Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Methyl 2-benzyl-1-benzyloxy-6a-methyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*b*]pyrrole-3a-carboxylate: hydrogen-bonded $R_4^4(24)$ sheets

John Nicolson Low,[a]* Justo Cobo,[b] Manuel Nogueras,[b] Alix Elena Loaiza[c] and Luz Marina Jaramillo-Gómez[c]

[a]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland., [b]Departamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, and [c]Departamento de Química, Universidad del Valle, AA 25360 Cali, Colombia

Correspondence e-mail: che562@abdn.ac.uk

Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.055
wR factor = 0.108
Data-to-parameter ratio = 19.3

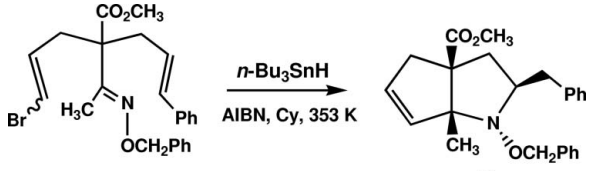
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 30 November 2005
Accepted 6 December 2005
Online 10 December 2005

In the title crystal structure, $C_{24}H_{27}NO_3$, molecules are linked by two C–H···O hydrogen bonds into $R_4^4(24)$ sheets.

Comment

Pyrrolidine-containing derivatives are present in a large number of biologically active natural products and numerous therapeutic agents. Radical cyclizations have emerged as a useful synthetic tool and have been reported in the synthesis of alkaloids and related pyrrolidinic compounds *via* the generation and trapping of nitrogen-centred radicals *e.g.* aminyl, iminyl, amidyl radicals *etc.* (Esker & Newcomb, 1993; Fallis & Brinza, 1997; Bowman *et al.* 1996; Guindon *et al.*, 2001) However, no reports about the capture of neutral alkyl–oxyaminyl radicals by a multiple function have been published up to date for the preparation of fused pyrrolidine derivatives. We describe here a fused pyrrolidine derivative, (I), prepared for the first time *via* an alkyl–oxyaminyl radical, which has been generated through the reductive intermolecular or intramolecular addition of carbon radicals to the carbon atom of oxime ethers (Friestad, 2001; Naito *et al.*, 2000; Tauh & Fallis, 1999; Marco-Contelles *et al.*, 1996; Enholm *et al.*, 1990). We carried out this reaction from methyl 2-[(*E*)-1-(benzyloxyimino)ethyl]-5-bromo-2-cinnamylpent-4-enoate by a double bond in a cascade process yielding the title compound, (I). This reaction involves two sequential 5-*exo* ring closures involving vinyl and neutral alkyl–oxyaminyl radicals, in a chain radical reaction, in which the attack of the radical is stereocontrolled by the carboxymethyl group, and hence determining the stereochemistry of the new bonds on the opposite face to that group.



AIBN = 2,2'-azobisisobutironitrile
Cy = cyclohexane

(I)

The title molecule, (I), is shown in Fig. 1. There are no unusual bonds lengths or angles in the structure. The puckering of the two five-membered rings N1/C2/C3/C3*A*/C6*A* and C3*A*/C4/C5/C6/C6*A* as defined by the pseudorotation parameters *P* and τ(*M*) (Rao *et al.*, 1981), are, for the former, *P* = 182.4 (1)°, τ(*M*) = 48.6 (1)°, reference bond N1—C2, corresponding to a twist on N1—C2 and, for the latter, *P* = 340.4 (6)°, τ(*M*) = 12.2 (1)°, reference bond C3*A*—C4, corresponding to an envelope on C3*A*.

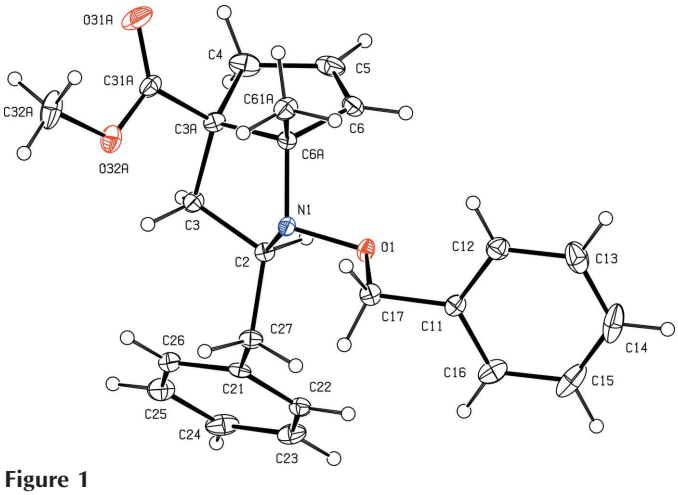


Figure 1
A view of (I), showing displacement ellipsoids drawn at the 30% probability level.

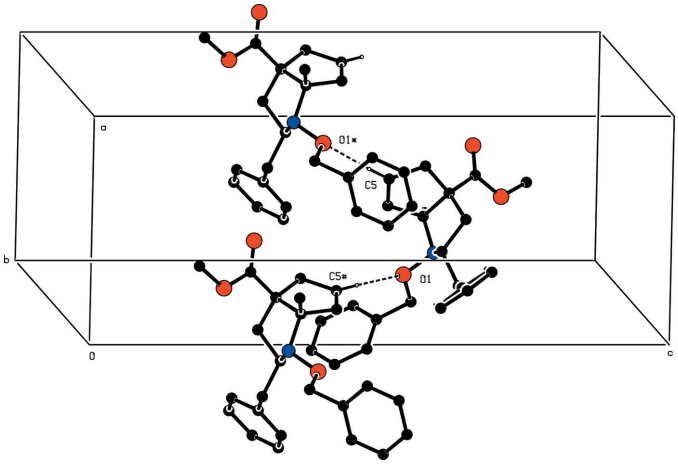


Figure 2
A view of the *C*6 chain formed by the C—H···O hydrogen bonds (dashed lines). The atoms labelled with and asterisk (*) and hash (#) are related by the symmetry operators $(\frac{1}{2}+x,\frac{1}{2}-y,1-z)$ and $(-\frac{1}{2}+x,\frac{1}{2}-y,1-z)$, respectively.

