an analogue of the antidepressant drug agomelatine. The cation is protonated at the carbonyl O atom of its amide group. The side chain at the 1-position adopts an extended conformation, with all non-H atoms lying in the same plane as the naphthalene ring. This is in contrast with the crystal structures known for three agomelatine polymorphs, and also with two known cocrystals containing agomelatine. The structure displays three types of hydrogen bond, namely  $C=O \cdots O$ ,  $N-H \cdots Br$  and  $O-H \cdots Br$ , which define a two-dimensional network parallel to the (100) plane. The naphthalene rings interdigitate in a 'zipper-like' fashion between these hydrogen-bonded networks, forming an offset arrangement. Direct face-to-face  $\pi-\pi$  contacts between naphthalene rings are not present in the structure.

## Comment

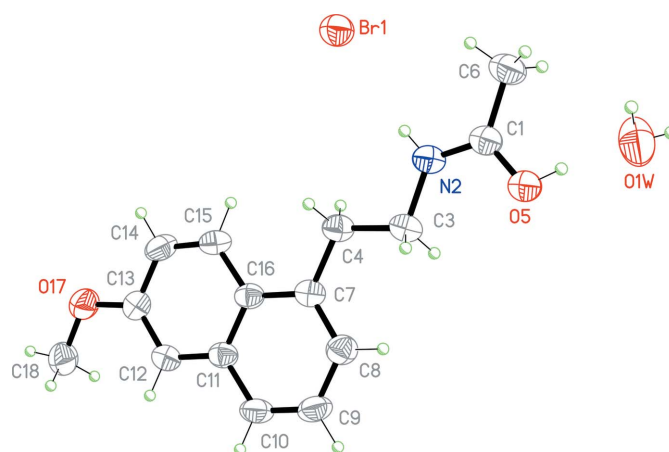
Agomelatine [*N*-[2-(7-methoxy-naphthalen-1-yl)ethyl]acetamide], (1), is an antidepressant developed by the pharmaceutical company Servier. It is classified as a norepinephrine-dopamine disinhibitor (NDDI) due to its antagonism of the 5-HT<sub>2C</sub> receptor. Agomelatine is also a potent agonist at melatonin receptors (MT1 and MT2 receptors), which makes it the first melatonergic antidepressant (Millan *et al.*, 2003). This overall favourable therapeutic profile makes it a very promising drug. Various crystallization attempts involving agomelatine have been made over recent years, involving multiple high-throughput screenings and conventional bench-top crystallizations. These have resulted in the discovery of at least six polymorphs and two cocrystals (Yous *et al.*, 1992; Coquerel *et al.*, 2007*a,b*, 2008, 2010; Souvie *et al.*, 2008; Zhu *et al.*, 2009; Zheng *et al.*, 2011). Five crystal structures have been reported so far (Tinant *et al.*, 1994; Zheng *et al.*, 2011).

During the synthesis of agomelatine in our laboratory, we observed that a white solid precipitated out of an agomelatine

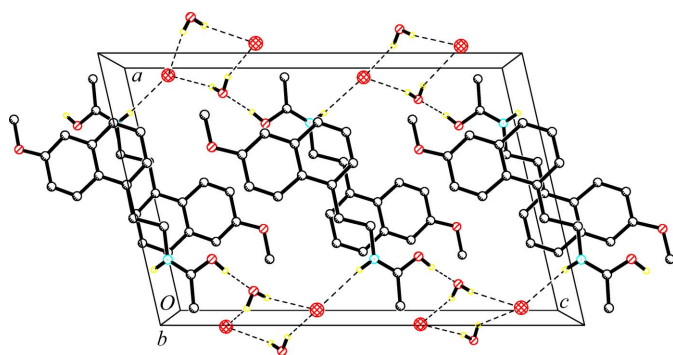
solution in ethyl acetate when it was titrated with one equivalent of dry HCl or dry HBr in ethyl acetate. Data obtained from elemental analysis suggested the formula to be agomelatine·HX. The solids formed with HCl or HBr were both unstable when stored in an unsealed condition and converted rapidly to the corresponding monohydrate. Further



investigation showed that the monohydrate could also be obtained directly by the addition of one equivalent of concentrated aqueous solutions of HCl or HBr. Since agomelatine has an acetamide and a methoxy group but no basic functional group, salt formation with HX was not immediately expected. To investigate this further, we synthesized the 6-methoxy analogue of agomelatine, *N*-[2-(6-methoxynaphthalen-1-yl)ethyl]acetamide, (2). This compound has also been reported as a melatonin receptor agonist (Depreux *et al.*, 1994; Mor *et al.*, 1998). Crystallization of (2) under the same conditions described for agomelatine produced the analogous compound (2)·HX·H<sub>2</sub>O. Single crystals of the title



