

Received 12 August 2016

Accepted 11 September 2016

Edited by G. Smith, Queensland University of  
Technology, Australia**Keywords:** intramolecular Diels–Alder furan  
(IMDAF) reaction; azaheterocycles; epimeriza-  
tion; tautomerism; crystal structure.**CCDC references:** 1503860; 1503859**Supporting information:** this article has  
supporting information at journals.iucr.org/e

# Crystal structures of the two epimers from the unusual thermal C6-epimerization of 5-oxo-1,2,3,5,5a,6,7,9b-octahydro-7,9a-epoxy-pyrrolo[2,1-*a*]isoindole-6-carboxylic acid, 5a(*RS*),6(*SR*),7(*RS*),9a(*SR*),9b(*SR*) and 5a(*RS*),6(*RS*),7(*RS*),9a(*SR*),9b(*SR*)

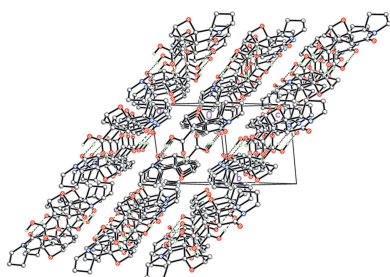
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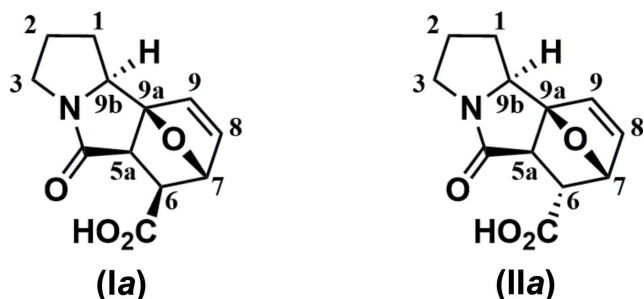
The isomeric title compounds, C<sub>12</sub>H<sub>13</sub>NO<sub>4</sub> (*Ia*) and C<sub>12</sub>H<sub>13</sub>NO<sub>4</sub> (*IIa*), the products of an usual thermal C6-epimerization of 5-oxo-1,2,3,5,5a,6,7,9b-octahydro-7,9a-epoxypyrrolo[2,1-*a*]isoindole-6-carboxylic acid, represent the two different diastereomers and have very similar molecular geometries. The molecules of both compounds comprise a fused tetracyclic system containing four five-membered rings (pyrrolidine, pyrrolidinone, dihydrofuran and tetrahydrofuran), all of which adopt the usual envelope conformations. The dihedral angle between the basal planes of the pyrrolidine and pyrrolidinone rings are 14.3 (2) and 16.50 (11)°, respectively, for (*Ia*) and (*IIa*). The nitrogen atom has a slightly pyramidalized geometry [bond-angle sum = 355.9 and 355.3°, for (*Ia*) and (*IIa*)], respectively. In the crystal of (*Ia*), molecules form zigzag-like hydrogen-bonded chains along [010] through strong O—H···O hydrogen bonds and are further linked by weak C—H···O hydrogen bonds into complex two-tier layers parallel to (100). Unlike (*Ia*), the crystal of (*IIa*) contains centrosymmetric cyclic hydrogen-bonded dimers [graph set R<sub>2</sub><sup>2</sup>(14)], formed through strong O—H···O hydrogen bonds and are further linked by weak C—H···O hydrogen bonds into ribbons extending across [101].

## 1. Chemical context

The intramolecular Diels–Alder furan (IMDAF) reaction between  $\alpha,\beta$ -unsaturated acid anhydrides and hydrogenated heterocycles, containing a furfurylamine moiety, has been studied for a long time (see, for example, Parker & Adamchuk, 1978; Blokzijl *et al.*, 1991; Varlamov *et al.*, 2006; Groenendaal *et al.*, 2008; Nakamura *et al.*, 2011; Zubkov *et al.*, 2011, 2012, 2014; Toze *et al.*, 2015) and used for diastereospecific synthesis of diverse fused-ring systems. It is arguable that the pathway with a simultaneous controlled formation of four or five new stereogenic centers is the best approach to epoxyisoindoles and affords target adducts under mild conditions with satisfactory yields. However, the simplest 2-furyl azaheterocycles (azetidene, pyrrolidine, piperidine, perhydroazepine) have not yet been studied in this reaction. One of the goals of our work is to fill the gap. Here we report on the



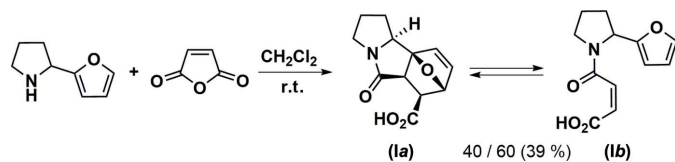
utilization of 2-furyl pyrrolidine as an initial reagent in the IMDAF reaction.



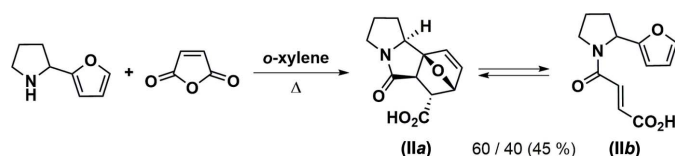
The interaction between 2-furyl pyrrolidine and maleic anhydride at room temperature leads to the mixture of cyclic (*Ia*) and open-chain (*Ib*) tautomers, the crystallization of which results in the cyclic form (*Ia*) only (Fig. 1). In contrast, the same reaction at 413 K leads to the maleic amide fragment isomerization and affords a mixture of the adduct (*IIa*) and the amide (*IIb*) (Fig. 2). Similarly, the mixture crystallization gives rise the cyclic tautomer (*IIa*) only. The crystal structures of both (*Ia*) and (*IIa*) using synchrotron X-ray diffraction data have been determined and are reported herein.

