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Crystal structure and Hirshfeld surface analysis of 3-({4-[(4-cyanophenoxy)carbonyl]phenoxy}carbonyl)phenyl 4-(benzyloxy)-3-chlorobenzoate

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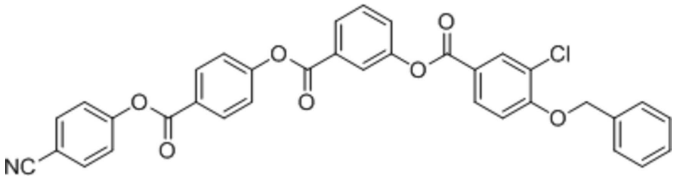
The title compound, $C_{35}H_{22}ClNO_7$, is a non-liquid crystal with a bent-shaped molecule. The dihedral angles between adjacent aromatic rings in the molecule (starting from the cyanobenzene ring) are 72.61 (2), 87.69 (4), 64.08 (2) and 88.23 (2)°, indicating that adjacent rings are close to perpendicular to each other. In the crystal, the molecules are linked by weak C—H···N and C—H···π interactions, thereby forming a two-dimensional supramolecular architecture in the *ac* plane. The most important contributions to the crystal packing arise from H···H (59.3%), S···H (27.4%) and O···H (7.5%) interactions, as determined by a Hirshfeld surface analysis.

1. Chemical context

Banana/bent-shaped liquid crystals (LCs) are of great interest in the field of display materials. In particular, the –CN groups at the terminal end (Walba *et al.*, 2000; Reddy & Sadashiva, 2004) of banana-shaped LCs have been linked to their bent or bow (twisted) anisometric phase with C_{2v} symmetry. Furthermore, they exhibit polar order, chirality and spontaneous polarization in the fluid phase. We have reported the crystal structures of LC intermediates and found that benzyloxy group-substituted molecules are prone to be hydrophobic (Kashi *et al.*, 2012; Al-Eryani *et al.*, 2011). Benzyloxy group-substituted molecules also play a significant role in synthesizing bent-shaped LCs and non-LCs (Palakshamurthy *et al.*, 2012). Hence, it is useful to study benzyloxy group-substituted bent-shaped molecules to understand the structural properties and the relationship between LCs and crystal structures.



In a continuation of this work, we investigated the title molecule, which possesses five aromatic rings with three ester groups and a benzyloxy group at one terminal end, presumably making the molecule highly polar. Furthermore, it has a chloro group at one side and a cyano group at the opposite terminal end of the molecule, inducing an unsymmetrical

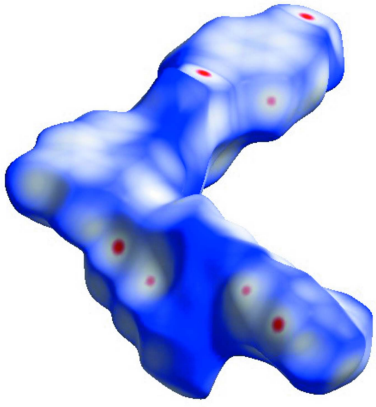


Table 1
Hydrogen-bond geometry (Å, °).

*Cg*4 and *Cg*5 are the centroids of the C23–C28 and C30–C35 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O2	0.944 (18)	2.411 (17)	2.7213 (19)	98.9 (12)
C12—H12···O4	0.93	2.42	2.733 (2)	100
C24—H24···O6	0.93	2.40	2.721 (2)	100
C17—H17···N1^{i}	0.93	2.62	3.504 (3)	158
C25—H25···*Cg*5^{ii}	0.93	2.86	3.744 (2)	158
C31—H31···*Cg*4^{iii}	0.93	2.82	3.702 (3)	158

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

structure (Hartung *et al.*, 2000). The molecule was subjected to LC characterization studies, but it did not show any LC properties, which may be due to the absence of a flexible alkyl chain. The title compound was synthesized according to the procedure described by Sadashiva *et al.* (2002) and its crystal structure is reported herein.

2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. The dihedral angles between the aromatic rings are as follows: *A*/*B* = 64.08 (2), *A*/*C*= 29.75 (2), *A*/*D* = 87.69 (4), *A*/*E* = 16.07 (3), *B*/*C* = 88.23 (2), *B*/*D* = 87.88 (4), *B*/*E* = 68.87 (4), *C*/*D* = 82.27 (3), *E*/*D* = 72.61 (2) and *C*/*E* = 37.46 (4)°, where *A*, *B*, *C*, *D* and *E* are the C1–C6, C23–C28, C30–C35, C8–C13 and C15–C20, rings, respectively. The torsion angles associated with the benzyloxy group are −7.2 (3) (C15—O4—C14—O3), −3.1 (3) (C8—O2—C7—O1) and −0.7 (2)° (C3—O6—C22—O5). Three short intramolecular C—H···O contacts (Table 1) may influence the molecular conformation.

3. Supramolecular features

In the crystal, the molecules are linked by weak C—H···N hydrogen bonds and weak C—H···π interactions (Table 1) to generate a two-dimensional supramolecular architecture propagating in the *ac* plane as shown in Fig. 2. Furthermore, the molecules are linked by centrosymmetric aromatic π–π stacking interactions with *Cg*4···*Cg*4 and *Cg*3···*Cg*3 = 3.6387 (10) Å (slippage = 1.086 Å) and 3.7740 (10) (slippage = 1.407 Å), respectively, as shown in Fig. 3 (*Cg*4 is the centroid of the C23–C28 ring and *Cg*3 is the centroid of the C15–C20 ring).

