



Synthesis, structure and Hirshfeld surface analysis of 2-oxo-2*H*-chromen-6-yl 4-*tert*-butylbenzoate: work carried out as part of the AFRAMED project

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Keywords: coumarin derivative; Hirshfeld surface; herringbone packing; crystal structure.

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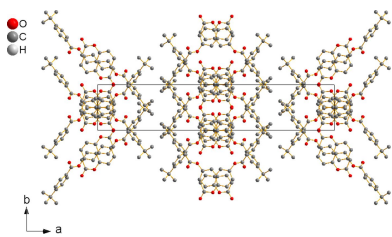
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In the title compound, C₂₀H₁₈O₄, the dihedral angle between the 2*H*-chromen-2-one ring system and the phenyl ring is 89.12 (5)°. In the crystal, the molecules are connected through C—H···O hydrogen bonds to generate [010] double chains that are reinforced by weak aromatic π – π stacking interactions. The unit-cell packing can be described as a tilted herringbone motif. The H···H, H···O/O···H, H···C/C···H and C···C contacts contribute 46.7, 24.2, 16.7 and 7.6%, respectively, to its Hirshfeld surface.

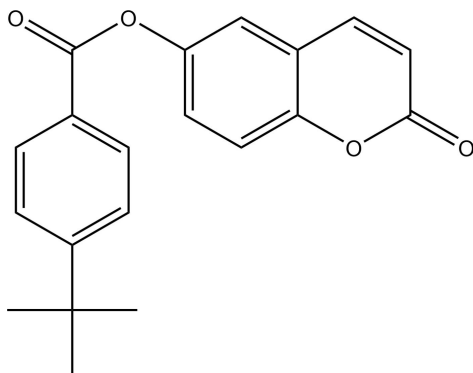
1. AFRAMED and chemical context

The AFRAMED (Supporting research and training in Africa through remote measurements; Abdel-Aal *et al.*, 2023) CNRS project was developed by the Chair of the IUCr Africa Initiative (Professor Claude Lecomte) and his team for Crystallography Education in Africa. The project is based on the remote control by an African laboratory of a diffractometer based in France (in fact now at CRM2) to perform X-ray single-crystal diffraction measurements for research and teaching purposes. Selected crystals are sent to the French partner by African researchers who control the data collection remotely and then receive the intensity data by e-mail. The project was launched in August 2022 and is co-financed by the French Centre National de la Recherche Scientifique (CNRS), the United Nations Educational, Scientific and Cultural Organization (UNESCO), and the International Union of Crystallography (IUCr). Two main steps define AFRAMED: first, four weeks training of African Partners (young lecturers with permanent positions) on a single-crystal diffractometer, and in the second step, the African researchers' laboratories are focal points to assist their colleagues for remote measurements. To date, representatives of Algeria, Cameroon; Congo Brazzaville; Cote d'Ivoire, Egypt, Gabon and Senegal have been trained at the CRM2 laboratory of the Université de Lorraine, France.

This paper presents one of the results of this training: the synthesis, crystal structure and Hirshfeld surface analysis of the title coumarin derivative, **I**, synthesized by colleagues from



Burkina Faso. Such coumarin derivatives have various biological activities such as anticancer (Lacy *et al.*, 2004; Kostova, 2005), anti-inflammatory (Todeschini *et al.*, 1998), antiviral (Borges *et al.*, 2005), anti-malarial (Agarwal *et al.*, 2005), anti-glaucoma (Ziki *et al.*, 2023) and anticoagulant (Maurer *et al.*, 1998) properties.



2. Structural commentary

As shown in Fig. 1, the C1–C9/O1/O2 2*H*-chromen-2-one ring system of **I** is almost planar (r.m.s. deviation = 0.044 Å) and the dihedral angle between this ring system and the C11–C16 phenyl group in the 4-*tert*-butylbenzoate moiety is 89.12 (5)°. This near perpendicular orientation has been observed in other coumarin derivatives with the same motif (Ji *et al.*, 2016). The dihedral angles between the linking C10/C11/O3/O4 ester group and the pendant C1–C9/O1/O2 and C11–C16 groupings are 64.38 (5) and 25.05 (6)°, respectively, indicating that the major twist in the molecule occurs about the C8–O3 bond. An inspection of the bond lengths shows that there is a slight asymmetry of electronic distribution around the coumarin ring: the difference between the C2=C3 [1.343 (2) Å] and C1–C2 [1.449 (2) Å] separations confirms the double-bond character of the former as indicated in the chemical scheme. Atom C20 of the *tert*-butyl group lies close to the plane of its attached ring [deviation = 0.226 (2) Å] whereas C18 and C19 are displaced either side of the ring [deviations = –1.465 (1) and 0.964 (1) Å, respectively].