**Figure 1**  
The molecular structure of (3). Displacement ellipsoids are drawn at the 50% probability level.

**Figure 2**

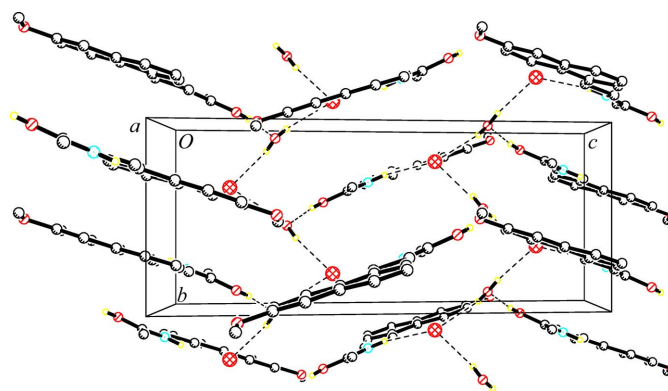
A view of the structure of (3), along the *b* axis. Dashed lines represent hydrogen bonds. The two-dimensional hydrogen-bond network lies in the (100) plane (horizontal).

HBr salt, (3), were prepared and the structure is described here; single crystals of the HCl salt were not obtained.

The molecular structure of (3) is shown in Fig. 1. The bond lengths and angles fall within normal ranges. The naphthalene system is planar within experimental error and the methoxy group lies close to the mean plane of the naphthalene system. The side chain adopts an extended conformation, with all non-H atoms in the same plane as the naphthalene system [torsion angle C16–C7–C4–C3 =  $-179.69$  ( $16^\circ$ )]. Interestingly, this conformation is different from those in all five of the previously reported structures containing agomelatine, including the two cocrystals with acetic acid and ethylene glycol. The corresponding torsion angle is  $79.7^\circ$  in agomelatine form I (Tinant *et al.*, 1994),  $79.4^\circ$  in form II,  $78.6^\circ$  in form III,  $90.5^\circ$  in the cocrystal with acetic acid and  $77.2^\circ$  in the cocrystal with ethylene glycol (Zheng *et al.*, 2011).

As shown in Fig. 1 and Table 1, the carbonyl O atom of the amide group is protonated, forming a C=O–H $\cdots$ O hydrogen bond with the water molecule, and the amide group forms an almost linear N–H $\cdots$ Br $^-$  hydrogen bond. The Br $^-$  anion also accepts O–H $\cdots$ Br $^-$  hydrogen bonds from two water molecules (Table 1) so that each anion accepts three hydrogen bonds in total. As shown in Figs. 2 and 3, the hydrogen-bond network is two-dimensional overall, lying parallel to the (100) plane. Between these hydrogen-bonded networks, the naphthalene systems interdigitate in a ‘zipper-like’ fashion. The rings form interfacial distances of 3.44 (1) [symmetry code ( $-x + 1, -y + 2, -z + 1$ )] and 3.58 (1) Å [symmetry code ( $-x + 1, -y + 1, -z + 1$ )] accompanied by significant lateral displacement [distances between the centroids of neighbouring C7–C11/C16 rings = 4.70 (1) and 5.44 (1) Å, respectively]. Direct face-to-face  $\pi$ – $\pi$  contacts are not present.

The packing arrangement in (3) differs considerably from that found in the five previously known crystal structures containing agomelatine. In agomelatine forms I–III, no solvent molecule is present, and the agomelatine molecules are linked by intermolecular hydrogen bonding between the amide N atom and the carbonyl O atom to form one-dimensional chains. The different polymorphs result mainly from different packing arrangements of these one-dimensional

**Figure 3**

A view of the structure of (3), along the *a* axis. Dashed lines represent hydrogen bonds.

chains. In the cocrystal with acetic acid, the latter molecule is inserted into the one-dimensional chain of the agomelatine molecules. In the cocrystal with ethylene glycol, a two-dimensional chiral sheet is formed.