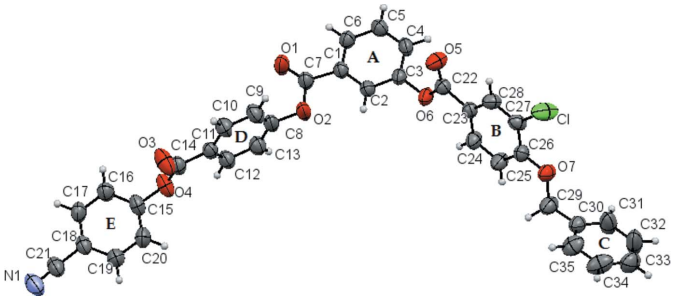


Figure 1
The molecular structure of the title compound, showing displacement ellipsoids drawn at the 50% probability level.

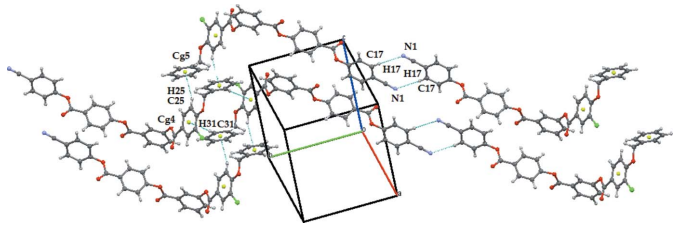


Figure 2
The molecular packing of the title compound. Dashed lines indicate the C—H···π interactions.

4. Database survey

A search of the Cambridge Structural Database (CSD, version 5.42, update of November 2020; Groom *et al.*, 2016) for molecules containing the (4-cyanophenoxy)carbonyl fragment resulted in four matches with CSD refcodes EWUSIA (Srinivasa *et al.*, 2015), IBUXOV (Ji *et al.*, 2017), IBUXUB (Yingchun *et al.*, 2016) and OCUTIS (Yingchun *et al.*, 2016). In all these structures there is a 4-cyanophenoxy grouping at the one end of the molecule, similar to the title compound. In IBUXOV, IBUXUB and OCUTIS the same core exists at both ends of the molecule. Sometimes the presence of a –CN group at both terminals of the molecule induces liquid-crystal properties.

In EWUSIA, the dihedral angles between the cyanobenzoate ring and the first neighbouring benzene ring, and between the second neighbour and the first and second benzene rings are 50.47 (2), 10.15 (3) and 50.02 (5)° compared to 72.61 (2), 16.06 (2) and 87.69 (4)° in the title molecule. In IBUXOV, the dihedral angles between the rings (cyanobenzoate ring and the neighbouring benzene ring) are 69.45 (2) and 64.20 (3)°, and 73.60 (3) and 84.16 (3)° between the adjacent cyanobenzoate and benzene rings themselves. In IBUXUB, the dihedral angles between the rings (cyanobenzoate and the neighbouring benzene ring) are 69.68 (2)

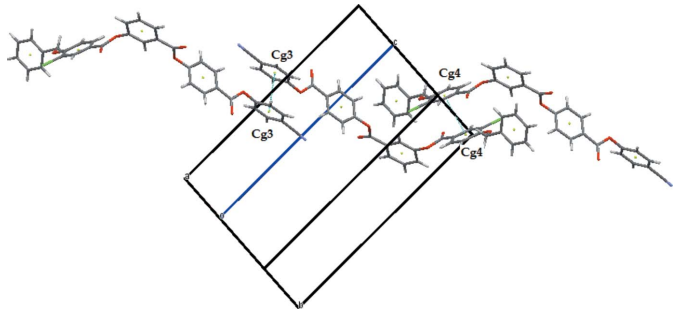


Figure 3
The molecular packing of the title compound. Dashed lines indicate the π–π stacking interactions.

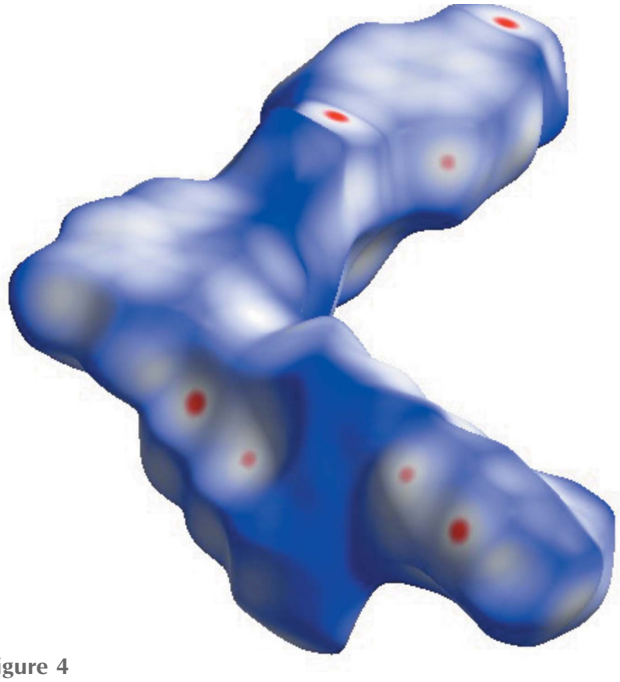


Figure 4
Hirshfeld surface of the title compound mapped with d_{norm}.

and 74.28 (4)°, and 48.87 (2) and 89.88 (4)° between the cyanobenzoate and benzene rings. In OCUTIS, the dihedral angles between adjacent cyanobenzoate and benzene rings are 81.21 (4) and 54.43 (2)° compared to angles between the cyanobenzoate and benzene rings of 55.02 (3) and 84.20 (3)°.

5. Hirshfeld surface analysis

CrystalExplorer17.5 (Turner *et al.*, 2017) was used to perform the Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) to further quantify the various intermolecular interactions.