3. Supramolecular features

In the crystal, the molecules of **I** are connected by C–H···O hydrogen bonds (Table 1) to build double chains propagating

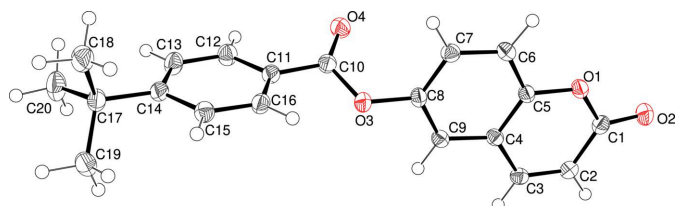


Figure 1

The molecular structure of **I** with displacement ellipsoids drawn at the 50% probability level.

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C9–H9···O1 ⁱ	0.987 (13)	2.584 (13)	3.5682 (14)	174.8 (10)
C6–H6···O3 ⁱⁱ	0.985 (15)	2.603 (15)	3.5835 (14)	173.9 (12)
C9–H9···O1 ⁱ	0.987 (13)	2.584 (13)	3.5682 (14)	174.8 (10)
C16–H16···O2 ⁱⁱⁱ	0.968 (14)	2.416 (15)	3.2628 (16)	146.0 (11)

Symmetry codes: (i) *x*, *y* + 1, *z*; (ii) *x*, *y* – 1, *z*; (iii) –*x*, –*y* + 1, –*z*.

in the [010] direction: this motif results in two adjacent $R_2^2(8)$ loops between each pair of molecules in one chain formed by the C3, C6 and C9 hydrogen bonds (Fig. 2). The C16 hydrogen bond provides the linkage to the second chain (Fig. 3). The pendant 4-*tert*-butylbenzoate moieties are parallel and shifted by translation along the *b* axis. Aromatic π – π stacking interactions between centrosymmetric pairs of C4–C9 rings reinforce the cohesion of the double chains [centroid–centroid separation = 3.6301 (8), slippage = 1.579 Å]. The unit-cell packing of **I** can be described as a tilted herringbone motif (Fig. 4), as also observed in the crystal structure of 1-(1,2-dihydrophthalazin-1-ylidene)-2-[1-(thiophen-2-yl)ethylidene]hydrazine (Majoumo-Mbe *et al.*, 2019).

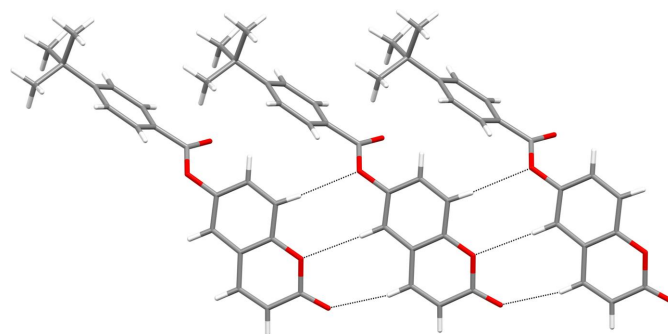


Figure 2

Fragment of a [010] chain in the structure of **I** showing the hydrogen bonds involving C3, C6 and C9 as black dashed lines.

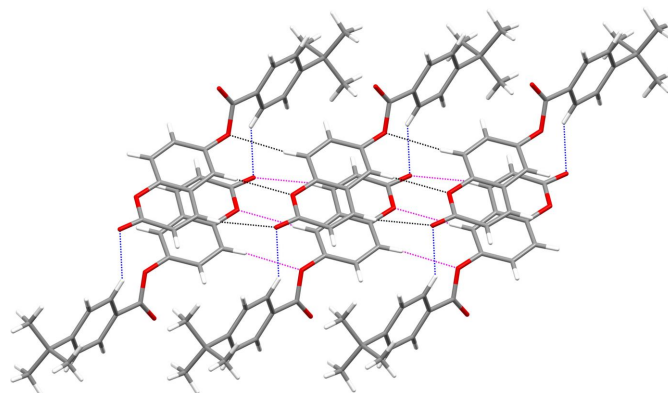


Figure 3

Partial packing diagram for **I** showing [010] double chains arising from C–H···O hydrogen bonds (black dashed lines in one chain, magenta dashed lines in the other and the C16 cross-linking bonds in blue).