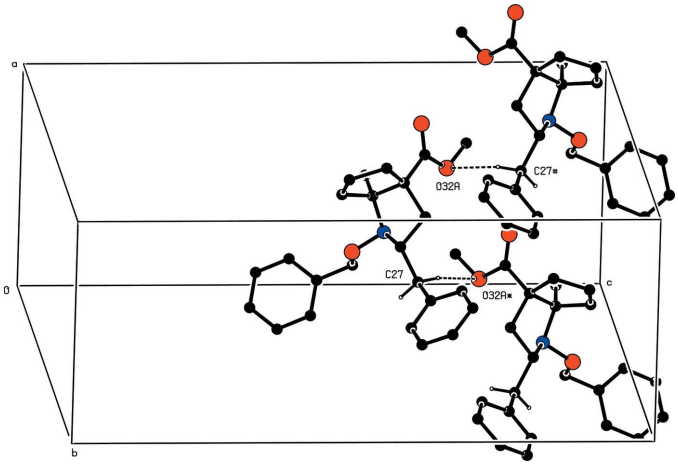


Figure 3
A view of the *C*(7) chain formed by the C—H···O hydrogen bonds (dashed lines). The atoms labelled asterisk (*) and hash (#) are related by the symmetry operators $(-\frac{1}{2}+x,y,\frac{3}{2}-z)$ and $(\frac{1}{2}+x,y,\frac{3}{2}-z)$, respectively.

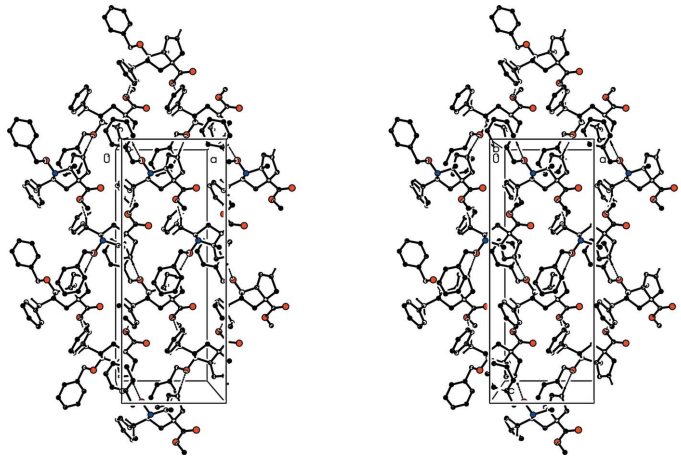


Figure 4
A stereoview of the (010) sheet showing the *C*6 and *C*8 chains and the $R_4^4(24)$ rings. Hydrogen bonds are shown as dashed lines

Two C—H···O hydrogen bonds are involved in the supramolecular stucture (Table 1). C5—H5···O1$(\frac{1}{2}+x,\frac{1}{2}-y,1-z)$ forms a *C*(6) chain (Fig. 2) (Bernstein *et al.*, 1995) and C27—H27*B*···O32*A* forms a *C*(7) chain (Fig. 3), both of which run parallel to the *a* axis. The latter hydrogen bond links antiparallel *C*6 chains of the former type into a sheet consisting of a network of $R_4^4(24)$ rings which lies parallel to (010) (Fig. 4). Atom C5 is a hydrogen donor to O1 in the molecule at $(\frac{1}{2}+x,\frac{1}{2}-y,1-z)$, atom C2a in this molecule is a hydrogen donor to O1 in the molecule at $(x,\frac{1}{2}-y,-\frac{1}{2}-z)$, C27 in this molecule is a hydrogen donor to O32*A* in the molecule at $(-\frac{1}{2}+x,\frac{1}{2}-y,1-z)$, while C5 is a hydrogen donor to O32*A* in the molecule at (x,y,z). Two such sheets occur in the unit cell; one in the range $0.0 > y > 0.5$ and $0.5 > y > 1.0$. There are no interactions between adjacent sheets, C—H···π or π–π interactions being absent.

Experimental

A solution of methyl 2-[(*E*)-1-(benzyloxyimino)ethyl]-5-bromo-2-cinnamylpent-4-enoate (350 mg, 0.77 mmol), 2,2′-azobisisobutyronitrile (39 mg, 0.23 mmol) and tributyltin hydride (0.26 ml, 0.92 mmol) in cyclohexane (39 ml) was degassed for 1 h by bubbling dry argon, and subsequently stirred at 353 K for 6–8 h. After cooling to room temperature the solution was evaporated under low pressure to dryness. Purification of the crude mixture by flash column chromatography with 5% (*v*/*v*) AcOEt/hexanes yielded a white solid (63 mg, 22% yield) mp 355 K. HRMS (EI) calcd for $C_{24}H_{27}NO_3$ 377.19909, found 377.19907. The solid was recrystallized from ethanol producing white crystals suitable for X-ray analysis.

Crystal data

$C_{24}H_{27}NO_3$
M_r = 377.47
Orthorhombic, *Pbca*
a = 8.8410 (17) Å
b = 20.584 (4) Å
c = 22.344 (2) Å
V = 4066.2 (12) Å^3
Z = 8
D_x = 1.233 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 4921 reflections
θ = 6.4–28.5°
μ = 0.08 mm^{-1}
T = 120 (2) K
Plate, colourless
0.38 × 0.33 × 0.12 mm

Data collection

Bruker–Nonius KappaCCD diffractometer	48795 measured reflections
φ–ω scans	4921 independent reflections
Absorption correction: multi-scan [*SADABS* (Sheldrick, 2003) and *EVALCCD* (Duisenberg *et al.*, 2003)]	3477 reflections with $I > 2\sigma(I)$
$T_{min} = 0.970$, $T_{max} = 0.990$	$R_{int} = 0.041$
	$\theta_{max} = 28.5^{\circ}$
	$h = -11 \rightarrow 11$
	$k = -26 \rightarrow 26$
	$l = -29 \rightarrow 27$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0174P)^2 + 3.2146P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.055$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.109$	$\Delta\rho_{max} = 0.36$ e Å^{-3}
$S = 1.11$	$\Delta\rho_{min} = -0.23$ e Å^{-3}
4921 reflections	
255 parameters	
H-atom parameters constrained	

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

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···O1^{i}	0.95	2.51	3.444 (2)	169
C27—H27B···O32A^{ii}	0.99	2.59	3.548 (2)	163

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

H atoms were treated as riding atoms, with aromatic C—H = 0.95 Å, CH_2 C—H = 0.99 Å, both with $U_{iso}(H) = 1.2U_{eq}(C)$, and methyl C—H = 0.98 Å, with $U_{iso}(H) = 1.5U_{eq}(C)$.