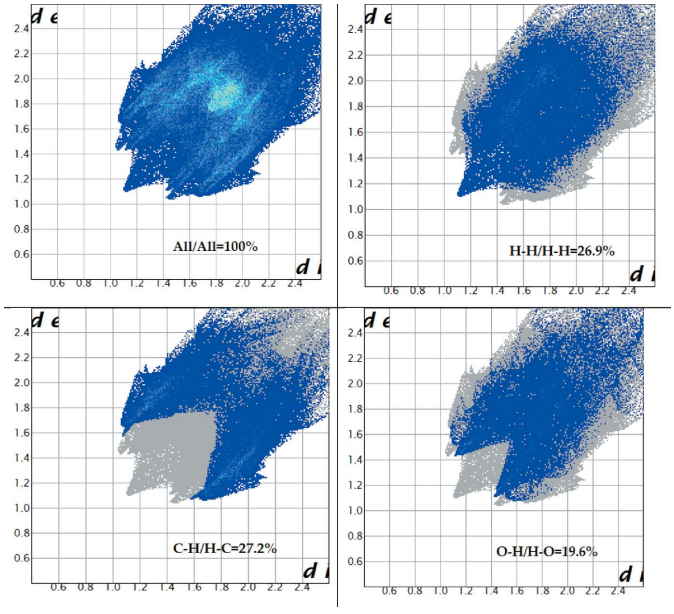


Figure 5
Two-dimensional fingerprint plots for the title compound.

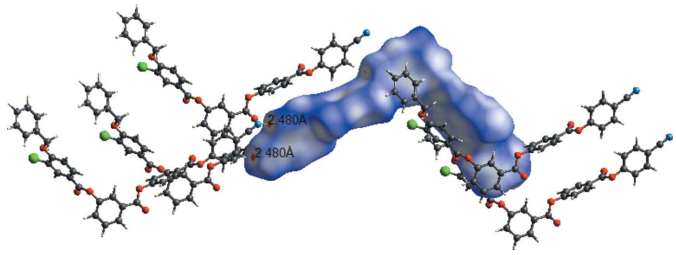


Figure 6
Hirshfeld surface of the title compound mapped over d_{norm}, showing the C—H···N interactions.

The Hirshfeld surface mapped over d_{norm} is illustrated in Fig. 4 and the associated two-dimensional fingerprint plots in Fig. 5. The major contributions to the crystal structure are from H···H (26.9%), C···H (27.2%) and O···H (19.6%) contacts. In Figs. 6 and 7, the red spots on the d_{norm} and d_e surfaces represent the C—H···π interactions.

6. Synthesis and crystallization

4-[(4-Cyanophenoxy)carbonyl]phenyl 3-hydroxybenzoate (1 mmol) and 4-(benzyloxy)-3-chlorobenzoic acid (1.2 mmol) were dissolved in dry chloroform (50 ml). After the addition of *N*,*N*-dicyclohexylcarbodiimide (1.2 mmol) and a catalytic amount of 4-(*N*,*N*-dimethylamino)pyridine (DMAP), the mixture was stirred at room temperature for about 12 h. The dicyclohexylurea that precipitated was filtered off and the filtrate diluted with chloroform. This solution was washed with 2% aqueous acetic acid solution

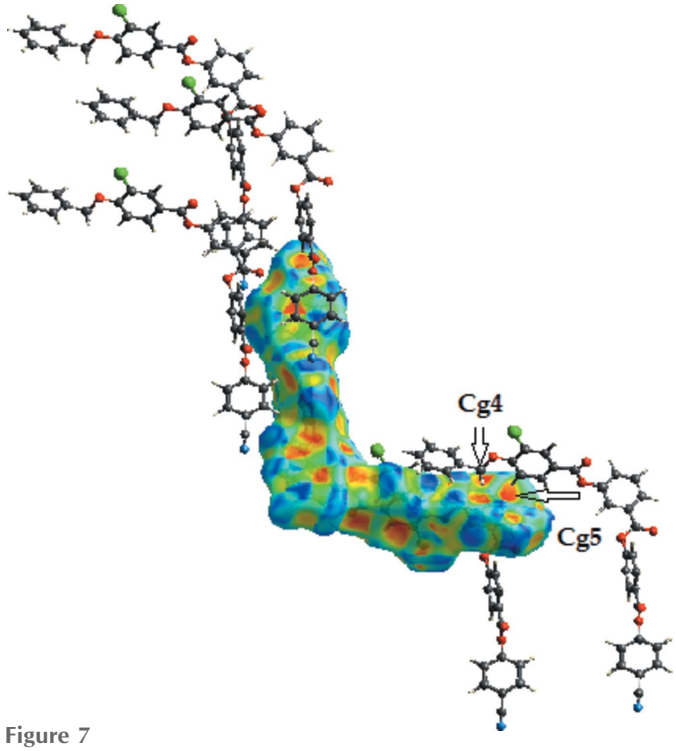


Figure 7
Hirshfeld surface of the title compound mapped over shape-index, showing the C—H···π interactions.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{35}H_{22}ClNO_7$
M_r	603.98
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	296
a, b, c (Å)	8.0202 (1), 9.8474 (2), 19.4712 (4)
α, β, γ (°)	95.422 (1), 94.693 (1), 103.857 (1)
V (Å^3)	1477.66 (5)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.18
Crystal size (mm)	0.19 × 0.18 × 0.16
Data collection	
Diffractometer	Bruker SMART APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2017)
T_{min}, T_{max}	0.966, 0.971
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25466, 5207, 4255
R_{int}	0.024
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.114, 1.03
No. of reflections	5207
No. of parameters	410
No. of restraints	6
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.26, −0.33

Computer programs: *APEX2* and *SAINT* (Bruker, 2017), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*) and *Mercury* (Macrae *et al.*, 2020).