## 2. Structural commentary

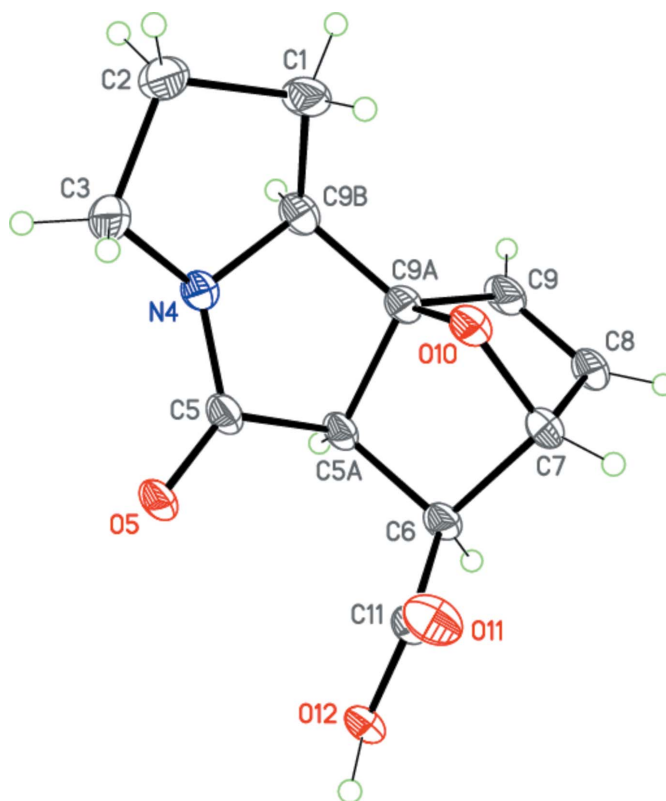
Compounds (*Ia*) and (*IIa*) represent two different diastereomers of 5-oxo-1,2,3,5,5a,6,7,9b-octahydro-7,9a-epoxypyrrolo[2,1-*a*]isindole-6-carboxylic acid and have very similar molecular geometries (Figs. 3, 4). The molecules of (*Ia*) and (*IIa*) each comprise a fused tetracyclic system containing four five-membered rings (pyrrolidine, pyrrolidinone, dihydrofuran and tetrahydrofuran), all of which adopt the usual envelope conformations. The dihedral angles between the basal planes of the pyrrolidine and pyrrolidinone rings are 14.3 (2) and 16.50 (11)°, respectively, for (*Ia*) and (*IIa*). The nitrogen N4 atom has a slightly pyramidalized geometry [sum of the bond angles = 355.9 and 355.3°, respectively, for (*Ia*) and (*IIa*)]. The bond lengths and angles in both epimers are in good agree-



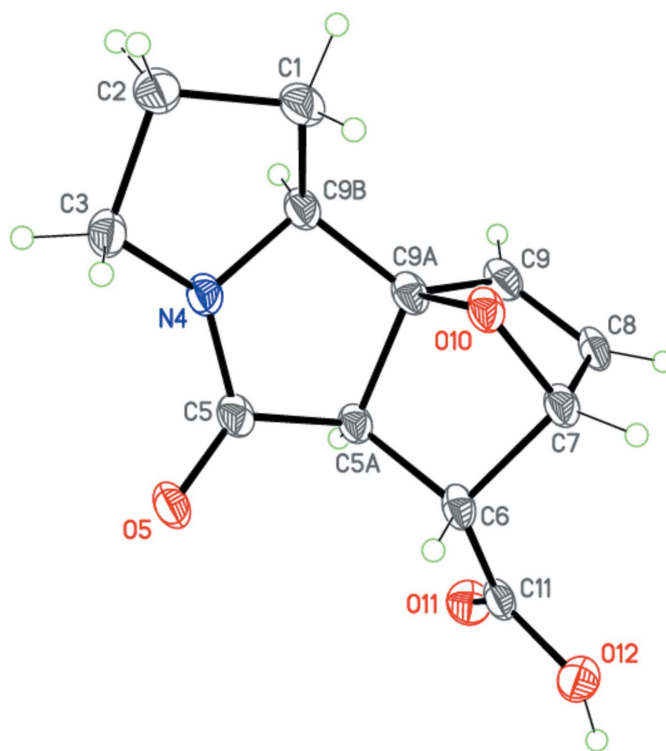
**Figure 1**  
Reaction of 2-furyl pyrrolidine and maleic anhydride at room temperature.



**Figure 2**  
Reaction of 2-furyl pyrrolidine and maleic anhydride at 413 K.



**Figure 3**  
Molecular structure and atom-numbering scheme for epimer (*Ia*). Displacement ellipsoids are drawn at the 50% probability level. H atoms are presented as small spheres of arbitrary radius.



**Figure 4**  
Molecular structure and atom-numbering scheme for epimer (*IIa*). Displacement ellipsoids are drawn at the 50% probability level. H atoms are presented as small spheres of arbitrary radius.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O12-H12\cdots O5^i$	0.90 (3)	1.75 (3)	2.613 (2)	157 (3)
$C5A-H5A\cdots O12^{ii}$	1.00	2.51	3.234 (3)	129

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O12-H12\cdots O5^i$	0.92	1.70	2.607 (2)	165
$C9-H9\cdots O11^{ii}$	0.95	2.42	3.362 (3)	172

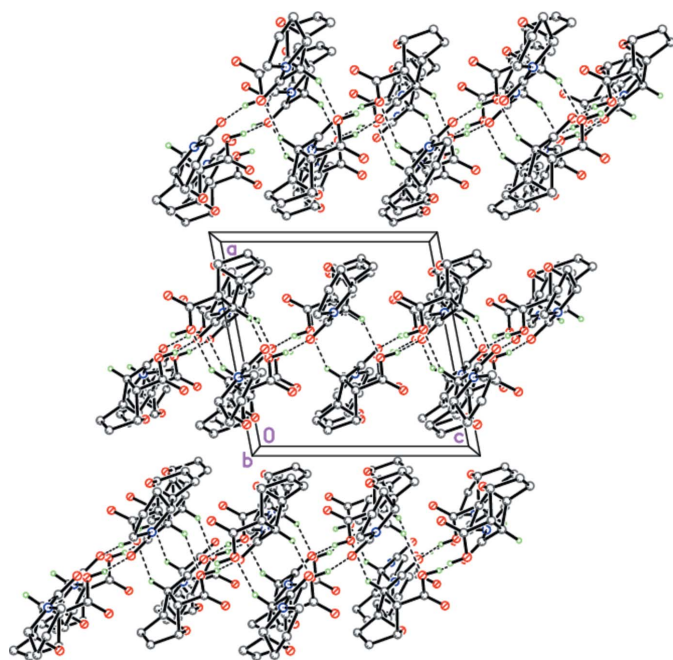
Symmetry codes: (i)  $-x + 2, -y + 1, -z + 1$ ; (ii)  $-x + 1, -y + 1, -z$ .

ment with those observed in a related structure (Lu *et al.*, 2013).

