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A $P2_12_12_1$ polymorph of (+)-clusianone

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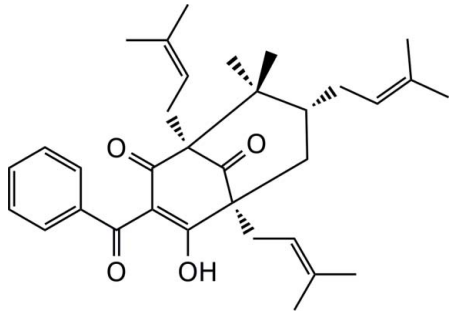
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.034; wR factor = 0.084; data-to-parameter ratio = 16.4.

The title compound, $C_{33}H_{42}O_4$ [systematic name: (1*S*,5*S*,7*R*)-3-benzoyl-4-hydroxy-8,8-dimethyl-1,5,7-tris(3-methylbut-2-enyl)bicyclo[3.3.1]nona-3-ene-2,9-dione], has a central bicyclo[3.3.1]nonane-2,4,9-trione surrounded by tetraprenylated and benzoyl groups. The compound was recrystallized several times in methanol using both a slow evaporation method and with a crystal-seeding technique. This subsequently produced diffraction-quality crystals which crystallize in the orthorhombic space group $P2_12_12_1$, in contrast to a previous report of a structure determination in the $Pna2_1$ space group [McCandlish *et al.* (1976). *Acta Cryst.* B**32**, 1793–1801]. The title compound has a melting point of 365–366 K, and a specific rotation $[\alpha]^{20}$ value of +51.94°. A strong intramolecular O—H···O hydrogen bond is noted. In the crystal, molecules are assembled in the *ab* plane by weak C—H···O interactions.

Related literature

For related structural studies, see: McCandlish *et al.* (1976); Santos *et al.* (1998, 2001). For background to *Clusiaceae* metabolites, see: Monache *et al.* (1991); de Oliveira *et al.* (1996). For discussion of polycyclic polyprenylated acylphloroglucinols, including their biological properties, see: Piccinelli *et al.* (2005); Garnsey *et al.* (2011); Simpkins (2013).



Experimental

Crystal data

$C_{33}H_{42}O_4$
M_r = 502.69
Orthorhombic, $P2_12_12_1$
a = 9.2035 (2) Å
b = 13.4629 (2) Å
c = 22.9607 (5) Å
V = 2844.96 (10) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 0.59 mm^{-1}
T = 100 K
0.21 × 0.14 × 0.08 mm

Data collection

Oxford Diffraction Gemini diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2002)
T_{min} = 0.86, T_{max} = 0.95
39826 measured reflections
5498 independent reflections
5269 reflections with $I > 2.0\sigma(I)$
R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.084
S = 0.96
5498 reflections
335 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}
Absolute structure: Flack (1983), 2383 Friedel pairs
Absolute structure parameter: −0.04 (15)

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

D—H···A	D—H	H···A	D···A	D—H···A
O11—H1···O1	0.98	1.48	2.4227 (14)	158
C27—H273···O1^{i}	0.99	2.63	3.330 (2)	128
C36—H363···O1^{ii}	0.94	2.67	3.523 (2)	151
C8—H81···O11^{iii}	0.95	2.62	3.300 (2)	129
C21—H211···O17^{iv}	0.96	2.70	3.610 (2)	158

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

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SUPERFLIP* (Palatinus & Chapuis, 2007); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003; Cooper *et al.*, 2010); molecular graphics: *CAMERON* (Watkin *et al.*, 1996) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK5270).

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supporting information

Acta Cryst. (2013). E**69**, o1799–o1800 [doi:10.1107/S1600536813031036]

A $P2_12_12_1$ polymorph of (+)-clusianone

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S1. Comment

Clusianone is a polycyclic polyprenylated acylpholroglucinols (PPAP) isolated from the plants of the family *Clusiacea*e (*Guttiferae*) and has gained considerable interest from both the natural product and synthetic chemistry community due to its potential bioactivity. Clusianone, both naturally occurring and synthetic, exhibits anti-HIV (Piccinelli *et al.*, 2005; Garnsey *et al.*, 2011) and anti-cancer properties (Simpkins, 2013).