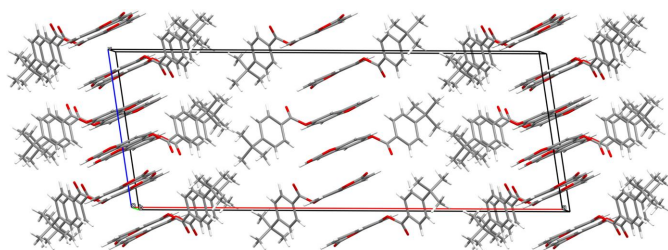


Figure 4
The unit-cell packing for **I** viewed down [010].

4. Database survey

A search of the Cambridge Structural Database (CSD, version 5.43; update 3, September 2022; Groom *et al.*, 2016) for structures having a coumarin motif similar to that of **I** returned five hits for the following molecules: 4-methyl-2-oxo-2H-1-benzopyran-6-yl pyridine-2-carboxylate (CSD refcode ATOROT; Ji *et al.*, 2016), 4-methyl-2-oxo-2H-1-benzopyran-6-yl pyridine-3-carboxylate (ATORUZ; Ji *et al.*, 2016), 4-methyl-2-oxo-2H-1-benzopyran-6-yl pyridine-4-carboxylate (ATOSAG; Ji *et al.*, 2016), 6-acetoxycoumarin (GASXON; Murthy *et al.*, 1988) and 4-methyl-2-oxo-2H-chromen-6-yl benzoate (YEFSOU; Ji *et al.*, 2017). ATORUZ only features a C6—H6···O3 hydrogen bond because a methyl group is bonded to C9 (according to the numbering scheme of **I**). This prevents the formation of layers like those found in the packing of **I**, although similar layers are found in GASXON.

5. Hirshfeld surface and Fingerprint plots

The interactions mentioned above are confirmed by the two-dimensional fingerprint plots of **I** (Fig. 5). The greatest contributions are the H···H and H···O/O···H contacts with 46.7 and 24.2%, respectively. The H···C/C···H and C···C contacts contribute 16.7 and 7.6%, respectively. The contri-

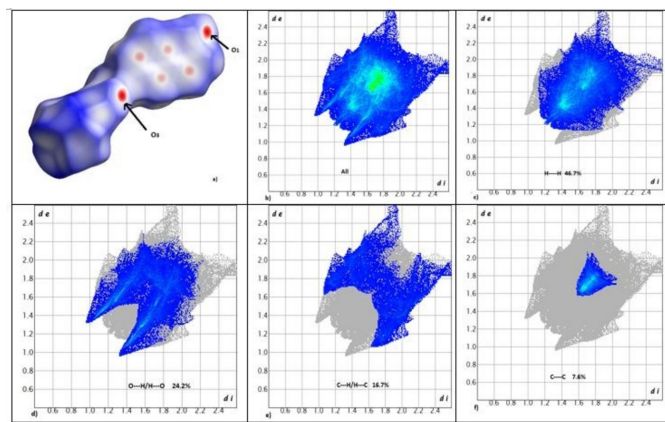


Figure 5
(a) Hirshfeld surface of **I** mapped over d_{norm} and (b) two-dimensional fingerprint plots of (b) overall and delineated into contributions from different contacts: (c) H—H, (d) H—O/O—H, (e) H—C/C—H and (f) C—C.

Table 2

Experimental details.

