



# Crystal structure of 22,24,25-trimethyl-8,11,14-trioxa-25-azatetracyclo[19.3.1.0<sup>2,7</sup>.0<sup>15,20</sup>]pentacosa-2,4,6,15(20),16,18-hexaen-23-one

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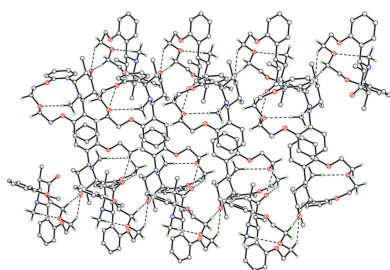
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The title compound, C<sub>24</sub>H<sub>29</sub>NO<sub>4</sub>, is the product of a Petrenko–Kritchenko condensation of 1,5-bis(2-formylphenoxy)-3-oxapentane, pentan-3-one and methylammonium acetate in ethanol. The molecule has mirror symmetry. The aza-14-crown-3 ether ring adopts a *bowl* conformation stabilized by a weak intramolecular C–H···O hydrogen bond. The conformation of the C–O–C–C–O–C–C–O–C polyether chain is t–g<sup>+</sup>–t–t–g<sup>–</sup>–t (t = *trans*, 180°; g = *gauche*, ±60°). The dihedral angle between the benzene rings fused to the aza-14-crown-4-ether moiety is 72.68 (4)°. The piperidinone ring adopts a *chair* conformation. The nitrogen atom has a trigonal–pyramidal geometry, the sum of the bond angles being 335.9°. In the crystal, the molecules are linked by weak C–H···O interactions, forming zigzag chains propagating along the [100] direction.

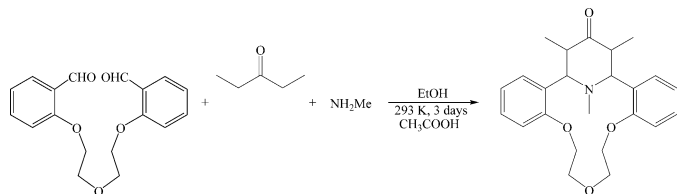
## 1. Chemical context

Macroheterocycles containing both crown ether and aza-heterocyclic moieties are prospective compounds not only as metal-ion receptors (Pedersen, 1988), but also as membrane ion-transporting vehicles (Gökel & Murillo, 1996), as active components of environmental chemistry (Bradshaw & Izatt, 1997), for the design of organic sensors (Costero *et al.*, 2005), in nanosized on-off switches and other molecular electronic devices (Natali & Giordani, 2012). Moreover, they can possess antibacterial (An *et al.*, 1998) and anticancer properties (Artiemenko *et al.*, 2002; Le *et al.*, 2014, 2015), and other useful biological activity (Anh & Soldatenkov, 2016; Tran *et al.*, 2016).

Recently, we have developed effective methods for the synthesis of azacrown ethers containing  $\gamma$ -piperidone (Levov *et al.*, 2006, 2008; Anh *et al.*, 2008, 2012*a,b,c*; Hieu *et al.* (2011, 2012*a,b*) or  $\gamma$ -arylpyridine (Anh & Soldatenkov, 2016; Tran *et al.*, 2016) subunits. This chemistry allowed us to make systematic studies of the fine structural features of a novel series of azacrown macrocycles using X-ray diffraction. Such data should be of use for the subsequent design of more certain drug-like macroheterocyclic molecules bearing new would-be pharmacophore groups.



In attempts to apply this chemistry for obtaining azacrown ethers which contain a 1,3,5-trimethyl-substituted  $\gamma$ -piperidine moiety, we studied the condensation of diethylketone and 1,5-bis(2-formylphenoxy)-3-oxapentane in the presence of methylammonium acetate taken both as the nitrogen source and as the template in ethanol/acetic acid solution. The reaction proceeded smoothly to give the expected azacrown title molecule, (I), with 32% yield.