## Experimental

The synthesis of *N*-[2-(6-methoxynaphthalen-1-yl)ethyl]acetamide, (2), was carried out according to the previously reported method for the preparation of agomelatine (Tang & Chen, 2008). The product was isolated in 31% yield (purity determined by high-performance liquid chromatography = 99%) and identified as (2) from MS, IR and NMR analyses. The compound was kept at 298 K in a sealed container.

For the preparation of (3), a solution of (2) (1 g) in ethyl acetate (10 ml) was cooled in an ice bath. To the mixture was added aqueous HBr (40%) (1 ml) dropwise over a period of 30 min. After stirring for 1 h, the crystallized product was collected by filtration, washed with ethyl acetate and dried in vacuo at 313 K to obtain a white powder, *viz.* (3) (yield 90%). Slow evaporation from a solution of (3) in methanol at room temperature gave single crystals suitable for X-ray diffraction analysis.

### Crystal data

$C_{15}H_{18}NO_2^+ \cdot Br^- \cdot H_2O$	$V = 1558.34$ (3) Å $^3$
$M_r = 342.23$	$Z = 4$
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation
$a = 11.9376$ (1) Å	$\mu = 3.66$ mm $^{-1}$
$b = 7.3761$ (1) Å	$T = 296$ K
$c = 18.1618$ (2) Å	$0.10 \times 0.10 \times 0.10$ mm
$\beta = 102.979$ (1) $^\circ$	

### Data collection

Bruker SMART APEXII area-detector diffractometer	5359 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2009)	2613 independent reflections
$T_{\min} = 0.711, T_{\max} = 0.711$	2486 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.014$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.071$	
$S = 1.08$	$\Delta\rho_{\max} = 0.31$ e Å $^{-3}$
2613 reflections	$\Delta\rho_{\min} = -0.26$ e Å $^{-3}$
199 parameters	
5 restraints	

**Table 1**

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···Br1	0.85 (1)	2.62 (1)	3.4478 (16)	167 (2)
O5—H5···O1W	0.82 (1)	1.70 (1)	2.507 (2)	167 (3)
O1W—H1W···Br1 <sup>i</sup>	0.83 (1)	2.51 (1)	3.312 (2)	164 (3)
O1W—H2W···Br1 <sup>ii</sup>	0.82 (1)	2.45 (1)	3.2614 (19)	170 (3)

Symmetry codes: (i)  $-x, -y + 1, -z + 1$ ; (ii)  $x, -y + \frac{3}{2}, z + \frac{1}{2}$ .

H atoms bound to C atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.93 (aromatic), 0.96 (methyl) or 0.97 Å (methylene), and with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl H atoms or  $1.2U_{\text{eq}}(\text{C})$  otherwise. Atoms H2 and H5 and the H atoms of the water molecule were located in a difference Fourier map, and refined with isotropic displacement parameters and bond-distance restraints of N—H = 0.86 (1) Å and O—H = 0.82 (1) Å. The H1W···H2W distance was restrained to 1.34 (1) Å.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Drug and Pharmaceutical Processes, Shanghai Institute of Pharmaceutical Industry.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BI3043). Services for accessing these data are described at the back of the journal.

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## supplementary materials

*Acta Cryst.* (2012). C68, o308–o310 [doi:10.1107/S0108270112029885]

## (1-{[2-(6-Methoxynaphthalen-1-yl)ethyl]amino}ethylidene)oxidanium bromide monohydrate

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### Crystal data

$C_{15}H_{18}NO_2^+ \cdot Br^- \cdot H_2O$

$M_r = 342.23$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 11.9376$  (1) Å

$b = 7.3761$  (1) Å

$c = 18.1618$  (2) Å

$\beta = 102.979$  (1)°

$V = 1558.34$  (3) Å<sup>3</sup>

$Z = 4$

$F(000) = 704$

$D_x = 1.459$  Mg m<sup>-3</sup>

Cu  $K\alpha$  radiation,  $\lambda = 1.54178$  Å

Cell parameters from 3863 reflections

$\theta = 3.8$ – $67.5$ °

$\mu = 3.66$  mm<sup>-1</sup>

$T = 296$  K

Block, colourless

$0.10 \times 0.10 \times 0.10$  mm

### Data collection

Bruker SMART APEXII area-detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2009)