(10 ml) and 5% ice-cold sodium hydroxide solution (10 ml) and finally washed with water and dried over anhydrous sodium sulfate. The crude residue obtained was chromatographed on silica gel using chloroform as an eluent. Removal of solvent from the eluate afforded the white target material, which was crystallized from a mixture of chloroform and acetonitrile. Single crystals in the form of colourless prisms suitable for diffraction studies were grown from a solution in ethyl alcohol by slow evaporation.

IR (nujol) λ_{max}: 3105, 3080, 2237, 1738, 1733, 1614, 1523, 1452, 1253, 1054 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ H: 8.22 (*m*, 3H, Ar—H) , 8.19 (*m*, 3H, Ar-H), 8.02 (*m*, 2H, Ar—H), 7.98–7.30 (*m*, 7H, Ar—H), 6.99 (*m*, 5H, Ar—H), 5.22 (*s*, 2H, Ar—O—CH_2–) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.2, 159.8, 154.6, 153.7, 151.2, 136.7, 132.6, 130.2, 129, 128.9, 128.6, 127.6, 127.1, 126.8, 123.9, 122.3, 121.3, 112.4 ppm. Micro elemental analysis calculated for $C_{35}H_{22}ClNO_7$; C, 69.60; H, 3.67; Cl, 5.87; N, 2.32; found C, 69.68; H, 3.72; Cl, 5.91; N, 2.35%.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Atoms H2, H4 and H6 were fully refined. Other H atoms were positioned with idealized geometry and refined using a riding model with C—H = 0.93–0.97 Å and U_{iso}(H) = 1.2–1.5U_{eq}(C).

Funding information

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Crystal structure and Hirshfeld surface analysis of 3-({4-[(4-cyanophenoxy)-carbonyl]phenoxy}carbonyl)phenyl 4-(benzyloxy)-3-chlorobenzoate

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Computing details

Data collection: *APEX2* (Bruker, 2017),; cell refinement: *SAINT* (Bruker, 2017); data reduction: *SAINT* (Bruker, 2017); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *SHELXL* (Sheldrick, 2015b).

3-({4-[(4-Cyanophenoxy)carbonyl]phenoxy}carbonyl)phenyl 4-(benzyloxy)-3-chlorobenzoate

Crystal data

$C_{35}H_{22}ClNO_7$
M_r = 603.98
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 8.0202 (1) Å
b = 9.8474 (2) Å
c = 19.4712 (4) Å
α = 95.422 (1)°
β = 94.693 (1)°
γ = 103.857 (1)°
V = 1477.66 (5) Å^3
Z = 2
$F(000)$ = 624
Prism
D_x = 1.357 Mg m^{-3}
Melting point: 445 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5212 reflections
θ = 1.0–25.0°
μ = 0.18 mm^{-1}
T = 296 K
Prism, colourless
0.19 × 0.18 × 0.16 mm

Data collection

Bruker SMART APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 2.06 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2017)
T_{min} = 0.966, T_{max} = 0.971
25466 measured reflections
5207 independent reflections
4255 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 25.0°, θ_{min} = 2.1°
h = −9→9
k = −11→11
l = −23→23

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.114
S = 1.03
5207 reflections
410 parameters
6 restraints
0 constraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0619P)^2 + 0.2788P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}
Extinction correction: SHELXL2018 (Sheldrick, 2015b), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0158 (18)

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O7	0.66155 (14)	1.37557 (12)	1.06583 (6)	0.0604 (3)
O6	0.23387 (14)	0.91624 (11)	0.82866 (6)	0.0562 (3)
O2	0.31260 (15)	0.47851 (13)	0.70608 (7)	0.0701 (4)
O4	0.70509 (18)	0.04285 (14)	0.58733 (6)	0.0691 (4)
O5	0.07952 (16)	0.85138 (14)	0.91636 (6)	0.0683 (4)
O3	0.6173 (2)	−0.06006 (17)	0.67969 (8)	0.0920 (5)
O1	0.06206 (16)	0.37006 (13)	0.64386 (7)	0.0734 (4)
N1	1.2423 (3)	−0.3715 (2)	0.52599 (11)	0.0906 (6)
C33	1.1312 (3)	1.7706 (3)	1.18897 (11)	0.0805 (6)
H33	1.200300	1.842548	1.220743	0.097*
C34	1.1522 (3)	1.6373 (3)	1.18768 (11)	0.0812 (6)
H34	1.235250	1.618164	1.218912	0.097*
C35	1.0499 (3)	1.5295 (2)	1.13982 (10)	0.0710 (5)
H35	1.066616	1.439064	1.138300	0.085*
C30	0.9239 (2)	1.55720 (18)	1.09471 (8)	0.0561 (4)
C29	0.8184 (2)	1.44647 (19)	1.03988 (9)	0.0652 (5)
H29A	0.790624	1.489441	0.999036	0.078*
H29B	0.883975	1.378979	1.026758	0.078*
C26	0.5546 (2)	1.27075 (17)	1.02142 (8)	0.0496 (4)
C25	0.5822 (2)	1.23457 (18)	0.95365 (9)	0.0599 (4)
H25	0.678848	1.285319	0.935657	0.072*
C24	0.4681 (2)	1.12408 (17)	0.91246 (8)	0.0550 (4)
H24	0.488830	1.101130	0.867042	0.066*
C23	0.32400 (19)	1.04740 (15)	0.93774 (8)	0.0456 (3)
C22	0.19929 (19)	0.92835 (16)	0.89583 (8)	0.0472 (4)
C3	0.1246 (2)	0.80725 (15)	0.78186 (8)	0.0476 (4)
C2	0.1912 (2)	0.69862 (16)	0.75737 (8)	0.0479 (4)
C1	0.08826 (19)	0.59329 (16)	0.70854 (7)	0.0449 (3)
C7	0.1464 (2)	0.46904 (17)	0.68174 (8)	0.0517 (4)
C8	0.3800 (2)	0.36353 (18)	0.68774 (9)	0.0577 (4)
C13	0.4822 (2)	0.37070 (19)	0.63451 (10)	0.0608 (4)
H13	0.499046	0.447392	0.609152	0.073*