Clusianone was isolated from the roots of *Clusia congestiflora* and analysis of X-ray diffraction has firmly established the equatorial orientation of the 3-methyl-2-butenyl group at C-7 which crystallized in the $Pna2_1$ space group (McCandlish *et al.*, 1976). Subsequent isolation of the compound from *Clusia Sandiensis* (Monache *et al.*, 1991) and *Clusia spiritu-santensis* (de Oliveira *et al.*, 1996) led to NMR studies of clusianone and its methyl derivative, respectively, but gave contradictory NMR data for clusianone. Unfortunately, due to the complexity of the data and the unavailability of authentic sample of clusianone, no report was made of the C7 stereochemistry. Santos and co-workers isolated 7-epiclusianone from *Rheedia gardneriana* and reported its NMR and X-ray crystal structure, showing the C7 exo isomerism (Santos *et al.*, 1998; Santos *et al.*, 2001). Thereafter, the absolute structure of (+)-7- epiclusianone possessing an axial C7-prenyl group while comparison to clusianone isolated from the roots of *Clusia congestiflora* (McCandlish *et al.*, 1976) had the C7-prenyl group as equatorial. The title compound's epimer (+)-7- epiclusianone crystallized in space group of $P2_12_12_1$ (Santos *et al.*, 1998).

To date, the absolute configuration of (+)-clusianone determined by X-ray crystallography at room temperature has been only confirmed by (McCandlish *et al.*, 1976). Previously reported clusianone isolated from *Clusia congestiflora* crystallizes in the $Pna2_1$ space group. The crystal was obtained from a 95% ethanol solution (McCandlish *et al.*,1976). However, the lack of the specific optical rotation of the clusianone isolated by McCandlish *et al.* (1976) indicates that further investigation might be required to discover the uncertainty in stereochemistry of this compound.

Herein, we report the clusianone with melting point 365–366 K and a specific rotation $[\alpha]^{20}$ value of +51.94 °. We report (+)-clusianone to crystallize in the orthorhombic space group $P2_12_12_1$, Fig. 1, when crystals were isolated from methanol solution. Intramolecular O—H···O hydrogen bonds are noted, Table 1. Supramolecular layers in the *ab* plane are stabilised by weak C—H···O interactions, Fig. 2. The different solvent used to crystallize the compound might be the reason for the polymorph occurance.

S2. Experimental

S2.1. Isolation and crystallization

G. Parvifolia leaves were collected from trees in a reserved forest, Sungai Congkak, Selangor, Malaysia. The leaves (133 g) were dried, powdered and macerated with n-hexane (3 x 1.0 L) frequently over three days. Each maceration were

filtered, evaporated and then dried using a rotary evaporator under reduced pressure at 40 °C. The hexane extract of the leaves (9.7 g) was then chromatographed on silica gel (70-230 mesh) and eluted with diethyl ether and evaporated. This fraction of the extract which contains a major portion of chlorophyll compounds was then mixed with silica gel:activated charcoal in proportion of 1:3:1, respectively, and placed in a column with a porous frit. The material was eluted with hexane (500 ml) followed by dichloromethane (500 ml) with the aid of vacuum pressure. To isolate the compound, the dichloromethane dried fractions (4.8 g) was further chromatographed on silica gel (70-230 mesh) and eluted with mixtures of cyclohexane/chloroform and chloroform/methanol of increasing polarity. A total of 122 fractions were collected in 20 ml vials and fractions from F51—F60 were crystallized *via* slow methanol evaporation. Growth of diffraction quality crystals were obtained through several recrystallizations in methanol using both slow evaporation method and crystal seeding technique over a period of 10 days. Yellow cubic crystals (119 mg) were obtained and the melting point was 365-366 K and the specific optical rotation $[\alpha]^{20}$ was +51.94 °. The specific optical rotation was measured using an ADP-440 Perkin Elmer digital polarimeter using a sodium lamp at 589 nm. The melting point was recorded on Stuart's melting point apparatus SMP100. All the data analysis relevant to melting point, specific rotation and X-ray diffraction analysis were repeated three times to determine the reproducibility of the data and various parameters.

S2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93–0.98 and O—H = 0.82 Å) and U_{iso}(H) (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints except the hydroxyl hydrogen which were refined freely (Cooper *et al.*, 2010).