Crystal data	
Chemical formula	$\text{C}_{20}\text{H}_{18}\text{O}_4$
M_r	322.34
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	100
a, b, c (Å)	35.908 (4), 6.8473 (6), 13.2661 (11)
β (°)	98.915 (4)
V (Å ³)	3222.3 (5)
Z	8
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.09
Crystal size (mm)	0.20 × 0.15 × 0.08
Data collection	
Diffractometer	Bruker D8 Venture
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
$T_{\text{min}}, T_{\text{max}}$	0.731, 0.895
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	60054, 4940, 3518
R_{int}	0.061
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.716
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.044, 0.124, 1.11
No. of reflections	4940
No. of parameters	289
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.30, -0.27

Computer programs: *APEX3* and *SAINT* (Bruker, 2019), *SHELXT* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

butions of the H···H interactions in **I** to Hirshfeld surface are greater than those found in 2-oxo-2H-chromen-3-yl 4-chlorobenzoate (Ziki *et al.* 2017); this can be related to the packing of the 2H-1-chromen-6-yl moieties of **I**. The H···O/O···H contacts are related to the C—H···O1 hydrogen bonds shown in Fig. 2. Their contact points are shown in red and are labelled on the Hirshfeld surface (see Fig. 5a).

6. Synthesis and crystallization

To 30 ml solution of 4-*tert*-butylbenzoyl chloride (1.2 g; 6.17 mmol) in dry tetrahydrofuran, were added dry triethylamine (2.6 ml; 3.1 mmol) and 6-hydroxycoumarin (1.00 g; 6.17 mmol) in small portions over 30 min. The mixture was then refluxed for 4 h and poured into 40 ml of chloroform. The solution was acidified with diluted hydrochloric acid until the pH was 2.5. The organic layer was extracted, washed with water to neutrality, dried over MgSO_4 and the solvent removed. The resulting precipitate was suction filtered, washed with petroleum ether and recrystallized from chloroform solution to give colorless prismatic crystals of **I** in a yield of 84%.

7. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 2. The H atoms were located in difference maps and their positions and U_{iso} values were freely refined.

Acknowledgements

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References

- Abdel-Aal, S. K., Kenfack, T. P., Bouraima, A., Djifa, H. A., Emmanuel, W., Bendeif, E.-E. & Lecomte, C. (2023). <https://www.iucr.org/news/newsletter/volume-31/number-1/appui-a-la-formation-et-la-recherche-a-travers-les-mesures-a-distance-afamed-a-recent-and-ambitious-project-for-the-development-of-crystallography-in-africa>.
- Agarwal, A., Srivastava, K., Puri, S. K. & Chauhan, P. M. S. (2005). *Bioorg. Med. Chem.* **13**, 4645–4650.
- 12
- Bruker (2019). *APEX3* and *SAINT*. Bruker AXS Inc. Madison, Wisconsin, USA.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Ji, W., Li, L., Eniola-Adefeso, O., Wang, Y., Liu, C. & Feng, C. (2017). *J. Mater. Chem. B*, **5**, 7790–7795.
- Ji, W., Liu, G., Li, Z. & Feng, C. (2016). *Appl. Mater. Interfaces*, **8**, 5188–5195.
- Kostova, I. (2005). *Curr. Med. Chem. Anti-Cancer Agents*, **5**, 29–46.
- Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
- Lacy, A. & O’Kennedy, R. (2004). *Curr. Pharm. Des.* **10**, 3797–3811.
- Majoumo-Mbe, F., Ngwang Nfor, E., Kenfack Tsobnang, P., Nguemmeni Eloundou, V. B., Ngwain Yong, J. & Iris Efeti, I. (2019). *Acta Cryst.* **E75**, 251–254.
- Maurer, H. H. & Arlt, J. W. J. (1998). *J. Chromatogr. B Biomed. Sci. Appl.* **714**, 181–195.
- Murthy, G. S., Ramamurthy, V. & Venkatesan, K. (1988). *Acta Cryst.* **C44**, 307–311.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Todeschini, A. R., de Miranda, A. L. P., da Silva, K. C. M., Parrini, S. C. & Barreiro, E. J. (1998). *Eur. J. Med. Chem.* **33**, 189–199.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Ziki, E., Akonon, L., Kouman, K. C., Dali, D., Megnassan, E., Kakou-Yao, R., Tenon, A. J., Frecer, V. & Miertus, S. J. (2023). *Pharm. Res. Int.* **35**, 10–33.
- Ziki, E., Sosso, S., Mansilla-Koblavi, F., Djandé, A. & Kakou-Yao, R. (2017). *Acta Cryst.* **E73**, 45–47.

supporting information

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Synthesis, structure and Hirshfeld surface analysis of 2-oxo-2*H*-chromen-6-yl 4-*tert*-butylbenzoate: work carried out as part of the AFRAMED project