Data collection: *COLLECT* (Hooft, 2004); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* (McArdle, 2003 and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *WORDPERFECT* macro *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the Servicios Técnicos de Investigación, Universidad de Jaén. JC and MN thank the Consejería de Educación y Ciencia (Junta de Andalucía, Spain) and the Universidad de Jaén for financial support. LMJ and AEL thank COLCIENCIAS and Universidad del Valle for financial support of this work.

References

Bernstein, J., Davis, R., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Engl.* **34**, 1555–1573.
Bowman, W. R., Stephenson, P. T. & Young, A. R. (1996). *Tetrahedron*, **52**, 11445–11462.
Duisenberg, A, J., Hooft, R. W. W., Schreurs, A. M. M. & Kroon, J. (2000). *J. Appl. Cryst.* **33**, 893–898.
Duisenberg, A, J., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.
Enholm, E., Jaramillo, L. M., Burroff, J. (1990). *Tetrahedron Lett.* **31**, 3727–3730.
Esker, J. L. & Newcomb, M. (1993). *Adv. Heterocycl. Chem.* **58**, 1–45.
Fallis, A. G. & Brinza, I. M. (1997). *Tetrahedron*, **53**, 17543–17594.
Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
Friestad, G. K. (2001). *Tetrahedron*, **57**, 5461–5496.
Guindon, I., Guérin, B. & Landry, S. R. (2001). *Org. Lett.* **3**, 2293–2296.
Hooft, R. W. W. (2004). *COLLECT*. Bruker–Nonius, Delft, The Netherlands.
Marco-Contelles, J., Destabel, C., Gallego, P., Chiara, J. L. & Bernabe, M. (1996). *J. Org. Chem.* **61**, 1354–1362.
McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
Naito, T., Miyabe, H., Ueda, M., Yoshioka, N. & Yamakawa, K. (2000). *Tetrahedron*, **56**, 2413–2420.
Rao, S. T., Westhof, E. & Sundaralingam, M. (1981). *Acta Cryst.* A**37**, 421–425.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2003) *SADABS*. Bruker–Nonius, Delft, The Netherlands.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Tauh, T. & Fallis, A. G. (1999). *J. Org. Chem.* **64**, 6960–6968.

supporting information

Acta Cryst. (2006). E**62**, o165–o167 [doi:10.1107/S1600536805040742]

Methyl 2-benzyl-1-benzyloxy-6a-methyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*b*]pyrrole-3a-carboxylate: hydrogen-bonded $R_4^4(24)$ sheets

John Nicolson Low, Justo Cobo, Manuel Nogueras, Alix Elena Loaiza and Luz Marina Jaramillo-Gómez

S1. Comment

Pyrrolidine-containing derivatives are present in a large number of biologically active natural products and numerous therapeutic agents. Radical cyclizations have emerged as a useful synthetic tool and have been reported in the synthesis of alkaloids and related pyrrolidinic compounds *via* generation and trapping of nitrogen-centered radicals *e.g.* aminyl, iminyl, amidyl radicals *etc*. (Esker & Newcomb, 1993; Fallis & Brinza, 1997; Bowman *et al.* 1996; Guindon *et al.*, 2001) However, no reports about the capture of neutral alkyl–oxyaminyl radicals by a multiple function have been published up to date for the preparation of fused pyrrolidine derivatives. We describe here a fused pyrrolidine derivative, (I), prepared for the first time *via* an alkyl–oxyaminyl radical, which has been generated through the reductive intermolecular or intramolecular addition of carbon radicals to the carbon atom of oxime ethers (Friestad, 2001; Naito *et al.*, 2000; Tauh & Fallis, 1999; Marco-Contelles *et al.*, 1996; Enholm *et al.*, 1990). We carried out this reaction by the intramolecular capture of an alkyl-oxyaminyl radical by a double bond in a cascade process yielding methyl 2-[(*E*)-1-(benzyloxyimino)-ethyl]-5-bromo-2-cinnamylpent-4-enoate. This reaction involves two sequential 5-*exo* ring closures involving vinyl and neutral alkyl–oxyaminyl radicals, in a chain radical reaction, in which the attack of the radical is stereo-controlled by the the carboxymethyl group, and hence determining the stereochemistry of the new stereogenic bonds on the opposite face to that group.

The title molecule is shown in Fig. 1. There are no unusual bonds lengths or angles in the structure. The puckering of the two five-membered rings N1/C2/C3/C3A/C6*A* and C3*A*/C4/C5/C6/C6*A* as defined by the pseudorotation parameters *P* and $\tau(M)$, (Rao *et al.*, 1981) are, for the former; P = 182.4 (1)°, $\tau(M)$ = 48.6 (1)°, reference bond N1—C2, corresponding to a twist on N1—C2 and for the latter; P = 340.4 (6)°, $\tau(M)$ = 12.2 (1)°, reference bond C3*A*—C4, corresponding to an envelope on C3*A*.