C12	0.5600 (2)	0.26220 (18)	0.61907 (9)	0.0572 (4)
H12	0.630774	0.266133	0.583388	0.069*
C11	0.53291 (19)	0.14754 (17)	0.65663 (8)	0.0494 (4)
C14	0.6184 (2)	0.03171 (19)	0.64397 (9)	0.0551 (4)
C15	0.8124 (2)	−0.04890 (18)	0.57562 (9)	0.0566 (4)
C20	0.9844 (2)	0.00167 (19)	0.59635 (10)	0.0654 (5)
H20	1.027213	0.091840	0.619681	0.078*
C19	1.0936 (2)	−0.08343 (19)	0.58204 (10)	0.0657 (5)
H19	1.211388	−0.050869	0.595875	0.079*
C18	1.0288 (2)	−0.21700 (18)	0.54721 (9)	0.0564 (4)
C21	1.1458 (3)	−0.3048 (2)	0.53442 (10)	0.0671 (5)
C27	0.40785 (19)	1.19401 (19)	1.04630 (8)	0.0526 (4)
C28	0.29494 (19)	1.08363 (18)	1.00565 (8)	0.0530 (4)
H28	0.198360	1.032683	1.023589	0.064*
C9	0.3515 (2)	0.2511 (2)	0.72563 (10)	0.0674 (5)
H9	0.281420	0.248249	0.761511	0.081*
C10	0.4279 (2)	0.1426 (2)	0.70986 (9)	0.0615 (4)
H10	0.408968	0.065641	0.735040	0.074*
C17	0.8540 (2)	−0.26542 (19)	0.52624 (9)	0.0621 (5)
H17	0.810392	−0.354934	0.502276	0.074*
C16	0.7448 (2)	−0.18100 (19)	0.54090 (9)	0.0632 (5)
H16	0.626763	−0.212940	0.527475	0.076*
C6	−0.0776 (2)	0.59977 (17)	0.68582 (8)	0.0501 (4)
C5	−0.1410 (2)	0.71063 (18)	0.71118 (9)	0.0558 (4)
H5	−0.252302	0.714786	0.695759	0.067*
C4	−0.0391 (2)	0.81545 (17)	0.75948 (9)	0.0538 (4)
C31	0.9056 (3)	1.6916 (2)	1.09726 (13)	0.0897 (7)
H31	0.821394	1.711933	1.066993	0.108*
C32	1.0097 (3)	1.7978 (3)	1.14393 (15)	0.1065 (9)
H32	0.996215	1.889094	1.144422	0.128*
Cl	0.37075 (6)	1.23731 (8)	1.13083 (2)	0.0967 (2)
H6	−0.146 (2)	0.5267 (19)	0.6546 (9)	0.057 (5)*
H2	0.303 (2)	0.6937 (18)	0.7740 (9)	0.061 (5)*
H4	−0.080 (2)	0.8914 (19)	0.7778 (9)	0.057 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O7	0.0531 (6)	0.0670 (7)	0.0505 (6)	0.0008 (5)	0.0086 (5)	−0.0123 (5)
O6	0.0596 (7)	0.0465 (6)	0.0544 (6)	0.0017 (5)	0.0134 (5)	−0.0115 (5)
O2	0.0542 (7)	0.0636 (8)	0.0892 (9)	0.0284 (6)	−0.0096 (6)	−0.0289 (6)
O4	0.0899 (9)	0.0714 (8)	0.0624 (7)	0.0493 (7)	0.0188 (6)	0.0061 (6)
O5	0.0600 (7)	0.0755 (8)	0.0566 (7)	−0.0063 (6)	0.0056 (6)	0.0044 (6)
O3	0.1290 (13)	0.0867 (10)	0.0914 (10)	0.0694 (10)	0.0423 (9)	0.0305 (9)
O1	0.0672 (8)	0.0598 (8)	0.0861 (9)	0.0257 (6)	−0.0185 (7)	−0.0296 (7)
N1	0.0917 (13)	0.0785 (12)	0.1191 (16)	0.0446 (10)	0.0413 (11)	0.0130 (11)
C33	0.0729 (13)	0.0866 (16)	0.0667 (12)	0.0043 (11)	−0.0038 (10)	−0.0185 (11)
C34	0.0696 (12)	0.0989 (17)	0.0638 (12)	−0.0017 (11)	−0.0122 (9)	0.0277 (11)