$T_{\min} = 0.711$ ,  $T_{\max} = 0.711$

5359 measured reflections

2613 independent reflections

2486 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.014$

$\theta_{\max} = 66.5$ °,  $\theta_{\min} = 3.8$ °

$h = -14 \rightarrow 13$

$k = -6 \rightarrow 8$

$l = -21 \rightarrow 19$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.026$

$wR(F^2) = 0.071$

$S = 1.08$

2613 reflections

199 parameters

5 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0368P)^2 + 0.593P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.31$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.26$  e Å<sup>-3</sup>

*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.

**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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.047030 (18)	0.82862 (3)	0.374825 (12)	0.05309 (11)
C1	0.18049 (16)	0.6564 (2)	0.59156 (11)	0.0396 (4)
N2	0.23448 (14)	0.7093 (2)	0.54133 (9)	0.0405 (4)
H2	0.1960 (19)	0.755 (3)	0.5004 (9)	0.056 (7)*
C3	0.36006 (15)	0.7004 (3)	0.55098 (11)	0.0399 (4)
H3A	0.3867	0.5776	0.5633	0.048*
H3B	0.3971	0.7795	0.5919	0.048*
C4	0.38986 (15)	0.7593 (3)	0.47803 (11)	0.0400 (4)
H4A	0.3548	0.6751	0.4386	0.048*
H4B	0.3559	0.8775	0.4643	0.048*
O5	0.24057 (12)	0.5884 (2)	0.65337 (8)	0.0484 (3)
H5	0.198 (2)	0.558 (4)	0.6812 (15)	0.087 (10)*
C6	0.05402 (18)	0.6761 (3)	0.57906 (14)	0.0547 (5)
H6A	0.0211	0.5633	0.5901	0.082*
H6B	0.0227	0.7087	0.5274	0.082*
H6C	0.0363	0.7691	0.6117	0.082*
C7	0.51665 (15)	0.7706 (2)	0.47987 (10)	0.0359 (4)
C8	0.59920 (17)	0.7316 (3)	0.54357 (11)	0.0428 (4)
H8A	0.5770	0.6948	0.5872	0.051*
C9	0.71684 (17)	0.7463 (3)	0.54415 (11)	0.0486 (5)
H9A	0.7712	0.7217	0.5883	0.058*
C10	0.75204 (16)	0.7961 (3)	0.48073 (12)	0.0453 (4)
H10A	0.8302	0.8033	0.4818	0.054*
C11	0.67075 (16)	0.8371 (2)	0.41334 (11)	0.0368 (4)
C12	0.70719 (16)	0.8917 (3)	0.34784 (11)	0.0394 (4)
H12A	0.7852	0.8970	0.3485	0.047*
C13	0.62818 (16)	0.9367 (3)	0.28367 (10)	0.0415 (4)
C14	0.50984 (17)	0.9290 (3)	0.28244 (11)	0.0476 (5)
H14A	0.4564	0.9610	0.2387	0.057*
C15	0.47317 (16)	0.8753 (3)	0.34453 (11)	0.0421 (4)
H15A	0.3947	0.8702	0.3423	0.051*
C16	0.55160 (15)	0.8264 (2)	0.41291 (10)	0.0349 (4)
O17	0.65468 (12)	0.9909 (2)	0.21755 (8)	0.0536 (4)
C18	0.77221 (19)	1.0213 (3)	0.21896 (12)	0.0550 (5)
H18A	0.7795	1.0691	0.1711	0.082*
H18B	0.8135	0.9090	0.2285	0.082*
H18C	0.8033	1.1065	0.2582	0.082*