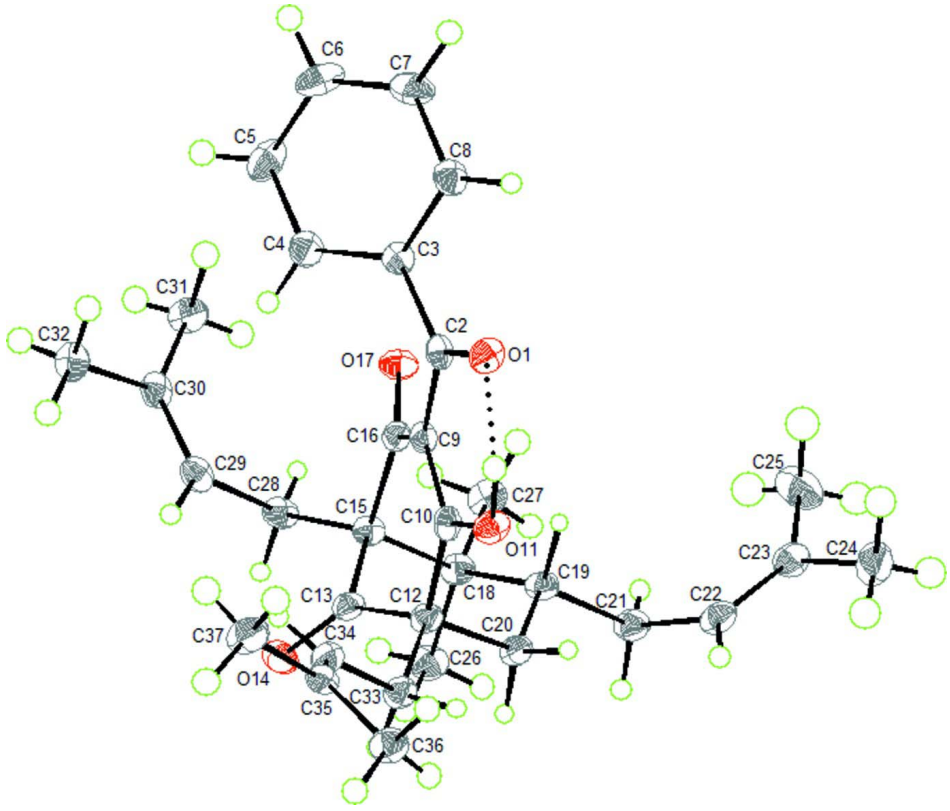

Figure 1

The title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radius. View of the molecule showing intramolecular hydrogen bond.

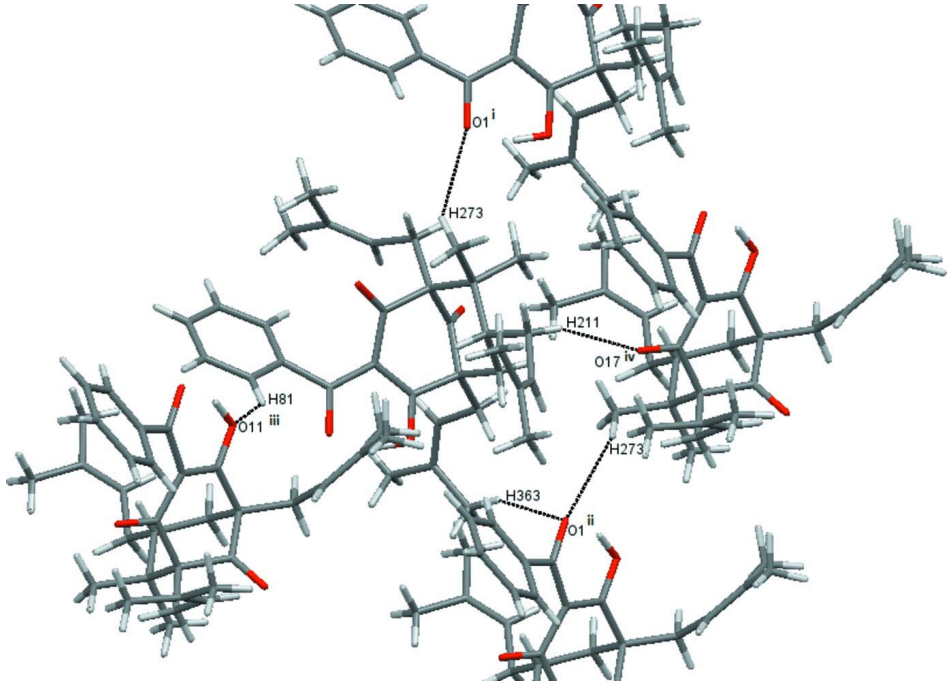

Figure 2

Partial packing diagram showing the C—H···O intermolecular interactions. Symmetry codes: (i) *x* - 1, *y*, *z*; (ii) -*x* + 2, *y* + 1/2, -*z* + 3/2; (iii) -*x* + 2, *y* - 1/2, -*z* + 3/2; (iv) -*x* + 1, *y* + 1/2, -*z* + 3/2.