C35	0.0744 (12)	0.0626 (11)	0.0720 (12)	0.0052 (9)	0.0026 (10)	0.0236 (9)
C30	0.0519 (9)	0.0587 (10)	0.0518 (9)	0.0056 (7)	0.0090 (7)	−0.0046 (7)
C29	0.0636 (10)	0.0634 (11)	0.0573 (10)	−0.0031 (8)	0.0135 (8)	−0.0061 (8)
C26	0.0488 (8)	0.0514 (9)	0.0461 (8)	0.0120 (7)	0.0033 (6)	−0.0037 (7)
C25	0.0622 (10)	0.0569 (10)	0.0510 (9)	−0.0031 (8)	0.0164 (8)	−0.0036 (7)
C24	0.0620 (10)	0.0524 (9)	0.0458 (8)	0.0062 (7)	0.0139 (7)	−0.0049 (7)
C23	0.0461 (8)	0.0443 (8)	0.0471 (8)	0.0146 (6)	0.0034 (6)	0.0019 (6)
C22	0.0464 (8)	0.0473 (8)	0.0490 (8)	0.0142 (7)	0.0053 (7)	0.0046 (7)
C3	0.0507 (8)	0.0411 (8)	0.0476 (8)	0.0066 (6)	0.0103 (7)	−0.0032 (6)
C2	0.0439 (8)	0.0497 (9)	0.0487 (8)	0.0123 (7)	0.0051 (7)	−0.0034 (7)
C1	0.0470 (8)	0.0447 (8)	0.0433 (8)	0.0145 (6)	0.0046 (6)	−0.0011 (6)
C7	0.0513 (9)	0.0517 (9)	0.0515 (9)	0.0187 (7)	−0.0001 (7)	−0.0068 (7)
C8	0.0485 (9)	0.0568 (10)	0.0656 (10)	0.0224 (7)	−0.0064 (8)	−0.0173 (8)
C13	0.0616 (10)	0.0555 (10)	0.0678 (11)	0.0238 (8)	0.0021 (8)	0.0005 (8)
C12	0.0581 (10)	0.0600 (10)	0.0575 (9)	0.0249 (8)	0.0076 (8)	−0.0016 (8)
C11	0.0477 (8)	0.0524 (9)	0.0474 (8)	0.0189 (7)	−0.0041 (6)	−0.0060 (7)
C14	0.0588 (10)	0.0564 (10)	0.0518 (9)	0.0239 (8)	−0.0010 (7)	−0.0045 (8)
C15	0.0700 (11)	0.0565 (10)	0.0516 (9)	0.0327 (8)	0.0109 (8)	0.0006 (7)
C20	0.0719 (12)	0.0497 (10)	0.0717 (11)	0.0170 (8)	0.0076 (9)	−0.0112 (8)
C19	0.0564 (10)	0.0588 (11)	0.0800 (12)	0.0158 (8)	0.0080 (9)	−0.0055 (9)
C18	0.0646 (10)	0.0527 (10)	0.0578 (9)	0.0240 (8)	0.0177 (8)	0.0026 (8)
C21	0.0734 (12)	0.0601 (11)	0.0766 (12)	0.0275 (9)	0.0263 (10)	0.0079 (9)
C27	0.0433 (8)	0.0724 (11)	0.0414 (8)	0.0163 (7)	0.0051 (6)	−0.0021 (7)
C28	0.0406 (8)	0.0688 (10)	0.0467 (8)	0.0082 (7)	0.0061 (6)	0.0052 (7)
C9	0.0664 (11)	0.0776 (13)	0.0630 (11)	0.0300 (9)	0.0144 (9)	−0.0054 (10)
C10	0.0645 (10)	0.0645 (11)	0.0591 (10)	0.0247 (8)	0.0076 (8)	0.0028 (8)
C17	0.0723 (11)	0.0507 (10)	0.0618 (10)	0.0198 (8)	0.0057 (8)	−0.0105 (8)
C16	0.0602 (10)	0.0657 (11)	0.0629 (10)	0.0224 (8)	−0.0004 (8)	−0.0083 (9)
C6	0.0513 (9)	0.0478 (9)	0.0492 (8)	0.0137 (7)	−0.0005 (7)	−0.0029 (7)
C5	0.0518 (9)	0.0562 (10)	0.0623 (10)	0.0225 (7)	0.0017 (7)	0.0016 (8)
C4	0.0614 (10)	0.0446 (9)	0.0594 (10)	0.0215 (7)	0.0121 (8)	−0.0013 (7)
C31	0.0782 (14)	0.0788 (14)	0.1071 (17)	0.0395 (11)	−0.0310 (12)	−0.0313 (12)
C32	0.0958 (17)	0.0809 (15)	0.133 (2)	0.0416 (13)	−0.0338 (16)	−0.0495 (15)
Cl	0.0578 (3)	0.1601 (6)	0.0491 (3)	−0.0054 (3)	0.0139 (2)	−0.0263 (3)

Geometric parameters (Å, º)

O7—C26	1.3545 (19)	C1—C6	1.385 (2)
O7—C29	1.441 (2)	C1—C7	1.476 (2)
O6—C22	1.3591 (19)	C8—C13	1.370 (3)
O6—C3	1.4086 (17)	C8—C9	1.372 (3)
O2—C7	1.3563 (19)	C13—C12	1.382 (2)
O2—C8	1.396 (2)	C13—H13	0.9300
O4—C14	1.350 (2)	C12—C11	1.386 (2)
O4—C15	1.4052 (19)	C12—H12	0.9300
O5—C22	1.1953 (19)	C11—C10	1.385 (2)
O3—C14	1.190 (2)	C11—C14	1.477 (2)
O1—C7	1.1909 (19)	C15—C20	1.363 (3)