## 2. Structural commentary

The title compound (Fig. 1), the product of a Petrenko–Kritchenko condensation of 1,5-bis(2-formylphenoxy)-3-oxapentane, pentan-3-one and methylammonium acetate in ethanol, crystallizes in the orthorhombic space group  $Pnma$  and, in the crystal, occupies a special position on a mirror plane. The aza-14-crown-3 ether ring adopts a *bowl* conformation stabilized by the weak intramolecular C16–H16B $\cdots$ O11 hydrogen bond (Table 1, Fig. 1). The distances from the center of the macrocycle cavity (defined as the centroid of atoms O8/O11/O8A/N14) to the O8, O11 and N14 atoms are 2.265 (2), 1.880 (2) and 2.393 (2) Å, respectively [atoms with the suffix *A* are related by the symmetry operation

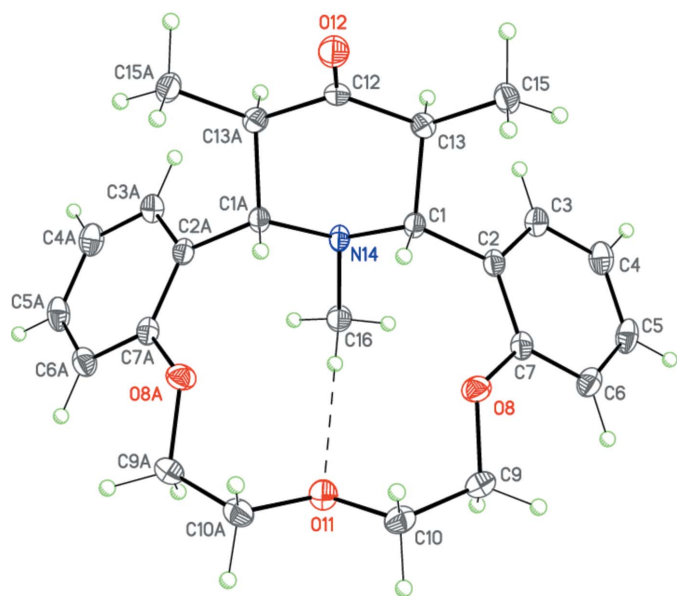


Figure 1

The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level. H atoms are presented as small spheres of arbitrary radius. The dashed line indicates the intramolecular C–H $\cdots$ O hydrogen bond. Atoms with the suffix *A* are related by the symmetry operation  $x, \frac{1}{2} - y, z$ .

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C10–H10B $\cdots$ O12 <sup>i</sup>	0.99	2.58	3.449 (2)	147
C16–H16B $\cdots$ O11	0.96	2.57	3.530 (3)	180

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

$x, \frac{1}{2} - y, z$ ]. The conformation of the C7–O8–C9–C10–O11–C10A–C9A–O8A–C7A polyether chain is  $t-g^+-t-t-g^-t$  ( $t = trans, 180^\circ$ ;  $g = gauche, \pm 60^\circ$ ). The dihedral angle between the planes of the benzene rings fused to the aza-14-crown-4-ether moiety is  $72.68(4)^\circ$ . The piperidinone ring adopts a *chair* conformation. The nitrogen N14 atom has a trigonal–pyramidal geometry (sum of the bond angles is  $335.9^\circ$ ).

The molecule of (I) possesses four asymmetric centers at the C1, C13, C13A and C1A carbon atoms and can have potentially numerous diastereomers. The crystal of (I) is racemic and consists of enantiomeric pairs with the following relative configuration of the centers:  $rac-1R^*, 13S^*, 13AR^*, 1AS^*$ .

## 3. Supramolecular features

In the crystal, molecules of (I) form zigzag chains along [100] *via* weak C–H $\cdots$ O interactions (Table 1, Figs. 2 and 3).  $\pi$ – $\pi$  stacking is observed in the crystal, the distance between

Table 2

Experimental details.