O1W	0.12755 (17)	0.4503 (3)	0.74000 (11)	0.0713 (5)
H1W	0.076 (2)	0.382 (4)	0.7181 (18)	0.101 (12)*
H2W	0.102 (2)	0.514 (4)	0.7696 (15)	0.095 (11)*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.04511 (16)	0.06130 (17)	0.05232 (16)	0.00216 (9)	0.00980 (10)	0.00548 (9)
C1	0.0350 (10)	0.0361 (9)	0.0471 (10)	-0.0004 (7)	0.0080 (8)	-0.0060 (8)
N2	0.0332 (8)	0.0404 (8)	0.0469 (9)	0.0010 (6)	0.0070 (7)	0.0030 (7)
C3	0.0315 (9)	0.0377 (9)	0.0500 (10)	0.0003 (7)	0.0083 (8)	0.0011 (8)
C4	0.0329 (9)	0.0407 (10)	0.0450 (10)	-0.0019 (7)	0.0060 (7)	0.0027 (8)
O5	0.0383 (7)	0.0608 (9)	0.0454 (8)	0.0019 (6)	0.0081 (6)	0.0053 (7)
C6	0.0361 (11)	0.0663 (14)	0.0621 (13)	0.0045 (9)	0.0122 (9)	0.0041 (10)
C7	0.0331 (9)	0.0293 (8)	0.0441 (9)	-0.0003 (7)	0.0063 (7)	-0.0002 (7)
C8	0.0414 (10)	0.0431 (10)	0.0434 (10)	0.0024 (8)	0.0084 (8)	0.0070 (8)
C9	0.0360 (10)	0.0598 (12)	0.0450 (10)	0.0058 (9)	-0.0015 (8)	0.0127 (10)
C10	0.0297 (9)	0.0526 (11)	0.0512 (11)	0.0067 (8)	0.0041 (8)	0.0084 (9)
C11	0.0331 (9)	0.0339 (9)	0.0419 (10)	0.0043 (7)	0.0051 (7)	0.0003 (7)
C12	0.0332 (9)	0.0404 (9)	0.0448 (10)	0.0035 (7)	0.0088 (7)	0.0005 (8)
C13	0.0440 (10)	0.0415 (10)	0.0380 (9)	-0.0006 (8)	0.0072 (8)	-0.0004 (8)
C14	0.0405 (10)	0.0569 (12)	0.0393 (10)	-0.0018 (9)	-0.0039 (8)	0.0037 (9)
C15	0.0297 (9)	0.0466 (10)	0.0459 (10)	-0.0026 (8)	-0.0004 (7)	0.0007 (8)
C16	0.0315 (9)	0.0306 (9)	0.0405 (9)	-0.0002 (6)	0.0038 (7)	-0.0014 (7)
O17	0.0510 (8)	0.0700 (10)	0.0391 (7)	-0.0006 (7)	0.0088 (6)	0.0066 (7)
C18	0.0567 (13)	0.0648 (13)	0.0464 (11)	-0.0033 (11)	0.0177 (9)	0.0033 (10)
O1W	0.0847 (13)	0.0761 (12)	0.0615 (10)	-0.0166 (10)	0.0338 (10)	-0.0112 (9)

*Geometric parameters (Å, °)*

C1—N2	1.290 (3)	C9—H9A	0.930
C1—O5	1.290 (2)	C10—C11	1.413 (3)
C1—C6	1.483 (3)	C10—H10A	0.930
N2—C3	1.471 (2)	C11—C12	1.414 (3)
N2—H2	0.85 (1)	C11—C16	1.423 (3)
C3—C4	1.511 (3)	C12—C13	1.366 (3)
C3—H3A	0.970	C12—H12A	0.930
C3—H3B	0.970	C13—O17	1.368 (2)
C4—C7	1.509 (2)	C13—C14	1.409 (3)
C4—H4A	0.970	C14—C15	1.357 (3)
C4—H4B	0.970	C14—H14A	0.930
O5—H5	0.82 (1)	C15—C16	1.424 (3)
C6—H6A	0.960	C15—H15A	0.930
C6—H6B	0.960	O17—C18	1.415 (3)
C6—H6C	0.960	C18—H18A	0.960
C7—C8	1.371 (3)	C18—H18B	0.960
C7—C16	1.432 (3)	C18—H18C	0.960
C8—C9	1.406 (3)	O1W—H1W	0.83 (1)
C8—H8A	0.930	O1W—H2W	0.82 (1)
C9—C10	1.362 (3)		