(1*S*,5*S*,7*R*)-3-Benzoyl-4-hydroxy-8,8-dimethyl-1,5,7-tris(3-methylbut-2-enyl)bicyclo[3.3.1]nona-3-ene-2,9-dione

Crystal data

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M_r = 502.69
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
a = 9.2035 (2) Å
b = 13.4629 (2) Å
c = 22.9607 (5) Å
V = 2844.96 (10) Å^3
Z = 4
F(000) = 1088
D_x = 1.174 Mg m^{-3}
Melting point: 365 K
Cu $K\alpha$ radiation, λ = 1.54180 Å
Cell parameters from 19011 reflections
θ = 3–71°
μ = 0.59 mm^{-1}
T = 100 K
Prismatic, colourless
0.21 × 0.14 × 0.08 mm

Data collection

Oxford Diffraction Gemini diffractometer
Radiation source: Cu Ka
Graphite monochromator
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2002)
T_{min} = 0.86, T_{max} = 0.95
39826 measured reflections
5498 independent reflections
5269 reflections with $I > 2.0\sigma(I)$
R_{int} = 0.034
θ_{max} = 71.6°, θ_{min} = 3.8°
h = −11→11
k = −16→16
l = −28→28

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.084

S = 0.96
5498 reflections
335 parameters
0 restraints
Primary atom site location: other
Hydrogen site location: difference Fourier map
H-atom parameters constrained

Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.04P)^2 + 1.02P]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}
Absolute structure: Flack (1983), 2383 Friedel pairs
Absolute structure parameter: −0.04 (15)

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems open-flow nitrogen cryostat with a nominal stability of 0.1 K.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	1.01156 (11)	0.23087 (8)	0.70014 (5)	0.0254
H1	0.9976	0.3386	0.7123	0.0500*
C2	0.89022 (15)	0.21427 (11)	0.67631 (6)	0.0196
C3	0.87580 (15)	0.11723 (10)	0.64619 (6)	0.0196
C4	0.81066 (17)	0.10926 (12)	0.59161 (7)	0.0252
C5	0.81469 (18)	0.01993 (13)	0.56225 (7)	0.0333
C6	0.87951 (19)	−0.06283 (13)	0.58714 (8)	0.0364
C7	0.94348 (19)	−0.05514 (12)	0.64160 (8)	0.0338
C8	0.94353 (17)	0.03472 (11)	0.67054 (7)	0.0260
C9	0.78010 (15)	0.29113 (10)	0.67650 (6)	0.0189
C10	0.82224 (15)	0.38637 (11)	0.69421 (6)	0.0200
O11	0.95023 (11)	0.40387 (7)	0.71561 (4)	0.0244
C12	0.72277 (16)	0.47533 (10)	0.69123 (6)	0.0207
C13	0.60033 (16)	0.45383 (10)	0.64825 (6)	0.0204
O14	0.56632 (12)	0.51181 (7)	0.61064 (5)	0.0285
C15	0.51798 (15)	0.35827 (10)	0.66056 (6)	0.0198
C16	0.62421 (15)	0.26982 (10)	0.66719 (6)	0.0187
O17	0.57659 (11)	0.18581 (7)	0.66667 (5)	0.0232
C18	0.43562 (16)	0.37607 (10)	0.72158 (6)	0.0215
C19	0.55121 (16)	0.40042 (10)	0.76906 (6)	0.0211
C20	0.64960 (16)	0.48756 (11)	0.75201 (6)	0.0220
C21	0.48510 (17)	0.42104 (11)	0.83005 (7)	0.0255
C22	0.59687 (18)	0.41885 (11)	0.87765 (7)	0.0268
C23	0.61287 (19)	0.35035 (12)	0.91878 (7)	0.0297
C24	0.7280 (2)	0.36145 (15)	0.96492 (8)	0.0415
C25	0.5211 (2)	0.25871 (14)	0.92400 (9)	0.0454
C26	0.32752 (17)	0.46277 (12)	0.71414 (7)	0.0286
C27	0.35104 (16)	0.28311 (12)	0.73993 (7)	0.0275
C28	0.41309 (16)	0.33433 (10)	0.60982 (6)	0.0227
C29	0.48887 (16)	0.31514 (11)	0.55260 (7)	0.0234
C30	0.48971 (16)	0.23037 (11)	0.52250 (6)	0.0235
C31	0.41774 (19)	0.13577 (11)	0.54147 (7)	0.0297