Crystal data	
Chemical formula	$C_{24}H_{29}NO_4$
$M_r$	395.48
Crystal system, space group	Orthorhombic, $Pnma$
Temperature (K)	120
$a, b, c$ (Å)	8.1468 (5), 20.3402 (11), 12.0155 (7)
$V$ (Å <sup>3</sup> )	1991.1 (2)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.09
Crystal size (mm)	0.20 $\times$ 0.15 $\times$ 0.15
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2003)
$T_{min}$ , $T_{max}$	0.970, 0.980
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	25079, 3128, 2469
$R_{int}$	0.065
$(\sin \theta/\lambda)_{max}$ (Å <sup>-1</sup> )	0.715
Refinement	
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.056, 0.130, 1.02
No. of reflections	3128
No. of parameters	140
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$ , $\Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.34, –0.23

Computer programs: *APEX2* (Bruker, 2001) and *SAINT* (Bruker, 2005), *SHELXT* (Sheldrick, 2015a), *SHELXL2015* (Sheldrick, 2015b) and *SHELXTL* (Sheldrick, 2008).

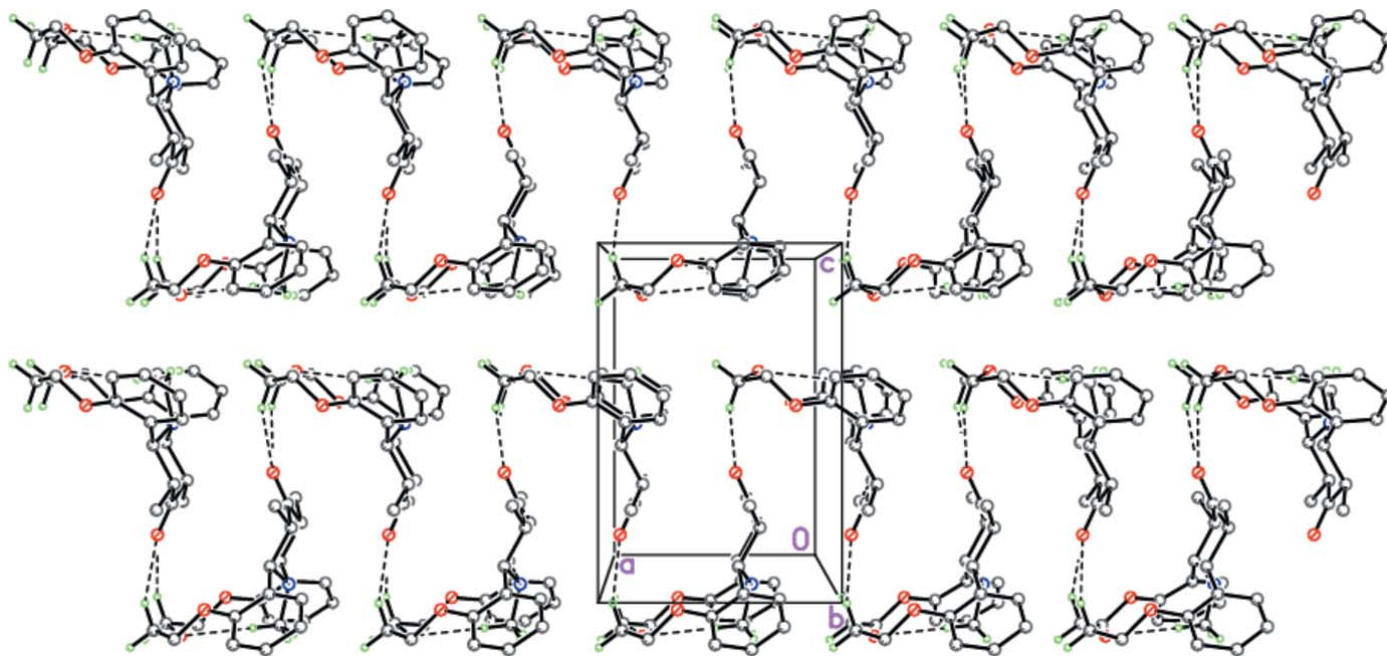


Figure 2  
Crystal packing of (I) along the *b* axis demonstrating the zigzag hydrogen-bonded chains along [100]. Dashed lines indicate the intra- and intermolecular C—H···O hydrogen bonds.