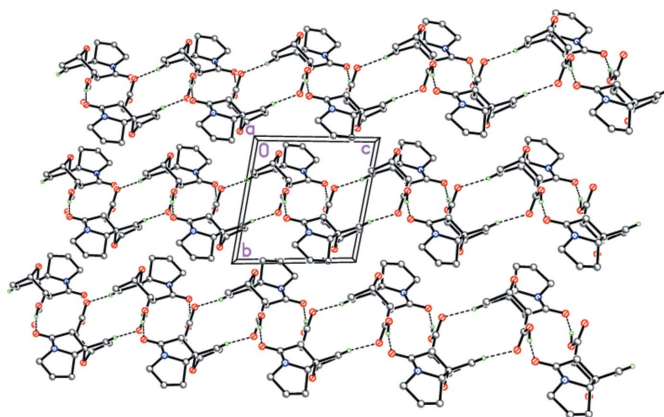
The molecules possess five asymmetric centers at the C5, C6, C7, C9a and C9b carbon atoms. The crystals of (Ia) and (IIa) are racemic and consist of enantiomeric pairs with the following relative configurations of the centers: 5a(*RS*),6(*SR*),7(*RS*),9a(*SR*),9b(*SR*) and 5a(*RS*),6(*RS*),7(*RS*),9a(*SR*),9b(*SR*)

### 3. Supramolecular features

Although the similarity of the molecular geometries might lead to similar packing motifs, this is not found in the case of (Ia) and (IIa). The intermolecular interactions, namely strong



**Figure 5**  
Crystal structure of (Ia) showing the two-tier layers parallel to (100). Dashed lines indicate the intermolecular  $O-H\cdots O$  and  $C-H\cdots O$  hydrogen bonds.



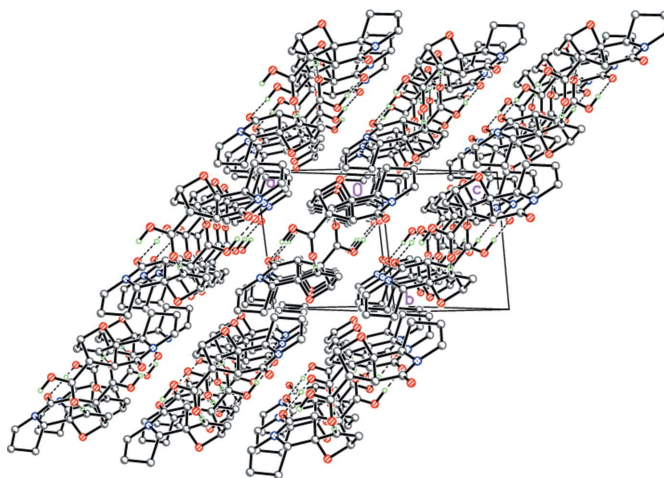
**Figure 6**  
The hydrogen-bonded chains of (IIa). Dashed lines indicate the intermolecular  $O-H\cdots O$  and  $C-H\cdots O$  hydrogen bonds.

$O-H\cdots O$  and weak  $C-H\cdots O$  hydrogen bonding, combined in a different way, give rise to different packing networks. In the crystal of (Ia), molecules form zigzag-like hydrogen-bonded chains extending along [010] through strong  $O12-H12\cdots O5^i$  hydrogen bonds, which are further linked by weak  $C5A-H5A\cdots O12^{ii}$  hydrogen bonds into complex two-tier layers lying parallel to (100) (Table 1, Fig. 5).

However, unlike (Ia), the crystal of (IIa) contains centrosymmetric hydrogen-bonded cyclic dimers [graph set  $R_2^2(14)$ ], formed through two strong  $O12-H12\cdots O5^i$  hydrogen bonds (Table 2, Fig. 6). The dimers are further linked by weak  $C9-H9\cdots O11^{ii}$  hydrogen bonds into ribbons extending across [101] (Table 2, Figs. 6 and 7).

### 4. Synthesis and crystallization

The initial 2-furyl pyrrolidine was synthesized according to the procedure described previously (Acher *et al.*, 1981; Shono *et al.*, 1981; Nikolic & Beak, 1997).



**Figure 7**  
Crystal structure of (IIa) along [101]. Dashed lines indicate the intermolecular  $O-H\cdots O$  and  $C-H\cdots O$  hydrogen bonds.

**Table 3**  
Experimental details.

	(Ia)	(IIa)
Crystal data		
Chemical formula	C <sub>12</sub> H <sub>13</sub> NO <sub>4</sub>	C <sub>12</sub> H <sub>13</sub> NO <sub>4</sub>
<i>M<sub>r</sub></i>	235.23	235.23
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.045 (2), 9.2023 (18), 11.062 (2)	8.4700 (17), 8.5100 (17), 8.5900 (17)
$\alpha$ , $\beta$ , $\gamma$ (°)	90, 100.91 (3), 90	94.04 (3), 111.12 (3), 105.17 (3)
<i>V</i> (Å <sup>3</sup> )	1104.1 (4)	548.0 (2)
<i>Z</i>	4	2
Radiation type	Synchrotron, $\lambda = 0.96990$ Å	Synchrotron, $\lambda = 0.96990$ Å
$\mu$ (mm <sup>-1</sup> )	0.23	0.23
Crystal size (mm)	0.20 × 0.15 × 0.15	0.15 × 0.10 × 0.10
Data collection		
Diffractometer	MAR CCD	MAR CCD
Absorption correction	Multi-scan ( <i>SCALA</i> ; Evans, 2006)	Multi-scan ( <i>SCALA</i> ; Evans, 2006)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.950, 0.960	0.960, 0.969
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	12183, 2329, 1864	7090, 2104, 1402
<i>R</i> <sub>int</sub>	0.085	0.061
(sin $\theta$ /λ) <sub>max</sub> (Å <sup>-1</sup> )	0.641	0.637
Refinement		
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.072, 0.189, 1.02	0.099, 0.240, 0.93
No. of reflections	2329	2104
No. of parameters	158	155
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.43, -0.43	0.45, -0.36

Computer programs: *Automar* (MarXperts, 2015), *iMOSFLM* (Battye *et al.*, 2011), *SHELXS97* and *SHELXTL* (Sheldrick, 2008) and *SHELXL2014* (Sheldrick, 2015).