N2—C1—O5	117.68 (17)	C10—C9—H9A	119.6
N2—C1—C6	121.02 (18)	C8—C9—H9A	119.6
O5—C1—C6	121.29 (18)	C9—C10—C11	120.51 (18)
C1—N2—C3	124.05 (17)	C9—C10—H10A	119.7
C1—N2—H2	118.7 (18)	C11—C10—H10A	119.7
C3—N2—H2	117.3 (18)	C10—C11—C12	120.55 (17)
N2—C3—C4	108.49 (15)	C10—C11—C16	118.95 (17)
N2—C3—H3A	110.0	C12—C11—C16	120.49 (17)
C4—C3—H3A	110.0	C13—C12—C11	120.22 (17)
N2—C3—H3B	110.0	C13—C12—H12A	119.9
C4—C3—H3B	110.0	C11—C12—H12A	119.9
H3A—C3—H3B	108.4	C12—C13—O17	124.65 (17)
C7—C4—C3	115.41 (15)	C12—C13—C14	120.11 (17)
C7—C4—H4A	108.4	O17—C13—C14	115.25 (16)
C3—C4—H4A	108.4	C15—C14—C13	120.52 (17)
C7—C4—H4B	108.4	C15—C14—H14A	119.7
C3—C4—H4B	108.4	C13—C14—H14A	119.7
H4A—C4—H4B	107.5	C14—C15—C16	121.82 (17)
C1—O5—H5	110 (2)	C14—C15—H15A	119.1
C1—C6—H6A	109.5	C16—C15—H15A	119.1
C1—C6—H6B	109.5	C11—C16—C15	116.84 (17)
H6A—C6—H6B	109.5	C11—C16—C7	119.53 (16)
C1—C6—H6C	109.5	C15—C16—C7	123.63 (17)
H6A—C6—H6C	109.5	C13—O17—C18	117.00 (15)
H6B—C6—H6C	109.5	O17—C18—H18A	109.5
C8—C7—C16	119.06 (17)	O17—C18—H18B	109.5
C8—C7—C4	122.30 (16)	H18A—C18—H18B	109.5
C16—C7—C4	118.63 (16)	O17—C18—H18C	109.5
C7—C8—C9	121.16 (18)	H18A—C18—H18C	109.5
C7—C8—H8A	119.4	H18B—C18—H18C	109.5
C9—C8—H8A	119.4	H1W—O1W—H2W	108.3 (16)
C10—C9—C8	120.77 (18)		
O5—C1—N2—C3	-1.4 (3)	C12—C13—C14—C15	-0.7 (3)
C6—C1—N2—C3	177.58 (18)	O17—C13—C14—C15	179.34 (19)
C1—N2—C3—C4	175.27 (17)	C13—C14—C15—C16	0.5 (3)
N2—C3—C4—C7	175.96 (15)	C10—C11—C16—C15	177.77 (17)
C3—C4—C7—C8	-0.6 (3)	C12—C11—C16—C15	-0.8 (3)
C3—C4—C7—C16	-179.69 (16)	C10—C11—C16—C7	-1.4 (3)
C16—C7—C8—C9	0.3 (3)	C12—C11—C16—C7	179.94 (16)
C4—C7—C8—C9	-178.85 (19)	C14—C15—C16—C11	0.2 (3)
C7—C8—C9—C10	-1.4 (3)	C14—C15—C16—C7	179.41 (19)
C8—C9—C10—C11	1.1 (3)	C8—C7—C16—C11	1.1 (3)
C9—C10—C11—C12	179.0 (2)	C4—C7—C16—C11	-179.73 (16)
C9—C10—C11—C16	0.3 (3)	C8—C7—C16—C15	-178.01 (18)
C10—C11—C12—C13	-177.87 (19)	C4—C7—C16—C15	1.1 (3)
C16—C11—C12—C13	0.7 (3)	C12—C13—O17—C18	-7.3 (3)
C11—C12—C13—O17	-179.96 (18)	C14—C13—O17—C18	172.68 (19)

C11—C12—C13—C14 0.0 (3)

*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···Br1	0.85 (1)	2.62 (1)	3.4478 (16)	167 (2)
O5—H5···O1 <i>W</i>	0.82 (1)	1.70 (1)	2.507 (2)	167 (3)
O1 <i>W</i> —H1 <i>W</i> ···Br1 <sup>i</sup>	0.83 (1)	2.51 (1)	3.312 (2)	164 (3)
O1 <i>W</i> —H2 <i>W</i> ···Br1 <sup>ii</sup>	0.82 (1)	2.45 (1)	3.2614 (19)	170 (3)

Symmetry codes: (i)  $-x, -y+1, -z+1$ ; (ii)  $x, -y+3/2, z+1/2$ .