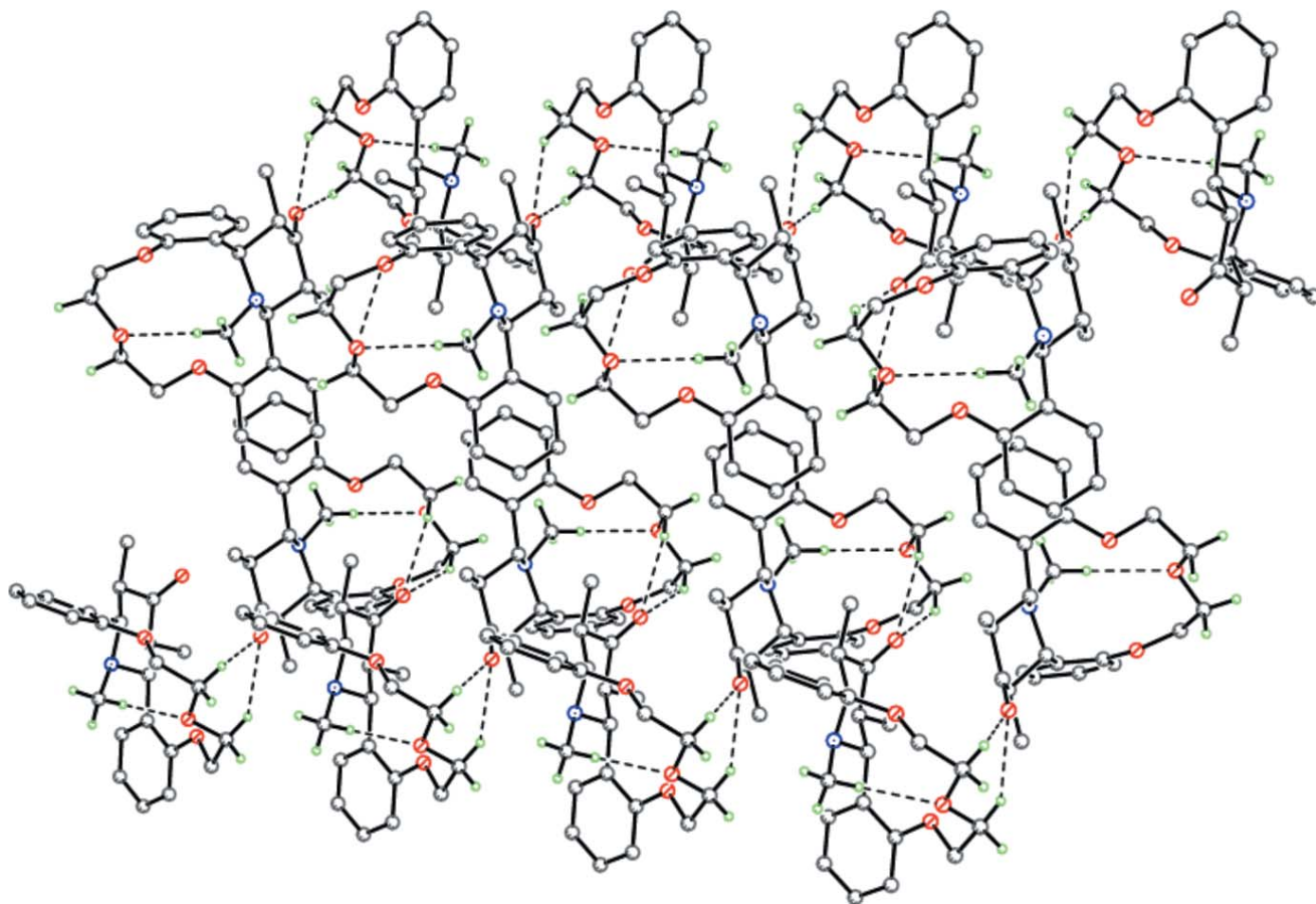


Figure 3  
A portion of the crystal packing of (I) indicating the intermolecular  $\pi$ - $\pi$  stacking interactions. Dashed lines indicate the intra- and intermolecular C—H···O hydrogen bonds.

parallel benzene rings is 3.446 (3) Å and the shortest intermolecular C5···C7<sup>i</sup> distance is 3.495 (2) Å [symmetry code: (i) 1 - x, 1 - y, -z].

#### 4. Synthesis and crystallization

Methylammonium acetate (3.85 g, 50 mmol) was added to a solution of 1,5-bis(2-formylphenoxy)-3-oxapentane (3.14 g, 10.0 mmol) and diethylketone (1.41 g, 10.0 mmol) in ethanol/acetic acid (40 mL/1 mL) mixture. The reaction mixture was stirred at 293 K for three days (monitored by TLC until the disappearance of the starting heterocyclic ketone spot). At the end of the reaction, the formed precipitate was filtered off, washed with ethanol and recrystallized from ethanol solution to give 2.1 g of crystals of (I) (yield 32% m.p. 485–487 K). IR (KBr),  $\nu/\text{cm}^{-1}$ : 1702. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 300 K):  $\delta$  = 0.89 (d, 6H, CH<sub>3</sub>, *J* = 6.7 Hz), 1.86 (c, 3H, NCH<sub>3</sub>), 3.19 (d, 2H, H1, H21, *J* = 10.8 Hz), 3.76–4.16 (m, 10H, H<sub>ether</sub> and H22, H24), 6.78–7.26 (m, 8H, H<sub>arom</sub>). Analysis calculated for C<sub>24</sub>H<sub>29</sub>NO<sub>4</sub>: C, 67.72; H, 7.31; N, 5.64. Found: C, 67.54; H, 7.42; N, 5.41.