**Synthesis of (Ia).** A mixture of the initial 2-furyl pyrrolidine (0.30 g, 2.2 mmol) and maleic anhydride (0.23 g, 2.3 mmol) in dichloromethane (6 mL) was stirred for 5 h at r.t. [monitoring by TLC until disappearance of the starting compound spot, eluent–EtOAc: hexane (1:3), Sorbfil]. On completion of the reaction, the solvent was evaporated. The isomer (Ia) was isolated as fine needles by slow recrystallization of the residue from a mixture of EtOAc–EtOH. Yield 39%; m.p. = 413–414 K. IR (KBr),  $\nu$  (cm<sup>-1</sup>): 1734, 1654. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 300 K):  $\delta$  = 1.98–1.69 (*m*, 4H, H1a, H1b, H2a, H2b), 2.42 (*d*, 1H, H6, *J*<sub>6,5a</sub> = 9.1), 2.94–2.88 (*m*, 2H, H3a, H3b), 3.10 (*d*, 1H, H5a, *J*<sub>5a,6</sub> = 9.1), 4.41 (*t*, 1H, H9b, *J*<sub>9b,1a</sub> = 7.5, *J*<sub>9b,1b</sub> = 7.5), 4.97 (*d*, 1H, H7, *J*<sub>7,8</sub> = 1.6), 6.44 (*dd*, 1H, H8, *J*<sub>8,9</sub> = 5.5, *J*<sub>8,7</sub> = 1.6), 6.54 (*d*, 1H, H9, *J*<sub>9,8</sub> = 5.5). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, 300 K):  $\delta$  = 23.5, 26.2, 41.9 (C1, C2, C3), 46.9, 53.8 (C6, C5a), 60.0 (C9b), 80.5 (C7), 93.5 (C9a), 133.9 (C9), 137.1 (C8), 171.7, 173.2 (NCO, COOH). EI–MS (70 eV), *m/z* (rel. intensity): 235 (22), 217 (91), 137 (41), 136 (100), 108 (39), 80 (45), 70 (32), 54 (29), 42 (25).

**Synthesis of (IIa).** A mixture of the initial 2-furyl pyrrolidine (0.3 g, 2.2 mmol) and maleic anhydride (0.23 g, 2.3 mmol) in *o*-xylene (6 mL) was heated at reflux for 3 h. At the end of the reaction, the solvent was evaporated. The isomer (IIa) was isolated as fine needles by slow recrystallization of the residue from a mixture of EtOAc–EtOH. Yield: 0.33 45%; m.p. = 414–416 K. IR (KBr),  $\nu$  (cm<sup>-1</sup>): 1738, 1658. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 300 K):  $\delta$  = 1.82–1.64 (*m*, 4H, H1a, H1b, H2a, H2b), 3.02 (*d*, 1H, H5a, *J*<sub>5a,6</sub> = 3.4), 3.17 (*dd*, 1H, H6, *J*<sub>6,5a</sub> = 3.4, *J*<sub>6,5a</sub> =

3.4), 3.36–3.32 (*m*, 2H, H3a, H3b), 4.52 (*t*, 1H, H9b, *J*<sub>9b,1a</sub> = 7.6, *J*<sub>9b,1b</sub> = 7.6), 5.20 (*dd*, 1H, H7, *J*<sub>7,8</sub> = 1.6, *J*<sub>7,6</sub> = 4.8), 6.34 (*dd*, 1H, H8, *J*<sub>8,9</sub> = 5.8, *J*<sub>8,7</sub> = 1.6), 6.66 (*d*, 1H, H9, *J*<sub>9,8</sub> = 5.8). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, 300 K):  $\delta$  = 23.5, 26.2, 42.1 (C1, C2, C3), 47.0, 55.1 (C6, C5a), 61.0 (C9b), 79.2 (C7), 93.5 (C9a), 133.9 (C8), 135.2 (C9), 171.7, 173.2 (NCO, COOH). EI–MS (70 eV), *m/z* (rel. intensity): 235 (22), 217 (91), 137 (41), 136 (100), 108 (39), 80 (45), 70 (32), 54 (38), 45 (29), 42 (25).

## 5. Refinement

Crystal data, data collection and refinement details are summarized in Table 3. X-ray diffraction studies were carried out on the ‘Belok’ beamline ( $\lambda = 0.96990$  Å) of the National Research Center “Kurchatov Institute” (Moscow, Russian Federation) using a MAR CCD detector.

The hydrogen atoms of the hydroxyl groups were localized in the difference-Fourier maps and refined in an isotropic approximation with fixed displacement parameters [*U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(O)] [for (Ia)] or included in the refinement with fixed positional (riding model) and isotropic displacement parameters [*U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(O)] [for (IIa)]. Other hydrogen atoms were placed in calculated positions with C–H = 0.95–1.00 Å and refined in the riding model with fixed isotropic displacement parameters [*U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C)].

The insufficient data completeness of 94.1% in the case of (IIa) is the result of the low (triclinic) crystal symmetry, making it very difficult to obtain good data completeness using

the  $\varphi$  scan mode only ('Belok' beamline limitation), even though we have used the two different crystal orientations.

### Acknowledgements

This work was supported by the Ministry of Education and Science of the Russian Federation (Agreement 02.a03.21.0008), and the Russian Foundation for Basic Research (grant No. 15-33-50016).

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## supporting information

*Acta Cryst.* (2016). E72, 1429-1433 [doi:10.1107/S2056989016014420]

**Crystal structures of the two epimers from the unusual thermal C6-epimerization of 5-oxo-1,2,3,5,5a,6,7,9b-octahydro-7,9a-epoxypyrrolo[2,1-a]isoindole-6-carboxylic acid, 5a(*RS*),6(*SR*),7(*RS*),9a(*SR*),9b(*SR*) and 5a(*RS*),6(*RS*),7(*RS*),9a(*SR*),9b(*SR*)**

**Dmitry S. Poplevin, Fedor I. Zubkov, Pavel V. Dorovatovskii, Yan V. Zubavichus and Victor N. Khrustalev**

**Computing details**

For both compounds, data collection: *Automar* (MarXperts, 2015); cell refinement: *iMOSFLM* (Battye *et al.*, 2011); data reduction: *iMOSFLM* (Battye *et al.*, 2011); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

**(1a) 5a(*RS*),6(*SR*),7(*RS*),9a(*SR*),9b(*SR*)-5-Oxo-1,2,3,5,5a,6,7,9b-octahydro-7,9a-epoxypyrrolo[2,1-a]isoindole-6-carboxylic acid**

*Crystal data*

C<sub>12</sub>H<sub>13</sub>NO<sub>4</sub>

*M<sub>r</sub>* = 235.23

Monoclinic, *P*2<sub>1</sub>/*c*

*a* = 11.045 (2) Å

*b* = 9.2023 (18) Å

*c* = 11.062 (2) Å

β = 100.91 (3)°

*V* = 1104.1 (4) Å<sup>3</sup>

*Z* = 4

*F*(000) = 496

*D<sub>x</sub>* = 1.415 Mg m<sup>-3</sup>

Melting point = 413–414 K

Synchrotron radiation, λ = 0.96990 Å

Cell parameters from 600 reflections

θ = 4.5–38.0°

μ = 0.23 mm<sup>-1</sup>

*T* = 100 K

Prism, colourless

0.20 × 0.15 × 0.15 mm

*Data collection*

MAR CCD

diffractometer

φ scan

Absorption correction: multi-scan

(*SCALA*; Evans, 2006)