Two C—H···O hydrogen bonds are involved in the supramolecular stucture (Table 1). C5—H5···O1($1/2 + x$, $1/2 - y$, $1 - z$) forms a *C*(6) chain (Fig. 2) (Bernstein *et al.*, 1995) and C27—H27*B*···O32*A* forms a*C*(7) chain (Fig. 3), both of which run parallel to the *a* axis. The latter hydrogen bond links antiparallel*C*6 chains of the former type into a sheet consisting of a network of $R_4^4(24)$ rings which lies parallel to (010) (Fig 4). Atom C5 is a hydrogen donor to O1 in the molecule at ($1/2 + x$, $1/2 - y$, $1 - z$), Atom C27 in this molecule is a hydrogen donor to O1 in the molecule at (x, $1/2 - y$, $-1/2 - z$), C27 in this molecule is a hydrogen donor to O32*A* in the molecule at ($-1/2 + x$, $1/2 - y$, $1 - z$), while C5 is a hydrogen donor to O32*A* in the molecule at (x, y, z). Two such sheets occur in the unit cell; one in the range $0.0 > y > 0.5$ and $0.5 > y > 1.0$. There are no interactions between adjacent sheets, C—H···π or π–π interactions being absent.

S2. Experimental

A solution of methyl 2-[(*E*)-1-(benzyloxyimino)ethyl]-5-bromo-2-cinnamylpent-4-enoate (350 mg, 0.77 mmol), 2,2′-azobisisobutironitrile (39 mg, 0.23 mmol) and tributyltin hydride (0.26 ml, 0.92 mmol) in cyclohexane (39 ml) was degassed for 1 h by bubbling dry argon, and subsequently stirred at 353 K for 6–8 h. After cooling to room temperature the solution was evaporated under low pressure to dryness. Purification of the crude mixture by flash column chromatography with 5% (*v*/*v*) AcOEt/hexanes yielded a white solid (63 mg, 22% yield) mp 355 K. HRMS (EI) calcd for $C_{24}H_{27}NO_3$ 377.19909, found 377.19907. The solid was recrystallized from hexanes producing white crystals suitable for X-ray analysis.

S3. Refinement

H atoms were treated as riding atoms, with aromatic C—H = 0.95 Å, CH_2 C—H = 0.99 Å, both with $U_{iso}(H) = 1.2U_{eq}(C)$, and methyl C—H = 0.98 Å, with $U_{iso}(H) = 1.5U_{eq}(C)$.

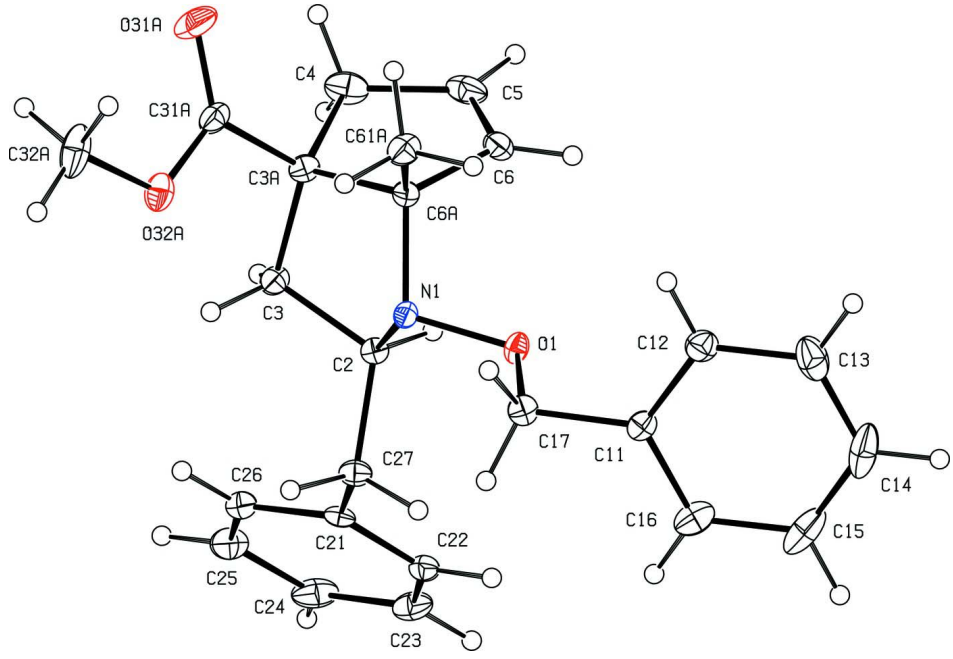


Figure 1

A view of (1), showing displacement ellipsoids drawn at the 30% probability level.

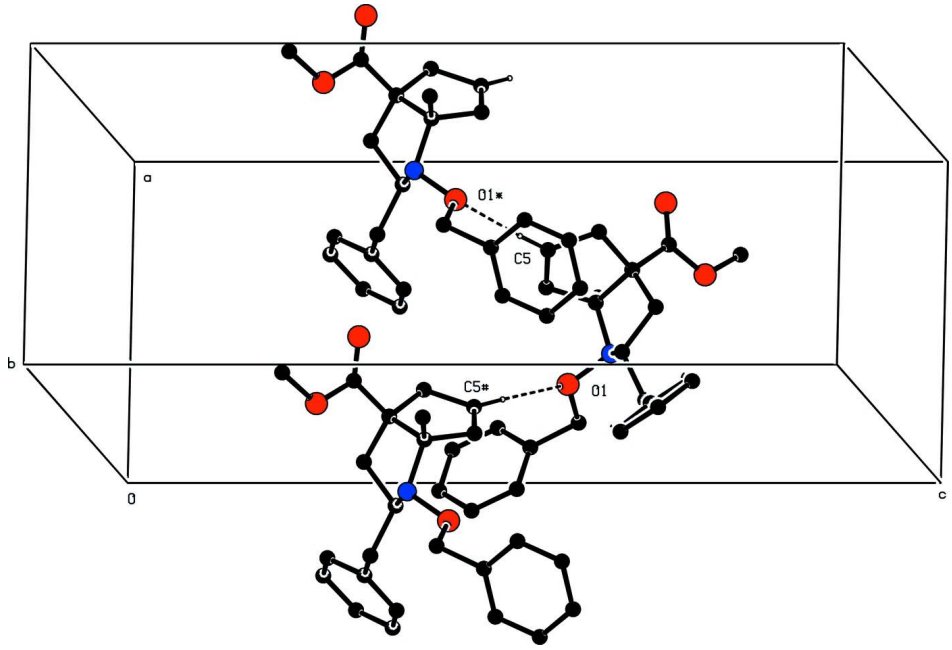


Figure 2

A view of the *C*6 chain formed by the C—H···O hydrogen bonds (dashed lines). The atoms labelled with and asterisk (*) and hash (#) are related by the symmetry operators (1/2 + *x*, 1/2 − *y*, 1 − *z*) and (−1/2 + *x*, 1/2 − *y*, 1 − *z*), respectively.