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Computing details

2-Oxo-2*H*-chromen-6-yl 4-*tert*-butylbenzoate

Crystal data

$C_{20}H_{18}O_4$

$M_r = 322.34$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 35.908\ (4)\ \text{\AA}$

$b = 6.8473\ (6)\ \text{\AA}$

$c = 13.2661\ (11)\ \text{\AA}$

$\beta = 98.915\ (4)^\circ$

$V = 3222.3\ (5)\ \text{\AA}^3$

$Z = 8$

$F(000) = 1360$

$D_x = 1.329\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 4940 reflections

$\theta = 2.3\text{--}30.6^\circ$

$\mu = 0.09\ \text{mm}^{-1}$

$T = 100\ \text{K}$

Prism, colourless

$0.20 \times 0.15 \times 0.08\ \text{mm}$

Data collection

Bruker D8 Venture

diffractometer

Radiation source: fine-focus sealed tube

Mirror monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Krause *et al.*, 2015)

$T_{\min} = 0.731$, $T_{\max} = 0.895$

60054 measured reflections

4940 independent reflections

3518 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.061$

$\theta_{\max} = 30.6^\circ$, $\theta_{\min} = 2.3^\circ$

$h = -51 \rightarrow 51$

$k = -9 \rightarrow 9$

$l = -18 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.124$

$S = 1.11$

4940 reflections

289 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: structure-
invariant direct methods

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0582P)^2 + 0.7544P]$

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

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

$\Delta\rho_{\max} = 0.30\ \text{e \AA}^{-3}$

$\Delta\rho_{\min} = -0.27\ \text{e \AA}^{-3}$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.01365 (2)	0.14244 (11)	0.13861 (6)	0.02265 (19)
O3	-0.07925 (2)	0.77690 (11)	0.03962 (6)	0.02359 (19)
C9	-0.01929 (3)	0.65096 (16)	0.10952 (8)	0.0204 (2)
O2	0.06636 (3)	0.00843 (12)	0.21536 (7)	0.0293 (2)
O4	-0.11921 (2)	0.70415 (12)	0.15117 (7)	0.0276 (2)
C5	-0.00869 (3)	0.30453 (15)	0.11373 (8)	0.0195 (2)
C2	0.06565 (3)	0.35501 (17)	0.20298 (9)	0.0225 (2)
C6	-0.04569 (3)	0.26950 (17)	0.07004 (9)	0.0219 (2)
C4	0.00547 (3)	0.49326 (15)	0.13275 (8)	0.0192 (2)
C1	0.05017 (3)	0.15982 (17)	0.18837 (9)	0.0227 (2)
C10	-0.11073 (3)	0.80567 (16)	0.08412 (9)	0.0222 (2)
C3	0.04453 (3)	0.51431 (17)	0.17689 (9)	0.0211 (2)
C11	-0.13230 (3)	0.97493 (16)	0.03591 (9)	0.0221 (2)
C7	-0.06982 (3)	0.42622 (17)	0.04737 (9)	0.0221 (2)
C8	-0.05615 (3)	0.61479 (16)	0.06872 (9)	0.0207 (2)
C16	-0.12922 (3)	1.03226 (17)	-0.06341 (9)	0.0231 (2)
C14	-0.17523 (3)	1.28898 (17)	-0.05714 (9)	0.0235 (2)
C15	-0.15077 (3)	1.18512 (17)	-0.10943 (9)	0.0236 (2)
C12	-0.15665 (4)	1.07610 (18)	0.08908 (10)	0.0272 (3)
C13	-0.17742 (4)	1.23237 (18)	0.04322 (10)	0.0280 (3)
C17	-0.19912 (3)	1.45327 (17)	-0.11186 (10)	0.0263 (3)
C19	-0.17461 (4)	1.58787 (19)	-0.16687 (12)	0.0327 (3)
C20	-0.21829 (5)	1.5761 (2)	-0.03849 (13)	0.0402 (4)
C18	-0.22939 (4)	1.3594 (2)	-0.19155 (13)	0.0375 (3)
H9	-0.0100 (4)	0.7858 (19)	0.1225 (9)	0.018 (3)*
H3	0.0540 (4)	0.644 (2)	0.1881 (10)	0.022 (3)*
H2	0.0923 (4)	0.3644 (18)	0.2369 (9)	0.019 (3)*
H6	-0.0534 (4)	0.132 (2)	0.0585 (11)	0.031 (4)*
H16	-0.1128 (4)	0.963 (2)	-0.1025 (11)	0.028 (4)*
H7	-0.0961 (4)	0.4084 (19)	0.0178 (10)	0.024 (3)*
H15	-0.1483 (4)	1.220 (2)	-0.1788 (11)	0.028 (4)*
H12	-0.1584 (4)	1.038 (2)	0.1596 (12)	0.033 (4)*
H13	-0.1935 (4)	1.302 (2)	0.0848 (12)	0.040 (4)*
H19A	-0.1646 (5)	1.519 (2)	-0.2236 (13)	0.042 (4)*
H18A	-0.2457 (5)	1.460 (2)	-0.2292 (12)	0.042 (4)*
H19B	-0.1528 (5)	1.642 (2)	-0.1159 (13)	0.046 (5)*
H20A	-0.2378 (4)	1.495 (2)	-0.0068 (12)	0.038 (4)*
H18B	-0.2453 (5)	1.273 (3)	-0.1618 (14)	0.054 (5)*
H20B	-0.1987 (4)	1.634 (2)	0.0198 (12)	0.041 (4)*