C32	0.56841 (18)	0.22262 (12)	0.46514 (7)	0.0286
C33	0.80586 (17)	0.57064 (11)	0.67524 (6)	0.0238
C34	0.90501 (18)	0.55841 (11)	0.62358 (6)	0.0269
C35	1.03353 (17)	0.60074 (10)	0.61558 (6)	0.0242
C36	1.10148 (18)	0.67277 (11)	0.65730 (7)	0.0283
C37	1.1235 (2)	0.57708 (12)	0.56262 (7)	0.0336
H41	0.7629	0.1648	0.5747	0.0322*
H51	0.7720	0.0154	0.5245	0.0408*
H61	0.8767	−0.1239	0.5662	0.0448*
H71	0.9882	−0.1120	0.6603	0.0423*
H81	0.9888	0.0410	0.7073	0.0323*
H191	0.6141	0.3413	0.7739	0.0240*
H201	0.7285	0.4939	0.7814	0.0255*
H202	0.5948	0.5492	0.7515	0.0250*
H211	0.4404	0.4855	0.8298	0.0302*
H212	0.4098	0.3724	0.8376	0.0308*
H221	0.6650	0.4724	0.8783	0.0333*
H241	0.7808	0.4252	0.9604	0.0629*
H242	0.6826	0.3587	1.0029	0.0630*
H243	0.7968	0.3064	0.9624	0.0633*
H251	0.4774	0.2571	0.9626	0.0712*
H252	0.4405	0.2558	0.8975	0.0712*
H253	0.5783	0.1996	0.9203	0.0711*
H261	0.2489	0.4460	0.6869	0.0435*
H262	0.3726	0.5228	0.7009	0.0443*
H263	0.2793	0.4760	0.7516	0.0424*
H271	0.2827	0.2989	0.7720	0.0415*
H272	0.4133	0.2300	0.7529	0.0415*
H273	0.2935	0.2588	0.7065	0.0413*
H281	0.3488	0.3913	0.6046	0.0275*
H282	0.3528	0.2790	0.6214	0.0274*
H291	0.5415	0.3699	0.5369	0.0295*
H311	0.3450	0.1161	0.5121	0.0463*
H312	0.3641	0.1421	0.5785	0.0443*
H313	0.4882	0.0812	0.5462	0.0471*
H321	0.5028	0.1978	0.4355	0.0443*
H322	0.6530	0.1781	0.4687	0.0436*
H323	0.6061	0.2878	0.4517	0.0438*
H331	0.8619	0.5902	0.7093	0.0268*
H332	0.7355	0.6225	0.6683	0.0297*
H341	0.8682	0.5150	0.5937	0.0329*
H361	1.1371	0.7325	0.6379	0.0438*
H362	1.1884	0.6436	0.6753	0.0454*
H363	1.0391	0.6926	0.6877	0.0428*
H371	1.1424	0.6355	0.5392	0.0501*
H372	1.0793	0.5284	0.5373	0.0518*
H373	1.2186	0.5520	0.5739	0.0518*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0188 (5)	0.0295 (5)	0.0279 (5)	0.0028 (4)	−0.0055 (4)	−0.0029 (4)
C2	0.0186 (7)	0.0247 (7)	0.0157 (6)	−0.0013 (6)	0.0009 (5)	0.0033 (5)
C3	0.0143 (6)	0.0228 (7)	0.0216 (7)	0.0013 (6)	0.0031 (5)	0.0010 (5)
C4	0.0223 (7)	0.0281 (8)	0.0250 (7)	0.0033 (6)	−0.0014 (6)	−0.0008 (6)
C5	0.0277 (8)	0.0415 (9)	0.0307 (8)	0.0014 (7)	−0.0041 (7)	−0.0124 (7)
C6	0.0330 (9)	0.0281 (8)	0.0480 (10)	0.0050 (7)	0.0038 (8)	−0.0156 (7)