*T<sub>min</sub>* = 0.950, *T<sub>max</sub>* = 0.960

12183 measured reflections

2329 independent reflections

1864 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.085

θ<sub>max</sub> = 38.5°, θ<sub>min</sub> = 4.5°

*h* = -13→14

*k* = -11→10

*l* = -13→13

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.072$

$wR(F^2) = 0.189$

$S = 1.02$

2329 reflections

158 parameters

0 restraints

Primary atom site location: difference Fourier map

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.08P)^2 + 1.P]$

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

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

$\Delta\rho_{\max} = 0.43 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.43 \text{ e } \text{\AA}^{-3}$

Extinction correction: SHELXL-2014/7 (Sheldrick, 2015),

$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.104 (9)

*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>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.8345 (2)	0.9330 (3)	0.5467 (2)	0.0330 (6)
H1A	0.8888	0.8929	0.4933	0.040*
H1B	0.8859	0.9780	0.6202	0.040*
C2	0.7415 (2)	1.0430 (3)	0.4762 (2)	0.0349 (6)
H2A	0.7799	1.1002	0.4177	0.042*
H2B	0.7123	1.1106	0.5341	0.042*
C3	0.6333 (2)	0.9507 (3)	0.4064 (2)	0.0312 (6)
H3A	0.5531	0.9989	0.4059	0.037*
H3B	0.6426	0.9320	0.3205	0.037*
N4	0.64418 (17)	0.8166 (2)	0.47832 (17)	0.0272 (5)
C5	0.60154 (19)	0.6839 (2)	0.4418 (2)	0.0253 (5)
O5	0.52224 (14)	0.65677 (18)	0.34888 (14)	0.0280 (5)
C5A	0.66529 (19)	0.5736 (2)	0.53586 (19)	0.0236 (5)
H5A	0.6166	0.5553	0.6019	0.028*
C6	0.7153 (2)	0.4306 (2)	0.4908 (2)	0.0254 (5)
H6	0.7007	0.3500	0.5470	0.030*
C7	0.8561 (2)	0.4655 (3)	0.5143 (2)	0.0296 (6)
H7	0.9050	0.4068	0.4645	0.035*
C8	0.9021 (2)	0.4591 (3)	0.6528 (2)	0.0330 (6)
H8	0.9504	0.3847	0.6980	0.040*
C9	0.8604 (2)	0.5799 (3)	0.6976 (2)	0.0302 (6)
H9	0.8737	0.6103	0.7812	0.036*
C9A	0.7874 (2)	0.6583 (2)	0.5868 (2)	0.0251 (5)
C9B	0.7500 (2)	0.8164 (3)	0.5827 (2)	0.0291 (6)
H9B	0.7224	0.8442	0.6606	0.035*
O10	0.85603 (14)	0.62038 (18)	0.49215 (14)	0.0276 (4)
C11	0.6649 (2)	0.3852 (2)	0.3585 (2)	0.0251 (5)

O11	0.71540 (16)	0.4123 (2)	0.27256 (16)	0.0374 (5)
O12	0.56401 (14)	0.30469 (18)	0.35042 (15)	0.0265 (4)
H12	0.539 (3)	0.275 (3)	0.272 (3)	0.040*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0350 (13)	0.0293 (13)	0.0289 (12)	-0.0063 (9)	-0.0086 (10)	-0.0015 (9)
C2	0.0433 (15)	0.0252 (13)	0.0318 (14)	-0.0031 (10)	-0.0039 (11)	0.0009 (9)
C3	0.0333 (13)	0.0261 (13)	0.0304 (13)	0.0025 (9)	-0.0033 (10)	0.0043 (9)
N4	0.0257 (10)	0.0236 (11)	0.0278 (10)	0.0004 (7)	-0.0064 (8)	0.0017 (7)
C5	0.0192 (10)	0.0290 (12)	0.0246 (11)	-0.0003 (8)	-0.0036 (8)	0.0016 (8)
O5	0.0233 (8)	0.0293 (9)	0.0259 (9)	-0.0010 (6)	-0.0098 (6)	0.0025 (6)
C5A	0.0190 (10)	0.0270 (12)	0.0214 (11)	-0.0001 (8)	-0.0052 (8)	0.0018 (8)
C6	0.0229 (11)	0.0254 (12)	0.0235 (11)	-0.0011 (8)	-0.0066 (8)	0.0011 (8)
C7	0.0215 (11)	0.0309 (13)	0.0314 (13)	0.0017 (9)	-0.0075 (9)	-0.0039 (9)
C8	0.0252 (11)	0.0324 (13)	0.0334 (14)	0.0030 (9)	-0.0148 (9)	0.0008 (9)
C9	0.0268 (12)	0.0341 (14)	0.0237 (12)	-0.0021 (9)	-0.0102 (9)	0.0011 (9)
C9A	0.0231 (11)	0.0260 (12)	0.0226 (11)	-0.0001 (8)	-0.0045 (8)	-0.0008 (8)
C9B	0.0269 (12)	0.0323 (14)	0.0236 (11)	0.0001 (9)	-0.0066 (9)	-0.0003 (9)
O10	0.0222 (8)	0.0303 (9)	0.0276 (9)	-0.0023 (6)	-0.0023 (6)	-0.0015 (7)
C11	0.0221 (11)	0.0246 (12)	0.0254 (12)	0.0003 (8)	-0.0036 (8)	0.0000 (8)
O11	0.0352 (10)	0.0471 (12)	0.0276 (10)	-0.0085 (8)	0.0004 (7)	-0.0016 (7)
O12	0.0205 (8)	0.0301 (9)	0.0251 (9)	-0.0027 (6)	-0.0053 (6)	-0.0030 (6)

*Geometric parameters (Å, °)*

C1—C9B	1.524 (4)	C6—C11	1.522 (3)
C1—C2	1.544 (3)	C6—C7	1.561 (3)
C1—H1A	0.9900	C6—H6	1.0000
C1—H1B	0.9900	C7—O10	1.446 (3)
C2—C3	1.548 (3)	C7—C8	1.522 (3)
C2—H2A	0.9900	C7—H7	1.0000
C2—H2B	0.9900	C8—C9	1.334 (4)
C3—N4	1.461 (3)	C8—H8	0.9500
C3—H3A	0.9900	C9—C9A	1.516 (3)
C3—H3B	0.9900	C9—H9	0.9500
N4—C5	1.343 (3)	C9A—O10	1.447 (3)
N4—C9B	1.480 (3)	C9A—C9B	1.511 (3)
C5—O5	1.243 (3)	C9B—H9B	1.0000
C5—C5A	1.527 (3)	C11—O11	1.216 (3)
C5A—C6	1.546 (3)	C11—O12	1.327 (3)
C5A—C9A	1.568 (3)	O12—H12	0.90 (3)
C5A—H5A	1.0000		
C9B—C1—C2	102.2 (2)	C11—C6—H6	108.8
C9B—C1—H1A	111.3	C5A—C6—H6	108.8
C2—C1—H1A	111.3	C7—C6—H6	108.8