H20C	-0.2317 (5)	1.687 (3)	-0.0776 (13)	0.051 (5)*
H19C	-0.1898 (5)	1.702 (2)	-0.1991 (12)	0.045 (4)*
H18C	-0.2170 (5)	1.281 (3)	-0.2455 (14)	0.055 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0223 (4)	0.0180 (4)	0.0272 (4)	0.0017 (3)	0.0023 (3)	0.0003 (3)
O3	0.0218 (4)	0.0213 (4)	0.0278 (4)	0.0041 (3)	0.0043 (3)	0.0037 (3)
C9	0.0228 (6)	0.0186 (5)	0.0200 (5)	-0.0004 (4)	0.0039 (4)	0.0008 (4)
O2	0.0292 (5)	0.0237 (4)	0.0349 (5)	0.0074 (3)	0.0046 (4)	0.0034 (4)
O4	0.0293 (5)	0.0255 (4)	0.0289 (5)	0.0011 (4)	0.0069 (4)	0.0031 (3)
C5	0.0218 (5)	0.0173 (5)	0.0197 (5)	0.0018 (4)	0.0044 (4)	0.0010 (4)
C2	0.0200 (5)	0.0251 (6)	0.0227 (6)	0.0001 (4)	0.0042 (4)	-0.0004 (4)
C6	0.0250 (6)	0.0184 (5)	0.0223 (6)	-0.0014 (4)	0.0035 (4)	-0.0009 (4)
C4	0.0215 (5)	0.0182 (5)	0.0178 (5)	-0.0005 (4)	0.0033 (4)	0.0007 (4)
C1	0.0219 (5)	0.0245 (6)	0.0225 (6)	0.0027 (4)	0.0058 (4)	0.0003 (4)
C10	0.0210 (5)	0.0211 (5)	0.0239 (6)	-0.0005 (4)	0.0017 (4)	-0.0027 (4)
C3	0.0223 (6)	0.0215 (5)	0.0199 (5)	-0.0023 (4)	0.0045 (4)	-0.0003 (4)
C11	0.0197 (5)	0.0206 (5)	0.0256 (6)	0.0001 (4)	0.0023 (4)	-0.0012 (4)
C7	0.0206 (6)	0.0226 (5)	0.0226 (6)	-0.0012 (4)	0.0021 (4)	0.0005 (4)
C8	0.0226 (6)	0.0188 (5)	0.0209 (5)	0.0038 (4)	0.0042 (4)	0.0017 (4)
C16	0.0211 (6)	0.0227 (5)	0.0258 (6)	0.0020 (4)	0.0043 (4)	-0.0019 (4)
C14	0.0190 (5)	0.0207 (5)	0.0297 (6)	-0.0001 (4)	0.0010 (4)	-0.0014 (4)
C15	0.0233 (6)	0.0240 (6)	0.0228 (6)	0.0007 (4)	0.0015 (4)	-0.0001 (4)
C12	0.0288 (6)	0.0282 (6)	0.0257 (6)	0.0037 (5)	0.0072 (5)	0.0014 (5)
C13	0.0275 (6)	0.0277 (6)	0.0299 (6)	0.0067 (5)	0.0081 (5)	-0.0014 (5)
C17	0.0232 (6)	0.0229 (6)	0.0318 (7)	0.0041 (5)	0.0008 (5)	-0.0002 (5)
C19	0.0331 (7)	0.0242 (6)	0.0396 (8)	0.0013 (5)	0.0017 (6)	0.0042 (5)
C20	0.0427 (9)	0.0341 (7)	0.0451 (9)	0.0169 (7)	0.0104 (7)	0.0018 (6)
C18	0.0288 (7)	0.0307 (7)	0.0482 (9)	0.0014 (6)	-0.0094 (6)	0.0017 (6)