C7	0.0331 (9)	0.0251 (7)	0.0432 (9)	0.0107 (7)	0.0017 (7)	0.0014 (7)
C8	0.0231 (7)	0.0299 (8)	0.0251 (7)	0.0045 (6)	−0.0002 (6)	0.0012 (6)
C9	0.0199 (7)	0.0209 (7)	0.0160 (6)	0.0006 (5)	0.0006 (5)	0.0015 (5)
C10	0.0192 (6)	0.0250 (7)	0.0157 (6)	−0.0026 (6)	0.0016 (5)	0.0013 (5)
O11	0.0215 (5)	0.0246 (5)	0.0270 (5)	−0.0021 (4)	−0.0028 (4)	−0.0040 (4)
C12	0.0222 (7)	0.0186 (7)	0.0215 (7)	−0.0026 (5)	0.0020 (6)	−0.0015 (5)
C13	0.0213 (7)	0.0186 (6)	0.0214 (7)	0.0034 (6)	0.0024 (6)	−0.0028 (5)
O14	0.0349 (6)	0.0215 (5)	0.0291 (6)	0.0015 (4)	−0.0056 (5)	0.0039 (4)
C15	0.0170 (6)	0.0196 (6)	0.0227 (7)	0.0005 (5)	−0.0002 (5)	−0.0006 (5)
C16	0.0194 (6)	0.0199 (6)	0.0169 (6)	0.0011 (5)	0.0005 (5)	−0.0007 (5)
O17	0.0195 (5)	0.0185 (5)	0.0318 (6)	−0.0007 (4)	0.0004 (4)	−0.0005 (4)
C18	0.0181 (7)	0.0214 (7)	0.0248 (7)	0.0010 (6)	0.0026 (6)	−0.0010 (5)
C19	0.0213 (7)	0.0179 (6)	0.0242 (7)	0.0021 (5)	0.0028 (6)	−0.0005 (5)
C20	0.0236 (7)	0.0200 (7)	0.0223 (7)	0.0000 (6)	0.0018 (6)	−0.0023 (5)
C21	0.0270 (7)	0.0222 (7)	0.0272 (7)	0.0026 (6)	0.0057 (6)	−0.0009 (6)
C22	0.0305 (8)	0.0241 (7)	0.0259 (7)	−0.0004 (6)	0.0081 (6)	−0.0059 (6)
C23	0.0340 (8)	0.0285 (8)	0.0267 (8)	0.0077 (7)	0.0078 (7)	−0.0029 (6)
C24	0.0491 (11)	0.0477 (10)	0.0278 (9)	0.0143 (9)	0.0009 (8)	−0.0037 (8)
C25	0.0507 (12)	0.0352 (10)	0.0503 (11)	0.0003 (9)	0.0050 (10)	0.0126 (8)
C26	0.0232 (7)	0.0291 (8)	0.0335 (8)	0.0066 (6)	0.0013 (7)	−0.0016 (7)
C27	0.0225 (8)	0.0293 (8)	0.0306 (8)	−0.0031 (6)	0.0043 (6)	−0.0013 (7)
C28	0.0178 (7)	0.0214 (6)	0.0290 (8)	0.0030 (5)	−0.0052 (6)	−0.0002 (6)
C29	0.0196 (7)	0.0252 (7)	0.0254 (7)	−0.0011 (6)	−0.0056 (6)	0.0039 (6)
C30	0.0187 (7)	0.0283 (7)	0.0235 (7)	0.0022 (6)	−0.0060 (6)	0.0012 (6)
C31	0.0312 (8)	0.0258 (7)	0.0322 (8)	0.0000 (7)	0.0025 (7)	−0.0028 (6)
C32	0.0283 (8)	0.0328 (8)	0.0247 (7)	−0.0003 (7)	−0.0015 (6)	0.0001 (6)
C33	0.0282 (8)	0.0199 (7)	0.0232 (7)	−0.0041 (6)	0.0019 (6)	−0.0015 (6)
C34	0.0381 (9)	0.0209 (6)	0.0217 (7)	−0.0045 (6)	0.0022 (7)	−0.0021 (6)
C35	0.0327 (8)	0.0173 (6)	0.0227 (7)	0.0020 (6)	0.0033 (6)	0.0028 (5)
C36	0.0280 (8)	0.0250 (7)	0.0317 (8)	−0.0024 (6)	0.0034 (6)	−0.0012 (6)
C37	0.0409 (9)	0.0267 (8)	0.0332 (9)	−0.0057 (7)	0.0124 (8)	−0.0030 (6)