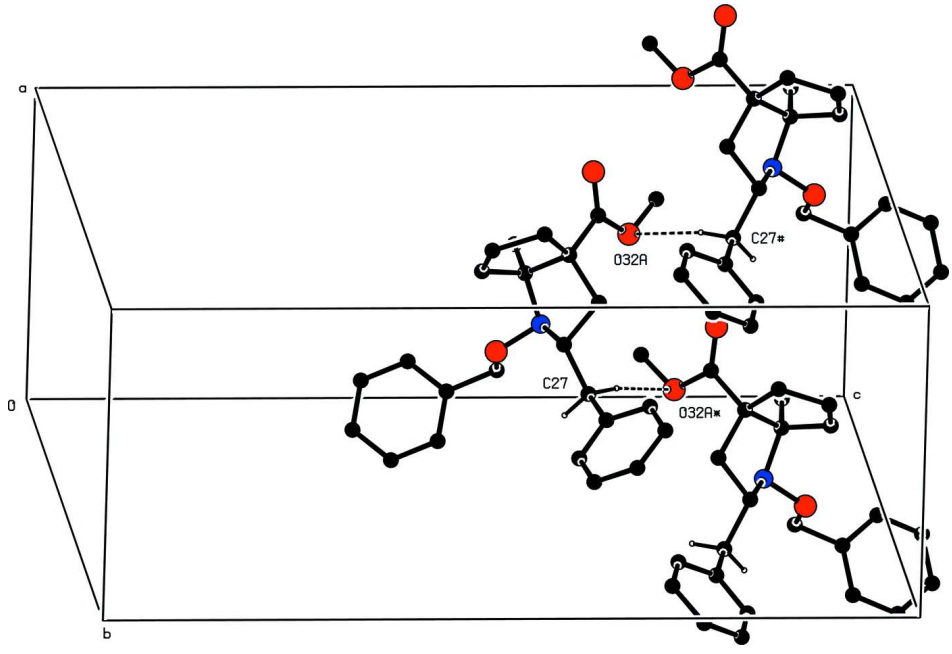


Figure 3

A view of the *C*(7) chain formed by the C—H···O hydrogen bonds (dashed lines). The atoms labelled asterisk (*) and hash (#) are related by the symmetry operators (−1/2 + *x*, *y*, 1.5 − *z*) and (1/2 + *x*, *y*, 1.5 − *z*), respectively.

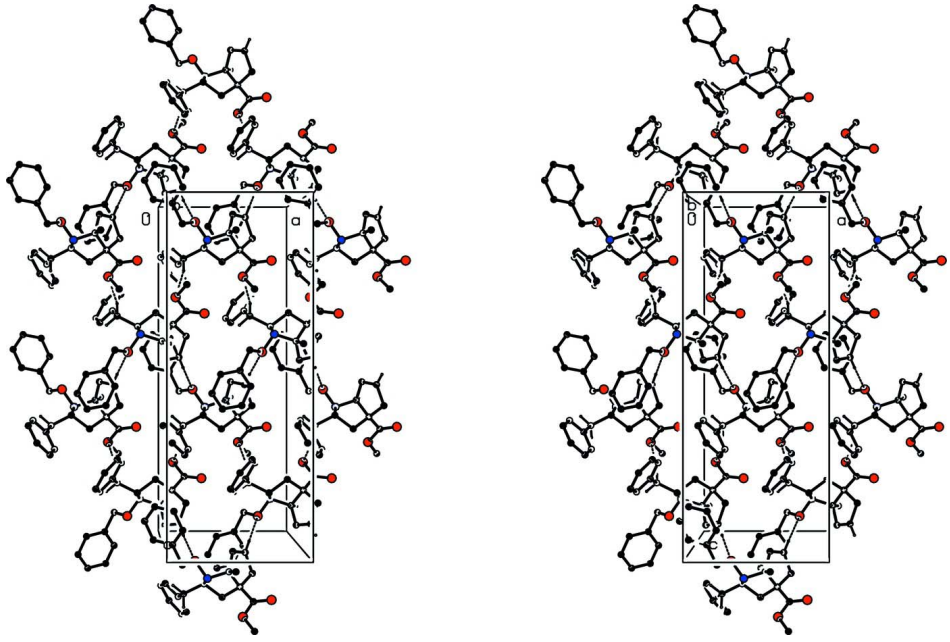


Figure 4

A stereoview of the (010) sheet showing the *C*6 and*C*8 chains and the $R_4^4(24)$ rings. Hydrogen bonds are shown as dashed lines

Methyl 2-benzyl-1-benzyloxy-6a-methyl-1,2,3,3a,4,6a-hexahydro- 1-azapentalene-3a-carboxylate

Crystal data

$C_{24}H_{27}NO_3$
$M_r = 377.47$
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
$a = 8.8410\ (17)$ Å
$b = 20.584\ (4)$ Å
$c = 22.344\ (2)$ Å
$V = 4066.2\ (12)$ Å^3
$Z = 8$
$F(000) = 1616$
$D_x = 1.233$ Mg m^{-3}
Melting point: 355 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4921 reflections
$\theta = 6.4$–$28.5°$
$\mu = 0.08$ mm^{-1}
$T = 120$ K
Plate, colourless
0.38 × 0.33 × 0.12 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ–ω scans
Absorption correction: multi-scan [*SADABS* (Sheldrick, 2003) and *EVALCCD* (Duisenberg et al., 2003)]
$T_{min} = 0.970$, $T_{max} = 0.990$
48795 measured reflections
4921 independent reflections
3477 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 28.5°$, $\theta_{min} = 6.4°$
$h = -11 \rightarrow 11$
$k = -26 \rightarrow 26$
$l = -29 \rightarrow 27$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.109$
$S = 1.11$
4921 reflections
255 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0174P)^2 + 3.2146P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Special details