#### 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All hydrogen atoms were placed in calculated positions with C–H = 0.95 Å (aryl-H), 0.96 Å (methyl-H), 0.98 Å (methylene-H) or 1.00 Å (methine-H) and refined using a riding model with fixed isotropic displacement parameters [ $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for the methyl groups and  $1.2U_{\text{eq}}(\text{C})$  for all other atoms].

#### Funding information

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## supporting information

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## Crystal structure of 22,24,25-trimethyl-8,11,14-trioxa-25-azatetracyclo-[19.3.1.0<sup>2,7</sup>.0<sup>15,20</sup>]pentacos-2,4,6,15(20),16,18-hexaen-23-one

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### Computing details

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2015* (Sheldrick, 2015b); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

### 22,24,25-Trimethyl-8,11,14-trioxa-25-azatetracyclo[19.3.1.0<sup>2,7</sup>.0<sup>15,20</sup>]pentacos-2,4,6,15 (20),16,18-hexaen-23-one

#### Crystal data

C<sub>24</sub>H<sub>29</sub>NO<sub>4</sub>

*M<sub>r</sub>* = 395.48

Orthorhombic, *Pnma*

*a* = 8.1468 (5) Å

*b* = 20.3402 (11) Å

*c* = 12.0155 (7) Å

*V* = 1991.1 (2) Å<sup>3</sup>

*Z* = 4

*F*(000) = 848

*D<sub>x</sub>* = 1.319 Mg m<sup>-3</sup>

Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 4090 reflections

θ = 3.0–29.2°

μ = 0.09 mm<sup>-1</sup>

*T* = 120 K

Prism, colourless

0.20 × 0.15 × 0.15 mm

#### Data collection

Bruker APEXII CCD  
diffractometer

Radiation source: fine-focus sealed tube

φ and ω scans

Absorption correction: multi-scan  
(*SADABS*; Bruker, 2003)