Geometric parameters (Å, º)

O1—C2	1.2635 (17)	C23—C24	1.506 (3)
H1—O11	0.984	C23—C25	1.500 (3)
C2—C3	1.4842 (19)	C24—H241	0.992
C2—C9	1.448 (2)	C24—H242	0.968
C3—C4	1.393 (2)	C24—H243	0.977

C3—C8	1.391 (2)	C25—H251	0.974
C4—C5	1.379 (2)	C25—H252	0.960
C4—H41	0.950	C25—H253	0.958
C5—C6	1.387 (3)	C26—H261	0.983
C5—H51	0.953	C26—H262	0.958
C6—C7	1.386 (3)	C26—H263	0.984
C6—H61	0.953	C27—H271	0.992
C7—C8	1.380 (2)	C27—H272	0.964
C7—H71	0.969	C27—H273	0.988
C8—H81	0.945	C28—C29	1.510 (2)
C9—C10	1.400 (2)	C28—H281	0.975
C9—C16	1.479 (2)	C28—H282	0.967
C10—O11	1.2979 (17)	C29—C30	1.334 (2)
C10—C12	1.509 (2)	C29—H291	0.953
C12—C13	1.526 (2)	C30—C31	1.500 (2)
C12—C20	1.5582 (19)	C30—C32	1.507 (2)
C12—C33	1.5381 (19)	C31—H311	0.987
C13—O14	1.2054 (18)	C31—H312	0.987
C13—C15	1.5198 (19)	C31—H313	0.986
C15—C16	1.5482 (19)	C32—H321	0.969
C15—C18	1.6110 (19)	C32—H322	0.986
C15—C28	1.5469 (19)	C32—H323	0.993
C16—O17	1.2131 (17)	C33—C34	1.506 (2)
C18—C19	1.558 (2)	C33—H331	0.973
C18—C26	1.543 (2)	C33—H332	0.966
C18—C27	1.533 (2)	C34—C35	1.326 (2)
C19—C20	1.5328 (19)	C34—H341	0.964
C19—C21	1.552 (2)	C35—C36	1.500 (2)
C19—H191	0.990	C35—C37	1.505 (2)
C20—H201	0.994	C36—H361	0.977
C20—H202	0.971	C36—H362	0.982
C21—C22	1.501 (2)	C36—H363	0.943
C21—H211	0.961	C37—H371	0.969
C21—H212	0.969	C37—H372	0.966
C22—C23	1.328 (2)	C37—H373	0.973
C22—H221	0.955		

O1—C2—C3	115.88 (13)	C22—C23—C25	124.43 (16)
O1—C2—C9	119.39 (13)	C24—C23—C25	114.94 (15)
C3—C2—C9	124.59 (12)	C23—C24—H241	110.9
C2—C3—C4	121.69 (13)	C23—C24—H242	109.1
C2—C3—C8	118.39 (13)	H241—C24—H242	109.8
C4—C3—C8	119.53 (14)	C23—C24—H243	109.8
C3—C4—C5	119.68 (15)	H241—C24—H243	109.4
C3—C4—H41	120.4	H242—C24—H243	107.7
C5—C4—H41	119.9	C23—C25—H251	108.9
C4—C5—C6	120.70 (15)	C23—C25—H252	114.7
C4—C5—H51	119.3	H251—C25—H252	104.9