N1—C21	1.141 (2)	C15—C16	1.371 (2)
C33—C32	1.349 (3)	C20—C19	1.376 (3)
C33—C34	1.360 (3)	C20—H20	0.9300
C33—H33	0.9300	C19—C18	1.381 (2)
C34—C35	1.393 (3)	C19—H19	0.9300
C34—H34	0.9300	C18—C17	1.382 (3)
C35—C30	1.378 (3)	C18—C21	1.441 (2)
C35—H35	0.9300	C27—C28	1.370 (2)
C30—C31	1.363 (3)	C27—Cl	1.7284 (15)
C30—C29	1.495 (2)	C28—H28	0.9300
C29—H29A	0.9700	C9—C10	1.376 (3)
C29—H29B	0.9700	C9—H9	0.9300
C26—C25	1.384 (2)	C10—H10	0.9300
C26—C27	1.388 (2)	C17—C16	1.372 (2)
C25—C24	1.379 (2)	C17—H17	0.9300
C25—H25	0.9300	C16—H16	0.9300
C24—C23	1.376 (2)	C6—C5	1.378 (2)
C24—H24	0.9300	C6—H6	0.929 (18)
C23—C28	1.390 (2)	C5—C4	1.380 (2)
C23—C22	1.471 (2)	C5—H5	0.9300
C3—C2	1.369 (2)	C4—H4	0.940 (18)
C3—C4	1.373 (2)	C31—C32	1.376 (3)
C2—C1	1.392 (2)	C31—H31	0.9300
C2—H2	0.944 (18)	C32—H32	0.9300

C26—O7—C29	115.72 (12)	C8—C13—H13	120.5
C22—O6—C3	118.29 (12)	C12—C13—H13	120.5
C7—O2—C8	117.25 (12)	C13—C12—C11	120.16 (16)
C14—O4—C15	117.53 (13)	C13—C12—H12	119.9
C32—C33—C34	119.68 (19)	C11—C12—H12	119.9
C32—C33—H33	120.2	C10—C11—C12	119.62 (15)
C34—C33—H33	120.2	C10—C11—C14	118.11 (16)
C33—C34—C35	120.33 (19)	C12—C11—C14	122.22 (15)
C33—C34—H34	119.8	O3—C14—O4	122.49 (15)
C35—C34—H34	119.8	O3—C14—O4	122.49 (15)
C30—C35—C34	119.8 (2)	O3—C14—C11	125.25 (16)
C30—C35—H35	120.1	O4—C14—C11	112.23 (15)
C34—C35—H35	120.1	O4—C14—C11	112.23 (15)
C31—C30—C35	118.56 (17)	C20—C15—C16	122.31 (16)
C31—C30—C29	119.80 (18)	C20—C15—O4	117.50 (16)
C35—C30—C29	121.44 (18)	C16—C15—O4	120.08 (16)
O7—C29—C30	109.61 (13)	C20—C15—O4	117.50 (16)
O7—C29—H29A	109.7	C16—C15—O4	120.08 (16)
C30—C29—H29A	109.7	C15—C20—C19	118.63 (16)
O7—C29—H29B	109.7	C15—C20—H20	120.7
C30—C29—H29B	109.7	C19—C20—H20	120.7
H29A—C29—H29B	108.2	C20—C19—C18	120.22 (17)
O7—C26—C25	124.66 (14)	C20—C19—H19	119.9

O7—C26—C27	117.23 (13)	C18—C19—H19	119.9
C25—C26—C27	118.10 (14)	C19—C18—C17	120.04 (16)
C24—C25—C26	120.76 (15)	C19—C18—C21	118.90 (17)
C24—C25—H25	119.6	C17—C18—C21	121.06 (16)
C26—C25—H25	119.6	N1—C21—C18	177.7 (2)
C23—C24—C25	120.81 (14)	C28—C27—C26	121.24 (14)
C23—C24—H24	119.6	C28—C27—Cl	119.84 (12)
C25—C24—H24	119.6	C26—C27—Cl	118.91 (12)
C24—C23—C28	118.75 (14)	C27—C28—C23	120.32 (14)
C24—C23—C22	122.69 (14)	C27—C28—H28	119.8
C28—C23—C22	118.56 (14)	C23—C28—H28	119.8
O5—C22—O6	122.68 (14)	C8—C9—C10	119.15 (17)
O5—C22—O6	122.68 (14)	C8—C9—H9	120.4
O5—C22—C23	125.70 (14)	C10—C9—H9	120.4
O6—C22—C23	111.61 (13)	C9—C10—C11	120.26 (18)
O6—C22—C23	111.61 (13)	C9—C10—H10	119.9
C2—C3—C4	122.09 (14)	C11—C10—H10	119.9
C2—C3—O6	117.58 (14)	C16—C17—C18	119.79 (16)
C4—C3—O6	120.24 (14)	C16—C17—H17	120.1
C2—C3—O6	117.58 (14)	C18—C17—H17	120.1
C4—C3—O6	120.24 (14)	C15—C16—C17	119.01 (17)
C3—C2—C1	118.53 (15)	C15—C16—H16	120.5
C3—C2—H2	120.9 (11)	C17—C16—H16	120.5
C1—C2—H2	120.5 (11)	C5—C6—C1	120.23 (15)
C6—C1—C2	119.99 (14)	C5—C6—H6	120.9 (11)
C6—C1—C7	117.75 (14)	C1—C6—H6	118.8 (11)
C2—C1—C7	122.20 (14)	C6—C5—C4	119.93 (15)
O1—C7—O2	122.12 (14)	C6—C5—H5	120.0
O1—C7—O2	122.12 (14)	C4—C5—H5	120.0
O1—C7—C1	126.23 (15)	C3—C4—C5	119.21 (15)
O2—C7—C1	111.65 (13)	C3—C4—H4	119.5 (11)
O2—C7—C1	111.65 (13)	C5—C4—H4	121.3 (11)
C13—C8—C9	121.82 (16)	C30—C31—C32	121.0 (2)
C13—C8—O2	118.33 (17)	C30—C31—H31	119.5
C9—C8—O2	119.73 (16)	C32—C31—H31	119.5
C13—C8—O2	118.33 (17)	C33—C32—C31	120.6 (2)
C9—C8—O2	119.73 (16)	C33—C32—H32	119.7
C8—C13—C12	118.98 (17)	C31—C32—H32	119.7