*T<sub>min</sub>* = 0.970, *T<sub>max</sub>* = 0.980

25079 measured reflections

3128 independent reflections

2469 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.065

θ<sub>max</sub> = 30.6°, θ<sub>min</sub> = 2.0°

*h* = -11→11

*k* = -29→29

*l* = -17→16

#### Refinement

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

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.056

*wR*(*F*<sup>2</sup>) = 0.130

*S* = 1.02

3128 reflections

140 parameters

0 restraints

Primary atom site location: difference Fourier  
map

Secondary atom site location: difference Fourier  
map

Hydrogen site location: mixed

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.046P)^2 + 1.66P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.34 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$$

### 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	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.58338 (18)	0.30912 (7)	-0.07447 (12)	0.0151 (3)
H1	0.4639	0.3029	-0.0903	0.018*
C2	0.60218 (18)	0.37109 (7)	-0.00494 (12)	0.0156 (3)
C3	0.75023 (19)	0.40480 (7)	0.00526 (13)	0.0190 (3)
H3	0.8432	0.3900	-0.0354	0.023*
C4	0.7652 (2)	0.45976 (7)	0.07366 (14)	0.0223 (3)
H4	0.8670	0.4822	0.0793	0.027*
C5	0.6301 (2)	0.48134 (7)	0.13342 (13)	0.0223 (3)
H5	0.6398	0.5188	0.1803	0.027*
C6	0.4808 (2)	0.44885 (7)	0.12557 (13)	0.0195 (3)
H6	0.3888	0.4637	0.1672	0.023*
C7	0.46690 (18)	0.39412 (7)	0.05590 (12)	0.0162 (3)
O8	0.32384 (13)	0.35995 (5)	0.04244 (9)	0.0194 (2)
C9	0.19912 (19)	0.36553 (8)	0.12588 (13)	0.0201 (3)
H9A	0.1387	0.4074	0.1172	0.024*
H9B	0.2488	0.3645	0.2011	0.024*
C10	0.08483 (19)	0.30816 (7)	0.11056 (13)	0.0197 (3)
H10A	-0.0119	0.3129	0.1597	0.024*
H10B	0.0462	0.3062	0.0325	0.024*
O11	0.17272 (19)	0.2500	0.13785 (13)	0.0192 (3)
C12	0.6367 (3)	0.2500	-0.24937 (18)	0.0157 (4)
O12	0.5743 (2)	0.2500	-0.34102 (13)	0.0219 (3)
C13	0.67442 (18)	0.31314 (7)	-0.18726 (12)	0.0160 (3)
H13	0.7951	0.3147	-0.1722	0.019*
N14	0.6428 (2)	0.2500	-0.01435 (14)	0.0148 (3)
C15	0.6282 (2)	0.37347 (7)	-0.25565 (13)	0.0192 (3)
H15A	0.6833	0.3715	-0.3281	0.029*
H15B	0.6626	0.4133	-0.2161	0.029*
H15C	0.5091	0.3744	-0.2667	0.029*
C16	0.6033 (3)	0.2500	0.10474 (17)	0.0186 (4)
H16A	0.6489	0.2885	0.1390	0.028*
H16B	0.4864	0.2500	0.1141	0.028*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0192 (7)	0.0111 (6)	0.0151 (6)	0.0006 (5)	0.0007 (5)	-0.0001 (5)
C2	0.0197 (7)	0.0118 (6)	0.0154 (6)	0.0002 (5)	-0.0012 (5)	0.0008 (5)
C3	0.0200 (7)	0.0152 (6)	0.0217 (7)	0.0009 (5)	-0.0016 (6)	0.0010 (5)
C4	0.0240 (8)	0.0169 (7)	0.0259 (8)	-0.0028 (6)	-0.0061 (6)	-0.0005 (6)
C5	0.0317 (8)	0.0133 (6)	0.0219 (7)	0.0005 (6)	-0.0075 (6)	-0.0042 (6)
C6	0.0248 (7)	0.0161 (7)	0.0177 (7)	0.0031 (6)	-0.0015 (6)	-0.0026 (5)
C7	0.0202 (7)	0.0124 (6)	0.0158 (7)	0.0003 (5)	-0.0018 (5)	0.0004 (5)
O8	0.0198 (5)	0.0201 (5)	0.0183 (5)	-0.0026 (4)	0.0035 (4)	-0.0054 (4)
C9	0.0208 (7)	0.0203 (7)	0.0193 (7)	0.0025 (6)	0.0038 (6)	-0.0033 (6)
C10	0.0176 (7)	0.0217 (7)	0.0199 (7)	0.0033 (6)	0.0015 (6)	-0.0008 (6)
O11	0.0177 (7)	0.0183 (7)	0.0216 (8)	0.000	-0.0020 (6)	0.000
C12	0.0152 (9)	0.0157 (9)	0.0162 (9)	0.000	0.0047 (7)	0.000
O12	0.0306 (9)	0.0190 (7)	0.0160 (7)	0.000	-0.0006 (6)	0.000
C13	0.0161 (6)	0.0149 (6)	0.0169 (7)	-0.0019 (5)	0.0014 (5)	-0.0001 (5)
N14	0.0193 (8)	0.0104 (7)	0.0147 (8)	0.000	-0.0017 (6)	0.000
C15	0.0245 (8)	0.0144 (6)	0.0187 (7)	-0.0008 (6)	-0.0002 (6)	0.0028 (5)
C16	0.0271 (11)	0.0154 (9)	0.0134 (9)	0.000	-0.0003 (8)	0.000