Experimental. The Tmin and Tmax values reported are those calculated from the *SHELX* SIZE command. The ratio of experimental transmission factors from *SADABS* is 0.239891

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.34560 (14)	0.15468 (6)	0.61087 (5)	0.0175 (3)
O1	0.25222 (12)	0.14741 (5)	0.55813 (5)	0.0203 (2)
C17	0.15344 (18)	0.09243 (8)	0.56498 (7)	0.0227 (3)
C11	0.07975 (17)	0.08382 (7)	0.50510 (7)	0.0207 (3)
C12	0.15277 (19)	0.05002 (8)	0.46007 (8)	0.0276 (4)
C13	0.0873 (2)	0.04383 (10)	0.40405 (8)	0.0399 (5)
C14	−0.0513 (3)	0.07179 (10)	0.39271 (9)	0.0470 (6)
C15	−0.1252 (2)	0.10536 (10)	0.43739 (11)	0.0447 (5)
C16	−0.06004 (19)	0.11148 (8)	0.49326 (9)	0.0322 (4)
C2	0.32646 (16)	0.22132 (7)	0.63345 (7)	0.0178 (3)
C27	0.17335 (17)	0.22926 (7)	0.66419 (7)	0.0219 (3)
C21	0.13840 (17)	0.29887 (7)	0.68005 (7)	0.0192 (3)
C22	0.04210 (18)	0.33563 (8)	0.64441 (7)	0.0228 (3)
C23	0.01202 (19)	0.40019 (9)	0.65715 (8)	0.0303 (4)
C24	0.0776 (2)	0.42919 (9)	0.70642 (9)	0.0351 (4)
C25	0.1720 (2)	0.39336 (9)	0.74298 (9)	0.0332 (4)
C26	0.20282 (18)	0.32876 (8)	0.72997 (7)	0.0255 (4)
C3	0.46432 (17)	0.22611 (8)	0.67422 (7)	0.0223 (3)
C3A	0.59306 (17)	0.19107 (8)	0.63972 (7)	0.0210 (3)
C31A	0.68804 (18)	0.14638 (8)	0.67829 (8)	0.0257 (4)
O31A	0.82136 (14)	0.13675 (7)	0.67205 (7)	0.0465 (4)
O32A	0.60534 (14)	0.11550 (6)	0.71958 (5)	0.0293 (3)
C32A	0.6850 (3)	0.06932 (9)	0.75659 (9)	0.0434 (5)
C4	0.6937 (2)	0.23914 (9)	0.60414 (9)	0.0342 (4)
C5	0.6389 (2)	0.23438 (9)	0.54132 (9)	0.0334 (4)
C6	0.53930 (19)	0.18767 (9)	0.53393 (8)	0.0285 (4)
C6A	0.50606 (17)	0.15025 (8)	0.59043 (7)	0.0192 (3)
C61A	0.54885 (19)	0.07899 (8)	0.58369 (8)	0.0277 (4)
H17A	0.0767	0.1009	0.5963	0.027*
H17B	0.2117	0.0532	0.5761	0.027*

H12	0.2487	0.0309	0.4676	0.033*
H13	0.1379	0.0203	0.3735	0.048*
H14	−0.0958	0.0680	0.3542	0.056*
H15	−0.2213	0.1243	0.4297	0.054*
H16	−0.1114	0.1348	0.5238	0.039*
H2	0.3358	0.2531	0.5998	0.021*
H27A	0.0931	0.2125	0.6374	0.026*
H27B	0.1722	0.2027	0.7011	0.026*
H22	−0.0041	0.3160	0.6105	0.027*
H23	−0.0536	0.4245	0.6320	0.036*
H24	0.0579	0.4736	0.7151	0.042*
H25	0.2162	0.4130	0.7772	0.040*
H26	0.2684	0.3047	0.7553	0.031*
H3A	0.4447	0.2045	0.7130	0.027*
H3B	0.4910	0.2721	0.6818	0.027*
H32A	0.7229	0.0337	0.7316	0.065*
H32B	0.6160	0.0519	0.7869	0.065*
H32C	0.7702	0.0910	0.7763	0.065*
H4A	0.6817	0.2839	0.6196	0.041*
H4B	0.8016	0.2266	0.6069	0.041*
H5	0.6724	0.2621	0.5100	0.040*
H6	0.4927	0.1784	0.4966	0.034*
H61A	0.5236	0.0556	0.6206	0.041*
H61B	0.6577	0.0754	0.5760	0.041*
H61C	0.4928	0.0600	0.5501	0.041*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0178 (6)	0.0182 (7)	0.0165 (6)	0.0012 (5)	−0.0025 (5)	−0.0002 (5)
O1	0.0219 (5)	0.0197 (6)	0.0193 (5)	−0.0041 (4)	−0.0061 (5)	0.0007 (4)
C17	0.0247 (8)	0.0193 (8)	0.0241 (8)	−0.0045 (6)	−0.0004 (7)	−0.0007 (6)
C11	0.0206 (8)	0.0161 (8)	0.0254 (8)	−0.0040 (6)	−0.0029 (6)	0.0010 (6)
C12	0.0251 (8)	0.0281 (9)	0.0295 (9)	−0.0037 (7)	−0.0002 (7)	−0.0024 (7)
C13	0.0526 (12)	0.0421 (11)	0.0251 (9)	−0.0177 (10)	0.0004 (9)	−0.0054 (8)
C14	0.0621 (14)	0.0423 (12)	0.0366 (11)	−0.0256 (11)	−0.0275 (11)	0.0143 (10)
C15	0.0361 (11)	0.0311 (11)	0.0670 (15)	−0.0054 (9)	−0.0284 (11)	0.0132 (10)
C16	0.0256 (9)	0.0221 (9)	0.0488 (11)	0.0010 (7)	−0.0056 (8)	−0.0010 (8)
C2	0.0183 (7)	0.0142 (7)	0.0209 (8)	−0.0009 (6)	0.0004 (6)	0.0012 (6)
C27	0.0193 (8)	0.0186 (8)	0.0277 (8)	−0.0018 (6)	0.0040 (6)	0.0014 (7)
C21	0.0145 (7)	0.0204 (8)	0.0229 (8)	−0.0018 (6)	0.0074 (6)	0.0011 (6)
C22	0.0185 (7)	0.0260 (9)	0.0238 (8)	−0.0021 (6)	0.0031 (6)	0.0004 (7)
C23	0.0215 (8)	0.0254 (9)	0.0440 (11)	0.0044 (7)	0.0025 (8)	0.0060 (8)
C24	0.0245 (9)	0.0237 (9)	0.0573 (12)	0.0026 (7)	0.0066 (9)	−0.0105 (9)
C25	0.0263 (9)	0.0353 (10)	0.0380 (10)	−0.0031 (8)	0.0017 (8)	−0.0159 (8)
C26	0.0201 (8)	0.0305 (9)	0.0259 (8)	0.0019 (7)	0.0006 (7)	−0.0015 (7)
C3	0.0208 (8)	0.0216 (9)	0.0245 (8)	0.0030 (6)	−0.0029 (7)	−0.0054 (7)
C3A	0.0191 (7)	0.0179 (8)	0.0260 (8)	−0.0017 (6)	−0.0004 (6)	−0.0004 (6)