C32—C33—C34—C35	0.5 (4)	C15—O4—C14—C11	170.88 (14)
C33—C34—C35—C30	−1.6 (3)	C10—C11—C14—O3	−7.1 (3)
C34—C35—C30—C31	1.5 (3)	C12—C11—C14—O3	170.25 (19)
C34—C35—C30—C29	176.40 (17)	C10—C11—C14—O4	174.84 (15)
C26—O7—C29—C30	−179.10 (15)	C12—C11—C14—O4	−7.8 (2)
C31—C30—C29—O7	−92.2 (2)	C10—C11—C14—O4	174.84 (15)
C35—C30—C29—O7	93.0 (2)	C12—C11—C14—O4	−7.8 (2)
C29—O7—C26—C25	−3.6 (3)	C14—O4—C15—C20	−98.2 (2)
C29—O7—C26—C27	175.84 (15)	C14—O4—C15—C16	85.5 (2)

O7—C26—C25—C24	178.60 (17)	C16—C15—C20—C19	−0.3 (3)
C27—C26—C25—C24	−0.9 (3)	O4—C15—C20—C19	−176.45 (16)
C26—C25—C24—C23	0.1 (3)	O4—C15—C20—C19	−176.45 (16)
C25—C24—C23—C28	0.2 (3)	C15—C20—C19—C18	0.2 (3)
C25—C24—C23—C22	−179.69 (16)	C20—C19—C18—C17	0.4 (3)
C3—O6—C22—O5	−0.7 (2)	C20—C19—C18—C21	−178.57 (18)
C3—O6—C22—C23	−179.61 (13)	O7—C26—C27—C28	−178.18 (15)
C24—C23—C22—O5	173.94 (17)	C25—C26—C27—C28	1.3 (3)
C28—C23—C22—O5	−6.0 (3)	O7—C26—C27—Cl	0.5 (2)
C24—C23—C22—O6	−7.2 (2)	C25—C26—C27—Cl	179.98 (14)
C28—C23—C22—O6	172.84 (14)	C26—C27—C28—C23	−1.0 (3)
C24—C23—C22—O6	−7.2 (2)	Cl—C27—C28—C23	−179.65 (13)
C28—C23—C22—O6	172.84 (14)	C24—C23—C28—C27	0.2 (2)
C22—O6—C3—C2	−110.45 (16)	C22—C23—C28—C27	−179.86 (15)
C22—O6—C3—C4	72.9 (2)	C13—C8—C9—C10	0.1 (3)
C4—C3—C2—C1	−0.3 (2)	O2—C8—C9—C10	−175.81 (15)
O6—C3—C2—C1	−176.95 (13)	O2—C8—C9—C10	−175.81 (15)
O6—C3—C2—C1	−176.95 (13)	C8—C9—C10—C11	0.3 (3)
C3—C2—C1—C6	−0.1 (2)	C12—C11—C10—C9	−0.3 (3)
C3—C2—C1—C7	−177.12 (15)	C14—C11—C10—C9	177.15 (16)
C8—O2—C7—O1	−3.1 (3)	C19—C18—C17—C16	−0.8 (3)
C8—O2—C7—C1	176.36 (15)	C21—C18—C17—C16	178.11 (17)
C6—C1—C7—O1	−2.8 (3)	C20—C15—C16—C17	−0.2 (3)
C2—C1—C7—O1	174.35 (17)	O4—C15—C16—C17	175.92 (16)
C6—C1—C7—O2	177.76 (14)	O4—C15—C16—C17	175.92 (16)
C2—C1—C7—O2	−5.1 (2)	C18—C17—C16—C15	0.7 (3)
C6—C1—C7—O2	177.76 (14)	C2—C1—C6—C5	0.3 (2)
C2—C1—C7—O2	−5.1 (2)	C7—C1—C6—C5	177.48 (15)
C7—O2—C8—C13	99.95 (19)	C1—C6—C5—C4	−0.1 (3)
C7—O2—C8—C9	−84.0 (2)	C2—C3—C4—C5	0.5 (3)
C9—C8—C13—C12	−0.6 (3)	O6—C3—C4—C5	177.03 (14)
O2—C8—C13—C12	175.35 (14)	O6—C3—C4—C5	177.03 (14)
O2—C8—C13—C12	175.35 (14)	C6—C5—C4—C3	−0.3 (3)
C8—C13—C12—C11	0.7 (2)	C35—C30—C31—C32	−0.3 (4)
C13—C12—C11—C10	−0.2 (2)	C29—C30—C31—C32	−175.3 (2)
C13—C12—C11—C14	−177.55 (15)	C34—C33—C32—C31	0.7 (4)
C15—O4—C14—O3	−7.2 (3)	C30—C31—C32—C33	−0.9 (4)

Hydrogen-bond geometry (Å, º)

*Cg*4 and *cg*5 are the centroids of the C23–C28 and C30–C35 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O2	0.944 (18)	2.411 (17)	2.7213 (19)	98.9 (12)
C12—H12···O4	0.93	2.42	2.733 (2)	100
C24—H24···O6	0.93	2.40	2.721 (2)	100
C17—H17···N1^{i}	0.93	2.62	3.504 (3)	158

C25—H25···*Cg*5^{ii}	0.93	2.86	3.744 (2)	158
C31—H31···*Cg*4^{iii}	0.93	2.82	3.702 (3)	158

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