Geometric parameters (Å, °)

O1—C1	1.3789 (14)	C7—H7	0.973 (13)
O1—C5	1.3791 (13)	C16—C15	1.3858 (16)
O3—C10	1.3680 (14)	C16—H16	0.967 (14)
O3—C8	1.4036 (13)	C14—C15	1.3956 (17)
C9—C8	1.3724 (16)	C14—C13	1.4005 (18)
C9—C4	1.4023 (15)	C14—C17	1.5281 (16)
C9—H9	0.987 (13)	C15—H15	0.967 (14)
O2—C1	1.2150 (14)	C12—C13	1.3895 (17)
O4—C10	1.2047 (14)	C12—H12	0.983 (15)
C5—C6	1.3855 (16)	C13—H13	0.983 (16)
C5—C4	1.3972 (15)	C17—C20	1.5286 (19)
C2—C3	1.3430 (16)	C17—C19	1.5347 (19)
C2—C1	1.4490 (16)	C17—C18	1.5348 (18)
C2—H2	0.993 (13)	C19—H19A	0.999 (17)

C6—C7	1.3829 (16)	C19—H19B	1.021 (17)
C6—H6	0.985 (14)	C19—H19C	1.007 (17)
C4—C3	1.4410 (16)	C20—H20A	1.034 (16)
C10—C11	1.4829 (16)	C20—H20B	1.040 (16)
C3—H3	0.956 (13)	C20—H20C	0.999 (18)
C11—C12	1.3903 (17)	C18—H18A	0.990 (16)
C11—C16	1.3955 (17)	C18—H18B	0.948 (18)
C7—C8	1.3949 (16)	C18—H18C	1.047 (18)
C1—O1—C5	121.32 (9)	C11—C16—H16	120.8 (8)
C10—O3—C8	119.20 (9)	C15—C14—C13	117.63 (11)
C8—C9—C4	119.17 (10)	C15—C14—C17	119.29 (11)
C8—C9—H9	121.0 (7)	C13—C14—C17	123.04 (11)
C4—C9—H9	119.8 (7)	C16—C15—C14	121.16 (11)
O1—C5—C6	116.43 (9)	C16—C15—H15	118.5 (8)
O1—C5—C4	121.28 (10)	C14—C15—H15	120.3 (8)
C6—C5—C4	122.28 (10)	C13—C12—C11	119.91 (12)
C3—C2—C1	121.66 (11)	C13—C12—H12	120.9 (8)
C3—C2—H2	122.0 (7)	C11—C12—H12	119.2 (8)
C1—C2—H2	116.3 (7)	C12—C13—C14	121.60 (11)
C7—C6—C5	118.98 (10)	C12—C13—H13	116.8 (9)
C7—C6—H6	123.8 (8)	C14—C13—H13	121.6 (9)
C5—C6—H6	117.2 (8)	C14—C17—C20	112.19 (11)
C5—C4—C9	118.16 (10)	C14—C17—C19	110.30 (10)
C5—C4—C3	118.03 (10)	C20—C17—C19	108.67 (11)
C9—C4—C3	123.80 (10)	C14—C17—C18	107.72 (10)
O2—C1—O1	116.33 (10)	C20—C17—C18	109.17 (12)
O2—C1—C2	126.25 (11)	C19—C17—C18	108.73 (12)
O1—C1—C2	117.41 (10)	C17—C19—H19A	111.9 (9)
O4—C10—O3	123.78 (10)	C17—C19—H19B	109.9 (9)
O4—C10—C11	126.47 (11)	H19A—C19—H19B	110.0 (13)
O3—C10—C11	109.74 (10)	C17—C19—H19C	110.8 (9)
C2—C3—C4	119.92 (10)	H19A—C19—H19C	106.1 (13)
C2—C3—H3	122.8 (8)	H19B—C19—H19C	107.9 (13)
C4—C3—H3	117.2 (8)	C17—C20—H20A	111.2 (9)
C12—C11—C16	119.14 (11)	C17—C20—H20B	111.4 (9)
C12—C11—C10	119.88 (11)	H20A—C20—H20B	109.1 (13)
C16—C11—C10	120.97 (10)	C17—C20—H20C	108.3 (10)
C6—C7—C8	119.02 (11)	H20A—C20—H20C	108.6 (14)
C6—C7—H7	121.8 (8)	H20B—C20—H20C	108.1 (13)
C8—C7—H7	119.2 (8)	C17—C18—H18A	110.9 (9)
C9—C8—C7	122.33 (10)	C17—C18—H18B	112.4 (11)
C9—C8—O3	117.29 (10)	H18A—C18—H18B	107.1 (14)
C7—C8—O3	120.12 (10)	C17—C18—H18C	110.8 (10)
C15—C16—C11	120.53 (11)	H18A—C18—H18C	107.2 (13)
C15—C16—H16	118.6 (8)	H18B—C18—H18C	108.3 (14)
C1—O1—C5—C6	-175.80 (10)	C5—C6—C7—C8	0.31 (17)