C31A	0.0213 (8)	0.0267 (9)	0.0290 (9)	0.0026 (7)	−0.0072 (7)	−0.0069 (7)
O31A	0.0217 (7)	0.0610 (10)	0.0567 (9)	0.0125 (6)	−0.0081 (6)	−0.0013 (7)
O32A	0.0356 (7)	0.0253 (6)	0.0270 (6)	0.0038 (5)	−0.0079 (5)	0.0021 (5)
C32A	0.0662 (14)	0.0262 (10)	0.0380 (11)	0.0072 (10)	−0.0269 (10)	−0.0011 (8)
C4	0.0307 (9)	0.0247 (9)	0.0473 (11)	−0.0084 (7)	0.0099 (8)	−0.0009 (8)
C5	0.0294 (9)	0.0318 (10)	0.0389 (10)	0.0067 (8)	0.0146 (8)	0.0131 (8)
C6	0.0255 (9)	0.0388 (10)	0.0212 (8)	0.0075 (8)	0.0051 (7)	0.0056 (7)
C6A	0.0185 (7)	0.0204 (8)	0.0187 (7)	0.0015 (6)	0.0006 (6)	−0.0005 (6)
C61A	0.0260 (8)	0.0248 (9)	0.0322 (9)	0.0051 (7)	−0.0036 (7)	−0.0079 (7)

Geometric parameters (Å, º)

N1—O1	1.4466 (15)	C23—H23	0.95
N1—C2	1.4713 (19)	C24—C25	1.382 (3)
N1—C6A	1.4931 (19)	C24—H24	0.95
O1—C17	1.4377 (18)	C25—C26	1.388 (2)
C17—C11	1.499 (2)	C25—H25	0.95
C17—H17A	0.99	C26—H26	0.95
C17—H17B	0.99	C3—C3A	1.552 (2)
C11—C12	1.383 (2)	C3—H3A	0.99
C11—C16	1.386 (2)	C3—H3B	0.99
C12—C13	1.385 (3)	C3A—C31A	1.515 (2)
C12—H12	0.95	C3A—C4	1.550 (2)
C13—C14	1.377 (3)	C3A—C6A	1.584 (2)
C13—H13	0.95	C31A—O31A	1.203 (2)
C14—C15	1.379 (3)	C31A—O32A	1.338 (2)
C14—H14	0.95	O32A—C32A	1.444 (2)
C15—C16	1.381 (3)	C32A—H32A	0.98
C15—H15	0.95	C32A—H32B	0.98
C16—H16	0.95	C32A—H32C	0.98
C2—C3	1.525 (2)	C4—C5	1.488 (3)
C2—C27	1.527 (2)	C4—H4A	0.99
C2—H2	1.00	C4—H4B	0.99
C27—C21	1.508 (2)	C5—C6	1.314 (3)
C27—H27A	0.99	C5—H5	0.95
C27—H27B	0.99	C6—C6A	1.508 (2)
C21—C22	1.390 (2)	C6—H6	0.95
C21—C26	1.395 (2)	C6A—C61A	1.522 (2)
C22—C23	1.385 (2)	C61A—H61A	0.98
C22—H22	0.95	C61A—H61B	0.98
C23—C24	1.380 (3)	C61A—H61C	0.98
O1—N1—C2	108.07 (11)	C24—C25—C26	120.40 (17)
O1—N1—C6A	106.66 (11)	C24—C25—H25	119.8
C2—N1—C6A	105.73 (12)	C26—C25—H25	119.8
C17—O1—N1	109.96 (11)	C25—C26—C21	120.64 (16)
O1—C17—C11	105.19 (12)	C25—C26—H26	119.7
O1—C17—H17A	110.7	C21—C26—H26	119.7