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

C1—N14	1.4840 (17)	C9—H9B	0.9900
C1—C2	1.5197 (19)	C10—O11	1.4211 (17)
C1—C13	1.547 (2)	C10—H10A	0.9900
C1—H1	1.0000	C10—H10B	0.9900
C2—C3	1.393 (2)	O11—C10 <sup>i</sup>	1.4211 (17)
C2—C7	1.403 (2)	C12—O12	1.213 (3)
C3—C4	1.393 (2)	C12—C13 <sup>i</sup>	1.5168 (18)
C3—H3	0.9500	C12—C13	1.5168 (18)
C4—C5	1.385 (2)	C13—C15	1.524 (2)
C4—H4	0.9500	C13—H13	1.0000
C5—C6	1.388 (2)	N14—C16	1.467 (3)
C5—H5	0.9500	N14—C1 <sup>i</sup>	1.4840 (17)
C6—C7	1.397 (2)	C15—H15A	0.9800
C6—H6	0.9500	C15—H15B	0.9800
C7—O8	1.3666 (18)	C15—H15C	0.9800
O8—C9	1.4319 (18)	C16—H16A	0.9595
C9—C10	1.504 (2)	C16—H16B	0.9593
C9—H9A	0.9900		
N14—C1—C2	111.82 (12)	H9A—C9—H9B	108.6
N14—C1—C13	108.23 (12)	O11—C10—C9	107.80 (13)
C2—C1—C13	112.92 (12)	O11—C10—H10A	110.1
N14—C1—H1	107.9	C9—C10—H10A	110.1
C2—C1—H1	107.9	O11—C10—H10B	110.1
C13—C1—H1	107.9	C9—C10—H10B	110.1