C9B—C1—H1B	111.3	O10—C7—C8	101.44 (18)
C2—C1—H1B	111.3	O10—C7—C6	101.91 (17)
H1A—C1—H1B	109.2	C8—C7—C6	107.0 (2)
C1—C2—C3	105.63 (19)	O10—C7—H7	115.0
C1—C2—H2A	110.6	C8—C7—H7	115.0
C3—C2—H2A	110.6	C6—C7—H7	115.0
C1—C2—H2B	110.6	C9—C8—C7	105.6 (2)
C3—C2—H2B	110.6	C9—C8—H8	127.2
H2A—C2—H2B	108.7	C7—C8—H8	127.2
N4—C3—C2	102.45 (18)	C8—C9—C9A	105.3 (2)
N4—C3—H3A	111.3	C8—C9—H9	127.3
C2—C3—H3A	111.3	C9A—C9—H9	127.3
N4—C3—H3B	111.3	O10—C9A—C9B	112.83 (19)
C2—C3—H3B	111.3	O10—C9A—C9	101.49 (18)
H3A—C3—H3B	109.2	C9B—C9A—C9	125.67 (19)
C5—N4—C3	128.07 (19)	O10—C9A—C5A	98.78 (16)
C5—N4—C9B	114.43 (18)	C9B—C9A—C5A	104.85 (17)
C3—N4—C9B	113.42 (18)	C9—C9A—C5A	110.12 (18)
O5—C5—N4	125.7 (2)	N4—C9B—C9A	101.29 (17)
O5—C5—C5A	126.3 (2)	N4—C9B—C1	103.16 (18)
N4—C5—C5A	108.04 (17)	C9A—C9B—C1	120.6 (2)
C5—C5A—C6	119.56 (18)	N4—C9B—H9B	110.3
C5—C5A—C9A	99.73 (17)	C9A—C9B—H9B	110.3
C6—C5A—C9A	101.74 (17)	C1—C9B—H9B	110.3
C5—C5A—H5A	111.5	C7—O10—C9A	95.65 (17)
C6—C5A—H5A	111.5	O11—C11—O12	124.4 (2)
C9A—C5A—H5A	111.5	O11—C11—C6	123.9 (2)
C11—C6—C5A	117.10 (17)	O12—C11—C6	111.56 (19)
C11—C6—C7	112.8 (2)	C11—O12—H12	109.4 (19)
C5A—C6—C7	100.16 (17)		
C9B—C1—C2—C3	-35.5 (3)	C6—C5A—C9A—O10	40.32 (19)
C1—C2—C3—N4	23.1 (3)	C5—C5A—C9A—C9B	33.7 (2)
C2—C3—N4—C5	-157.3 (2)	C6—C5A—C9A—C9B	156.88 (18)
C2—C3—N4—C9B	-1.6 (3)	C5—C5A—C9A—C9	171.42 (19)
C3—N4—C5—O5	-16.7 (4)	C6—C5A—C9A—C9	-65.4 (2)
C9B—N4—C5—O5	-172.2 (2)	C5—N4—C9B—C9A	13.2 (3)
C3—N4—C5—C5A	164.6 (2)	C3—N4—C9B—C9A	-146.0 (2)
C9B—N4—C5—C5A	9.0 (3)	C5—N4—C9B—C1	138.6 (2)
O5—C5—C5A—C6	45.6 (3)	C3—N4—C9B—C1	-20.6 (3)
N4—C5—C5A—C6	-135.7 (2)	O10—C9A—C9B—N4	77.5 (2)
O5—C5—C5A—C9A	155.1 (2)	C9—C9A—C9B—N4	-157.9 (2)
N4—C5—C5A—C9A	-26.1 (2)	C5A—C9A—C9B—N4	-29.0 (2)
C5—C5A—C6—C11	-18.4 (3)	O10—C9A—C9B—C1	-35.3 (3)
C9A—C5A—C6—C11	-126.8 (2)	C9—C9A—C9B—C1	89.3 (3)
C5—C5A—C6—C7	103.9 (2)	C5A—C9A—C9B—C1	-141.8 (2)
C9A—C5A—C6—C7	-4.5 (2)	C2—C1—C9B—N4	33.3 (2)
C11—C6—C7—O10	92.5 (2)	C2—C1—C9B—C9A	145.2 (2)

C5A—C6—C7—O10	−32.8 (2)	C8—C7—O10—C9A	−50.66 (19)
C11—C6—C7—C8	−161.48 (19)	C6—C7—O10—C9A	59.66 (18)
C5A—C6—C7—C8	73.2 (2)	C9B—C9A—O10—C7	−171.63 (16)
O10—C7—C8—C9	32.0 (3)	C9—C9A—O10—C7	51.38 (18)
C6—C7—C8—C9	−74.4 (2)	C5A—C9A—O10—C7	−61.36 (16)
C7—C8—C9—C9A	0.9 (3)	C5A—C6—C11—O11	95.3 (3)
C8—C9—C9A—O10	−33.6 (2)	C7—C6—C11—O11	−20.2 (3)
C8—C9—C9A—C9B	−162.9 (2)	C5A—C6—C11—O12	−88.8 (2)
C8—C9—C9A—C5A	70.3 (3)	C7—C6—C11—O12	155.70 (19)
C5—C5A—C9A—O10	−82.84 (18)		

*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>
O12—H12...O5 <sup>i</sup>	0.90 (3)	1.75 (3)	2.613 (2)	157 (3)
C5A—H5A...O12 <sup>ii</sup>	1.00	2.51	3.234 (3)	129

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

**(IIa) 5a(RS),6(RS),7(RS),9a(SR),9b(SR)-5-Oxo-1,2,3,5,5a,6,7,9b-octahydro-7,9a-epoxy pyrrolo[2,1-a]isoindole-6-carboxylic acid***Crystal data*C<sub>12</sub>H<sub>13</sub>NO<sub>4</sub>*M<sub>r</sub>* = 235.23Triclinic, *P*1̄*a* = 8.4700 (17) Å*b* = 8.5100 (17) Å*c* = 8.5900 (17) Å $\alpha$  = 94.04 (3)° $\beta$  = 111.12 (3)° $\gamma$  = 105.17 (3)°*V* = 548.0 (2) Å<sup>3</sup>*Z* = 2*F*(000) = 248*D<sub>x</sub>* = 1.426 Mg m<sup>−3</sup>