C1—O1—C5—C4	3.67 (16)	C4—C9—C8—C7	-1.38 (17)
O1—C5—C6—C7	177.35 (10)	C4—C9—C8—O3	-175.41 (10)
C4—C5—C6—C7	-2.11 (17)	C6—C7—C8—C9	1.43 (18)
O1—C5—C4—C9	-177.29 (10)	C6—C7—C8—O3	175.30 (10)
C6—C5—C4—C9	2.15 (17)	C10—O3—C8—C9	-120.25 (11)
O1—C5—C4—C3	1.60 (16)	C10—O3—C8—C7	65.57 (14)
C6—C5—C4—C3	-178.97 (10)	C12—C11—C16—C15	-1.48 (18)
C8—C9—C4—C5	-0.39 (16)	C10—C11—C16—C15	177.09 (10)
C8—C9—C4—C3	-179.21 (10)	C11—C16—C15—C14	1.79 (18)
C5—O1—C1—O2	173.38 (10)	C13—C14—C15—C16	-0.42 (17)
C5—O1—C1—C2	-6.99 (15)	C17—C14—C15—C16	-178.56 (11)
C3—C2—C1—O2	-175.08 (12)	C16—C11—C12—C13	-0.18 (18)
C3—C2—C1—O1	5.34 (17)	C10—C11—C12—C13	-178.76 (11)
C8—O3—C10—O4	3.51 (16)	C11—C12—C13—C14	1.6 (2)
C8—O3—C10—C11	-175.37 (9)	C15—C14—C13—C12	-1.26 (18)
C1—C2—C3—C4	-0.26 (17)	C17—C14—C13—C12	176.81 (12)
C5—C4—C3—C2	-3.21 (16)	C15—C14—C17—C20	-168.91 (12)
C9—C4—C3—C2	175.60 (11)	C13—C14—C17—C20	13.06 (17)
O4—C10—C11—C12	24.57 (18)	C15—C14—C17—C19	-47.60 (15)
O3—C10—C11—C12	-156.59 (11)	C13—C14—C17—C19	134.37 (13)
O4—C10—C11—C16	-153.99 (12)	C15—C14—C17—C18	70.93 (15)
O3—C10—C11—C16	24.85 (15)	C13—C14—C17—C18	-107.11 (14)

Hydrogen-bond geometry (\AA , $^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C9—H9 \cdots O1 ⁱ	0.987 (13)	2.584 (13)	3.5682 (14)	174.8 (10)
C6—H6 \cdots O3 ⁱⁱ	0.985 (14)	2.603 (15)	3.5835 (14)	173.9 (12)
C9—H9 \cdots O1 ⁱ	0.987 (13)	2.584 (13)	3.5682 (14)	174.8 (10)
C16—H16 \cdots O2 ⁱⁱⁱ	0.968 (14)	2.416 (15)	3.2628 (16)	146.0 (11)

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