C6—C5—H51	120.0	C23—C25—H253	111.5
C5—C6—C7	119.63 (15)	H251—C25—H253	106.8
C5—C6—H61	118.2	H252—C25—H253	109.5
C7—C6—H61	122.1	C18—C26—H261	111.8
C6—C7—C8	120.00 (15)	C18—C26—H262	113.2
C6—C7—H71	121.4	H261—C26—H262	108.1
C8—C7—H71	118.6	C18—C26—H263	109.3
C3—C8—C7	120.41 (14)	H261—C26—H263	105.5
C3—C8—H81	119.0	H262—C26—H263	108.7
C7—C8—H81	120.6	C18—C27—H271	110.6
C2—C9—C10	117.48 (13)	C18—C27—H272	112.9
C2—C9—C16	122.67 (13)	H271—C27—H272	107.8
C10—C9—C16	119.24 (13)	C18—C27—H273	109.2
C9—C10—O11	121.85 (13)	H271—C27—H273	108.0
C9—C10—C12	123.08 (13)	H272—C27—H273	108.3
O11—C10—C12	115.06 (12)	C15—C28—C29	113.75 (11)
H1—O11—C10	102.2	C15—C28—H281	107.9
C10—C12—C13	109.07 (11)	C29—C28—H281	107.9
C10—C12—C20	107.79 (11)	C15—C28—H282	108.1
C13—C12—C20	106.27 (11)	C29—C28—H282	111.9
C10—C12—C33	111.80 (12)	H281—C28—H282	107.0
C13—C12—C33	111.78 (12)	C28—C29—C30	126.86 (14)
C20—C12—C33	109.91 (11)	C28—C29—H291	115.6
C12—C13—O14	122.17 (13)	C30—C29—H291	117.5
C12—C13—C15	114.12 (11)	C29—C30—C31	124.98 (14)
O14—C13—C15	123.50 (13)	C29—C30—C32	120.98 (14)
C13—C15—C16	110.76 (11)	C31—C30—C32	114.03 (13)
C13—C15—C18	105.69 (11)	C30—C31—H311	109.2
C16—C15—C18	109.03 (11)	C30—C31—H312	113.4
C13—C15—C28	110.33 (11)	H311—C31—H312	105.8
C16—C15—C28	107.93 (11)	C30—C31—H313	112.0
C18—C15—C28	113.10 (11)	H311—C31—H313	108.7
C15—C16—C9	118.54 (12)	H312—C31—H313	107.4
C15—C16—O17	119.21 (13)	C30—C32—H321	109.7
C9—C16—O17	122.20 (13)	C30—C32—H322	110.4
C15—C18—C19	108.57 (11)	H321—C32—H322	110.0
C15—C18—C26	108.64 (12)	C30—C32—H323	112.3
C19—C18—C26	111.01 (12)	H321—C32—H323	107.7
C15—C18—C27	110.89 (12)	H322—C32—H323	106.7
C19—C18—C27	109.04 (12)	C12—C33—C34	113.47 (12)
C26—C18—C27	108.70 (12)	C12—C33—H331	107.3
C18—C19—C20	112.70 (11)	C34—C33—H331	110.0
C18—C19—C21	113.66 (12)	C12—C33—H332	108.0
C20—C19—C21	108.97 (11)	C34—C33—H332	110.8
C18—C19—H191	108.0	H331—C33—H332	107.0
C20—C19—H191	107.4	C33—C34—C35	127.09 (14)
C21—C19—H191	105.7	C33—C34—H341	114.5
C19—C20—C12	113.78 (11)	C35—C34—H341	118.4

C19—C20—H201	108.9	C34—C35—C36	124.15 (14)
C12—C20—H201	107.5	C34—C35—C37	120.78 (14)
C19—C20—H202	110.5	C36—C35—C37	115.06 (14)
C12—C20—H202	107.7	C35—C36—H361	112.4
H201—C20—H202	108.2	C35—C36—H362	110.5
C19—C21—C22	112.63 (12)	H361—C36—H362	104.3
C19—C21—H211	108.9	C35—C36—H363	113.8
C22—C21—H211	108.4	H361—C36—H363	108.0
C19—C21—H212	108.7	H362—C36—H363	107.3
C22—C21—H212	110.3	C35—C37—H371	112.1
H211—C21—H212	107.8	C35—C37—H372	113.5
C21—C22—C23	127.39 (15)	H371—C37—H372	106.9
C21—C22—H221	116.5	C35—C37—H373	110.7
C23—C22—H221	116.1	H371—C37—H373	105.5
C22—C23—C24	120.62 (16)	H372—C37—H373	107.6

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O11—H1···O1	0.98	1.48	2.4227 (14)	158
C27—H273···O1^{i}	0.99	2.63	3.330 (2)	128
C36—H363···O1^{ii}	0.94	2.67	3.523 (2)	151
C8—H81···O11^{iii}	0.95	2.62	3.300 (2)	129
C21—H211···O17^{iv}	0.96	2.70	3.610 (2)	158

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