Melting point = 414–416 K

Synchrotron radiation,  $\lambda$  = 0.96990 Å

Cell parameters from 500 reflections

 $\theta$  = 3.6–36.0° $\mu$  = 0.23 mm<sup>−1</sup>*T* = 100 K

Prism, colourless

0.15 × 0.10 × 0.10 mm

*Data collection*

MAR CCD

diffractometer

 $\phi$  scan

Absorption correction: multi-scan

(SCALA; Evans, 2006)

*T<sub>min</sub>* = 0.960, *T<sub>max</sub>* = 0.969

7090 measured reflections

2104 independent reflections

1402 reflections with *I* > 2σ(*I*)*R<sub>int</sub>* = 0.061 $\theta_{\max}$  = 38.1°,  $\theta_{\min}$  = 3.4°*h* = −10→10*k* = −10→10*l* = −10→10*Refinement*Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.099*wR*(*F*<sup>2</sup>) = 0.240*S* = 0.93

2104 reflections

155 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

 $w = 1/[\sigma^2(F_o^2) + (0.06P)^2]$ where  $P = (F_o^2 + 2F_c^2)/3$

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

$$\Delta\rho_{\max} = 0.45 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.36 \text{ e } \text{\AA}^{-3}$$

Extinction correction: SHELXL-2014/7  
(Sheldrick, 2015),  
 $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$   
Extinction coefficient: 0.138 (11)

### 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	0.1779 (3)	0.0068 (2)	0.2264 (2)	0.0322 (5)
H1A	0.0733	-0.0331	0.1171	0.039*
H1B	0.2531	-0.0668	0.2374	0.039*
C2	0.1215 (3)	0.0169 (2)	0.3765 (2)	0.0324 (5)
H2A	0.0900	-0.0932	0.4081	0.039*
H2B	0.0181	0.0592	0.3486	0.039*
C3	0.2874 (2)	0.1392 (2)	0.5222 (2)	0.0288 (5)
H3A	0.2529	0.2089	0.5934	0.035*
H3B	0.3628	0.0797	0.5949	0.035*
N4	0.37879 (19)	0.23864 (17)	0.42848 (16)	0.0261 (4)
C5	0.5531 (2)	0.3199 (2)	0.4832 (2)	0.0250 (4)
O5	0.65982 (17)	0.35299 (15)	0.63512 (13)	0.0299 (3)
C5A	0.5950 (2)	0.3619 (2)	0.3297 (2)	0.0233 (4)
H5A	0.5949	0.4769	0.3127	0.028*
C6	0.7574 (2)	0.32415 (19)	0.3142 (2)	0.0245 (4)
H6	0.8150	0.2754	0.4140	0.029*
C7	0.6593 (3)	0.1818 (2)	0.1503 (2)	0.0276 (5)
H7	0.7338	0.1138	0.1333	0.033*
C8	0.5722 (2)	0.2548 (2)	-0.0027 (2)	0.0264 (5)
H8	0.6108	0.2775	-0.0921	0.032*
C9	0.4292 (3)	0.2805 (2)	0.0152 (2)	0.0284 (5)
H9	0.3431	0.3223	-0.0598	0.034*
C9A	0.4358 (2)	0.2276 (2)	0.1826 (2)	0.0256 (5)
C9B	0.2840 (2)	0.1875 (2)	0.24142 (19)	0.0267 (5)
H9B	0.2022	0.2541	0.1950	0.032*
O10	0.51146 (16)	0.09341 (13)	0.18544 (14)	0.0258 (3)
C11	0.8967 (2)	0.4657 (2)	0.2990 (2)	0.0259 (5)
O11	0.88416 (17)	0.60281 (15)	0.27854 (15)	0.0338 (4)
O12	1.04071 (16)	0.42233 (14)	0.31124 (15)	0.0312 (4)
H12	1.1355	0.5093	0.3163	0.047*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0352 (10)	0.0244 (9)	0.0294 (8)	-0.0016 (8)	0.0132 (7)	-0.0032 (7)

C2	0.0364 (10)	0.0254 (9)	0.0311 (8)	-0.0003 (8)	0.0158 (7)	0.0030 (7)
C3	0.0365 (9)	0.0234 (9)	0.0290 (8)	0.0035 (8)	0.0201 (6)	0.0019 (7)
N4	0.0308 (8)	0.0214 (7)	0.0246 (6)	0.0012 (6)	0.0152 (5)	-0.0014 (5)
C5	0.0316 (9)	0.0159 (7)	0.0263 (8)	0.0045 (7)	0.0131 (6)	-0.0028 (6)
O5	0.0364 (7)	0.0281 (6)	0.0205 (5)	0.0017 (5)	0.0130 (4)	-0.0033 (5)
C5A	0.0284 (9)	0.0177 (8)	0.0227 (7)	0.0022 (7)	0.0131 (6)	-0.0005 (6)
C6	0.0355 (9)	0.0164 (8)	0.0232 (7)	0.0043 (7)	0.0165 (6)	0.0005 (6)
C7	0.0335 (9)	0.0192 (8)	0.0277 (8)	-0.0004 (7)	0.0169 (6)	-0.0048 (6)
C8	0.0373 (10)	0.0199 (8)	0.0209 (7)	0.0025 (7)	0.0158 (6)	-0.0026 (6)
C9	0.0368 (10)	0.0211 (8)	0.0229 (8)	0.0029 (8)	0.0118 (7)	-0.0001 (6)
C9A	0.0344 (9)	0.0168 (8)	0.0239 (7)	0.0043 (7)	0.0128 (6)	0.0000 (6)
C9B	0.0327 (9)	0.0214 (8)	0.0240 (8)	0.0032 (7)	0.0134 (6)	-0.0021 (6)
O10	0.0337 (6)	0.0164 (5)	0.0277 (5)	0.0033 (5)	0.0165 (4)	-0.0009 (4)
C11	0.0316 (9)	0.0227 (9)	0.0204 (7)	0.0024 (7)	0.0126 (6)	-0.0045 (6)
O11	0.0375 (7)	0.0228 (6)	0.0390 (6)	0.0042 (6)	0.0170 (5)	0.0031 (5)
O12	0.0309 (7)	0.0232 (6)	0.0403 (6)	0.0040 (5)	0.0189 (5)	0.0015 (5)