C11—C17—H17A	110.7	C2—C3—C3A	105.04 (12)
O1—C17—H17B	110.7	C2—C3—H3A	110.7
C11—C17—H17B	110.7	C3A—C3—H3A	110.7
H17A—C17—H17B	108.8	C2—C3—H3B	110.7
C12—C11—C16	118.94 (16)	C3A—C3—H3B	110.7
C12—C11—C17	120.39 (15)	H3A—C3—H3B	108.8
C16—C11—C17	120.63 (15)	C31A—C3A—C4	111.19 (14)
C11—C12—C13	120.56 (17)	C31A—C3A—C3	113.96 (13)
C11—C12—H12	119.7	C4—C3A—C3	112.26 (13)
C13—C12—H12	119.7	C31A—C3A—C6A	110.03 (13)
C14—C13—C12	119.99 (19)	C4—C3A—C6A	105.10 (13)
C14—C13—H13	120.0	C3—C3A—C6A	103.63 (12)
C12—C13—H13	120.0	O31A—C31A—O32A	122.47 (17)
C13—C14—C15	119.87 (18)	O31A—C31A—C3A	125.26 (17)
C13—C14—H14	120.1	O32A—C31A—C3A	112.21 (13)
C15—C14—H14	120.1	C31A—O32A—C32A	116.18 (15)
C14—C15—C16	120.15 (19)	O32A—C32A—H32A	109.5
C14—C15—H15	119.9	O32A—C32A—H32B	109.5
C16—C15—H15	119.9	H32A—C32A—H32B	109.5
C15—C16—C11	120.48 (18)	O32A—C32A—H32C	109.5
C15—C16—H16	119.8	H32A—C32A—H32C	109.5
C11—C16—H16	119.8	H32B—C32A—H32C	109.5
N1—C2—C3	99.98 (12)	C5—C4—C3A	104.79 (14)
N1—C2—C27	110.86 (12)	C5—C4—H4A	110.8
C3—C2—C27	115.67 (13)	C3A—C4—H4A	110.8
N1—C2—H2	110.0	C5—C4—H4B	110.8
C3—C2—H2	110.0	C3A—C4—H4B	110.8
C27—C2—H2	110.0	H4A—C4—H4B	108.9
C21—C27—C2	112.90 (12)	C6—C5—C4	112.63 (16)
C21—C27—H27A	109.0	C6—C5—H5	123.7
C2—C27—H27A	109.0	C4—C5—H5	123.7
C21—C27—H27B	109.0	C5—C6—C6A	113.52 (16)
C2—C27—H27B	109.0	C5—C6—H6	123.2
H27A—C27—H27B	107.8	C6A—C6—H6	123.2
C22—C21—C26	117.91 (15)	N1—C6A—C6	114.21 (13)
C22—C21—C27	120.55 (14)	N1—C6A—C61A	108.98 (13)
C26—C21—C27	121.54 (14)	C6—C6A—C61A	111.16 (13)
C23—C22—C21	121.49 (16)	N1—C6A—C3A	102.49 (12)
C23—C22—H22	119.3	C6—C6A—C3A	102.50 (13)
C21—C22—H22	119.3	C61A—C6A—C3A	117.33 (13)
C24—C23—C22	119.89 (17)	C6A—C61A—H61A	109.5
C24—C23—H23	120.1	C6A—C61A—H61B	109.5
C22—C23—H23	120.1	H61A—C61A—H61B	109.5
C23—C24—C25	119.65 (17)	C6A—C61A—H61C	109.5
C23—C24—H24	120.2	H61A—C61A—H61C	109.5
C25—C24—H24	120.2	H61B—C61A—H61C	109.5
C2—N1—O1—C17	−125.72 (12)	C2—C3—C3A—C6A	−16.77 (16)

C6A—N1—O1—C17	121.00 (13)	C4—C3A—C31A—O31A	−17.8 (2)
N1—O1—C17—C11	−171.95 (11)	C3—C3A—C31A—O31A	−145.89 (17)
O1—C17—C11—C12	83.28 (18)	C6A—C3A—C31A—O31A	98.2 (2)
O1—C17—C11—C16	−94.45 (17)	C4—C3A—C31A—O32A	165.07 (13)
C16—C11—C12—C13	−0.1 (2)	C3—C3A—C31A—O32A	36.98 (18)
C17—C11—C12—C13	−177.82 (16)	C6A—C3A—C31A—O32A	−78.90 (16)
C11—C12—C13—C14	0.4 (3)	O31A—C31A—O32A—C32A	−0.2 (2)
C12—C13—C14—C15	−0.7 (3)	C3A—C31A—O32A—C32A	177.03 (13)
C13—C14—C15—C16	0.6 (3)	C31A—C3A—C4—C5	130.43 (15)
C14—C15—C16—C11	−0.3 (3)	C3—C3A—C4—C5	−100.56 (16)
C12—C11—C16—C15	0.0 (2)	C6A—C3A—C4—C5	11.41 (17)
C17—C11—C16—C15	177.75 (16)	C3A—C4—C5—C6	−7.3 (2)
O1—N1—C2—C3	−163.08 (11)	C4—C5—C6—C6A	−0.5 (2)
C6A—N1—C2—C3	−49.17 (14)	O1—N1—C6A—C6	43.33 (16)
O1—N1—C2—C27	74.40 (14)	C2—N1—C6A—C6	−71.55 (16)
C6A—N1—C2—C27	−171.70 (12)	O1—N1—C6A—C61A	−81.64 (14)
N1—C2—C27—C21	−171.53 (13)	C2—N1—C6A—C61A	163.48 (12)
C3—C2—C27—C21	75.59 (17)	O1—N1—C6A—C3A	153.37 (11)
C2—C27—C21—C22	100.61 (17)	C2—N1—C6A—C3A	38.49 (14)
C2—C27—C21—C26	−78.34 (18)	C5—C6—C6A—N1	117.80 (16)
C26—C21—C22—C23	0.9 (2)	C5—C6—C6A—C61A	−118.39 (16)
C27—C21—C22—C23	−178.05 (15)	C5—C6—C6A—C3A	7.77 (18)
C21—C22—C23—C24	−0.4 (3)	C31A—C3A—C6A—N1	110.13 (14)
C22—C23—C24—C25	−0.5 (3)	C4—C3A—C6A—N1	−130.07 (13)
C23—C24—C25—C26	0.9 (3)	C3—C3A—C6A—N1	−12.09 (15)
C24—C25—C26—C21	−0.4 (3)	C31A—C3A—C6A—C6	−131.22 (13)
C22—C21—C26—C25	−0.5 (2)	C4—C3A—C6A—C6	−11.43 (15)
C27—C21—C26—C25	178.44 (15)	C3—C3A—C6A—C6	106.55 (14)
N1—C2—C3—C3A	39.62 (15)	C31A—C3A—C6A—C61A	−9.17 (19)
C27—C2—C3—C3A	158.67 (13)	C4—C3A—C6A—C61A	110.63 (16)
C2—C3—C3A—C31A	−136.34 (13)	C3—C3A—C6A—C61A	−131.39 (14)
C2—C3—C3A—C4	96.12 (15)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O1^{i}	0.95	2.51	3.444 (2)	169
C27—H27*B*···O32*A*^{ii}	0.99	2.59	3.548 (2)	163

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