C3—C2—C7	118.03 (13)	H10A—C10—H10B	108.5
C3—C2—C1	122.95 (13)	C10—O11—C10 <sup>i</sup>	112.69 (16)
C7—C2—C1	118.96 (13)	O12—C12—C13 <sup>i</sup>	122.11 (9)
C2—C3—C4	121.51 (15)	O12—C12—C13	122.11 (9)
C2—C3—H3	119.2	C13 <sup>i</sup> —C12—C13	115.71 (18)
C4—C3—H3	119.2	C12—C13—C15	111.50 (13)
C5—C4—C3	119.40 (15)	C12—C13—C1	106.80 (12)
C5—C4—H4	120.3	C15—C13—C1	113.36 (12)
C3—C4—H4	120.3	C12—C13—H13	108.3
C4—C5—C6	120.68 (14)	C15—C13—H13	108.3
C4—C5—H5	119.7	C1—C13—H13	108.3
C6—C5—H5	119.7	C16—N14—C1 <sup>i</sup>	113.80 (10)
C5—C6—C7	119.40 (14)	C16—N14—C1	113.80 (10)
C5—C6—H6	120.3	C1 <sup>i</sup> —N14—C1	108.27 (15)
C7—C6—H6	120.3	C13—C15—H15A	109.5
O8—C7—C6	123.03 (14)	C13—C15—H15B	109.5
O8—C7—C2	116.00 (12)	H15A—C15—H15B	109.5
C6—C7—C2	120.97 (14)	C13—C15—H15C	109.5
C7—O8—C9	118.82 (11)	H15A—C15—H15C	109.5
O8—C9—C10	106.99 (12)	H15B—C15—H15C	109.5
O8—C9—H9A	110.3	N14—C16—H16A	109.5
C10—C9—H9A	110.3	N14—C16—H16B	109.4
O8—C9—H9B	110.3	H16A—C16—H16B	109.5
C10—C9—H9B	110.3		
N14—C1—C2—C3	80.51 (18)	C2—C7—O8—C9	159.44 (13)
C13—C1—C2—C3	-41.84 (19)	C7—O8—C9—C10	-161.82 (12)
N14—C1—C2—C7	-96.59 (16)	O8—C9—C10—O11	67.31 (16)
C13—C1—C2—C7	141.06 (13)	C9—C10—O11—C10 <sup>i</sup>	-171.15 (10)
C7—C2—C3—C4	0.1 (2)	O12—C12—C13—C15	-1.4 (2)
C1—C2—C3—C4	-177.05 (14)	C13 <sup>i</sup> —C12—C13—C15	-178.58 (11)
C2—C3—C4—C5	0.3 (2)	O12—C12—C13—C1	122.9 (2)
C3—C4—C5—C6	-0.1 (2)	C13 <sup>i</sup> —C12—C13—C1	-54.2 (2)
C4—C5—C6—C7	-0.5 (2)	N14—C1—C13—C12	58.80 (16)
C5—C6—C7—O8	-179.15 (14)	C2—C1—C13—C12	-176.87 (13)
C5—C6—C7—C2	0.9 (2)	N14—C1—C13—C15	-178.02 (12)
C3—C2—C7—O8	179.34 (13)	C2—C1—C13—C15	-53.68 (16)
C1—C2—C7—O8	-3.41 (19)	C2—C1—N14—C16	38.57 (19)
C3—C2—C7—C6	-0.7 (2)	C13—C1—N14—C16	163.56 (14)
C1—C2—C7—C6	176.59 (13)	C2—C1—N14—C1 <sup>i</sup>	166.15 (9)
C6—C7—O8—C9	-20.6 (2)	C13—C1—N14—C1 <sup>i</sup>	-68.85 (18)

Symmetry code: (i)  $x, -y+1/2, z$ .*Hydrogen-bond geometry* ( $\text{\AA}, ^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C10—H10B $\cdots$ O12 <sup>ii</sup>	0.99	2.58	3.449 (2)	147



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C16—H16B···O11	0.96	2.57	3.530 (3)	180
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Symmetry code: (ii)  $x-1/2, -y+1/2, -z-1/2$ .