*Geometric parameters (Å, °)*

C1—C2	1.532 (3)	C6—C11	1.500 (3)
C1—C9B	1.534 (3)	C6—C7	1.590 (2)
C1—H1A	0.9900	C6—H6	1.0000
C1—H1B	0.9900	C7—O10	1.427 (2)
C2—C3	1.552 (2)	C7—C8	1.521 (3)
C2—H2A	0.9900	C7—H7	1.0000
C2—H2B	0.9900	C8—C9	1.344 (3)
C3—N4	1.472 (2)	C8—H8	0.9500
C3—H3A	0.9900	C9—C9A	1.522 (2)
C3—H3B	0.9900	C9—H9	0.9500
N4—C5	1.341 (2)	C9A—O10	1.446 (2)
N4—C9B	1.485 (2)	C9A—C9B	1.513 (3)
C5—O5	1.250 (2)	C9B—H9B	1.0000
C5—C5A	1.526 (3)	C11—O11	1.218 (2)
C5A—C6	1.540 (3)	C11—O12	1.336 (2)
C5A—C9A	1.576 (2)	O12—H12	0.9239
C5A—H5A	1.0000		
C2—C1—C9B	102.15 (14)	C11—C6—H6	108.7
C2—C1—H1A	111.3	C5A—C6—H6	108.7
C9B—C1—H1A	111.3	C7—C6—H6	108.7
C2—C1—H1B	111.3	O10—C7—C8	102.71 (15)
C9B—C1—H1B	111.3	O10—C7—C6	99.48 (13)
H1A—C1—H1B	109.2	C8—C7—C6	109.15 (14)
C1—C2—C3	104.39 (16)	O10—C7—H7	114.6
C1—C2—H2A	110.9	C8—C7—H7	114.6
C3—C2—H2A	110.9	C6—C7—H7	114.6
C1—C2—H2B	110.9	C9—C8—C7	105.52 (17)
C3—C2—H2B	110.9	C9—C8—H8	127.2

H2A—C2—H2B	108.9	C7—C8—H8	127.2
N4—C3—C2	102.16 (13)	C8—C9—C9A	104.59 (17)
N4—C3—H3A	111.3	C8—C9—H9	127.7
C2—C3—H3A	111.3	C9A—C9—H9	127.7
N4—C3—H3B	111.3	O10—C9A—C9B	111.77 (14)
C2—C3—H3B	111.3	O10—C9A—C9	102.12 (14)
H3A—C3—H3B	109.2	C9B—C9A—C9	126.44 (16)
C5—N4—C3	127.10 (15)	O10—C9A—C5A	100.18 (14)
C5—N4—C9B	115.10 (15)	C9B—C9A—C5A	105.83 (13)
C3—N4—C9B	113.07 (13)	C9—C9A—C5A	107.50 (14)
O5—C5—N4	124.50 (18)	N4—C9B—C9A	102.11 (13)
O5—C5—C5A	127.21 (17)	N4—C9B—C1	101.06 (14)
N4—C5—C5A	108.28 (14)	C9A—C9B—C1	120.38 (16)
C5—C5A—C6	117.75 (15)	N4—C9B—H9B	110.7
C5—C5A—C9A	101.00 (14)	C9A—C9B—H9B	110.7
C6—C5A—C9A	101.86 (13)	C1—C9B—H9B	110.7
C5—C5A—H5A	111.7	C7—O10—C9A	96.02 (13)
C6—C5A—H5A	111.7	O11—C11—O12	123.30 (17)
C9A—C5A—H5A	111.7	O11—C11—C6	125.93 (18)
C11—C6—C5A	117.00 (15)	O12—C11—C6	110.77 (15)
C11—C6—C7	113.55 (15)	C11—O12—H12	113.8
C5A—C6—C7	99.72 (13)		
C9B—C1—C2—C3	-40.2 (2)	C6—C5A—C9A—O10	32.99 (16)
C1—C2—C3—N4	24.99 (19)	C5—C5A—C9A—C9B	27.56 (18)
C2—C3—N4—C5	-154.32 (18)	C6—C5A—C9A—C9B	149.26 (14)
C2—C3—N4—C9B	-0.1 (2)	C5—C5A—C9A—C9	165.01 (15)
C3—N4—C5—O5	-16.0 (3)	C6—C5A—C9A—C9	-73.29 (18)
C9B—N4—C5—O5	-169.80 (16)	C5—N4—C9B—C9A	8.4 (2)
C3—N4—C5—C5A	163.66 (15)	C3—N4—C9B—C9A	-149.09 (15)
C9B—N4—C5—C5A	9.9 (2)	C5—N4—C9B—C1	133.04 (17)
O5—C5—C5A—C6	47.1 (2)	C3—N4—C9B—C1	-24.4 (2)
N4—C5—C5A—C6	-132.62 (15)	O10—C9A—C9B—N4	85.85 (15)
O5—C5—C5A—C9A	156.89 (18)	C9—C9A—C9B—N4	-148.99 (15)
N4—C5—C5A—C9A	-22.81 (19)	C5A—C9A—C9B—N4	-22.27 (18)
C5—C5A—C6—C11	-123.93 (16)	O10—C9A—C9B—C1	-24.8 (2)
C9A—C5A—C6—C11	126.75 (15)	C9—C9A—C9B—C1	100.3 (2)
C5—C5A—C6—C7	113.23 (14)	C5A—C9A—C9B—C1	-132.96 (15)
C9A—C5A—C6—C7	3.91 (16)	C2—C1—C9B—N4	38.51 (18)
C11—C6—C7—O10	-165.65 (15)	C2—C1—C9B—C9A	149.76 (16)
C5A—C6—C7—O10	-40.40 (16)	C8—C7—O10—C9A	-49.46 (13)
C11—C6—C7—C8	-58.5 (2)	C6—C7—O10—C9A	62.79 (14)
C5A—C6—C7—C8	66.71 (18)	C9B—C9A—O10—C7	-171.68 (12)
O10—C7—C8—C9	30.75 (16)	C9—C9A—O10—C7	50.59 (14)
C6—C7—C8—C9	-74.15 (18)	C5A—C9A—O10—C7	-59.96 (14)
C7—C8—C9—C9A	1.83 (16)	C5A—C6—C11—O11	-8.9 (2)
C8—C9—C9A—O10	-33.38 (16)	C7—C6—C11—O11	106.5 (2)
C8—C9—C9A—C9B	-162.43 (15)	C5A—C6—C11—O12	171.02 (12)

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C8—C9—C9A—C5A	71.53 (17)	C7—C6—C11—O12	-73.58 (19)
C5—C5A—C9A—O10	-88.71 (15)		

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*Hydrogen-bond geometry (Å, °)*

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O12—H12...O5 <sup>i</sup>	0.92	1.70	2.607 (2)	165
C9—H9...O11 <sup>ii</sup>	0.95	2.42	3.362 (3)	172

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