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

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The title compound, C 35H22ClNO7, 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)/C14, indicating that adjacent rings are close to perpendicular to each other. In the crystal, the molecules are linked by weak C—H/C1/C1/C1 and C—H/C25 interactions, thereby forming a two-dimensional supramolecular architecture in the ac plane. The most important contributions to the crystal packing arise from H/C1/C1/C1H (59.3%), S/C1/C1/C1H (27.4%) and O/C1/C1/C1H (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
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 = 16.06 (2), 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), −69.45 (2), −3.1 (3), −3.6387 (10) Å (slippage = 1.086 Å) and 3.7740 (10) Å (slippage = 1.407 Å), respectively, as shown in Fig. 3 (Cg4 is the centroid of the C23–C28 ring and Cg3 is the centroid of the C15–C20 ring).

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 Cg4⋯Cg4 and Cg3⋯Cg3 = 3.6387 (10) Å (slippage = 1.086 Å) and 3.7740 (10) Å (slippage = 1.407 Å), respectively, as shown in Fig. 3 (Cg4 is the centroid of the C23–C28 ring and Cg3 is the centroid of the C15–C20 ring).

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 (Srinivas 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 group 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 cyano-benzoate 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 (cyano-benzoate ring and the neighbouring benzene ring) are 69.45 (2) and 64.20 (3)°, 73.60 (3) and 84.16 (3)° between the adjacent cyanobenzoate and benzene rings themselves. In IBUXUB, the dihedral angles between the rings (cyano-benzoate and the neighbouring benzene ring) are 69.68 (2)

### Table 1

Hydrogen-bond geometry (Å, °).

| 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 | 0.93 | 2.62 | 3.504 (3) | 158 |
| C25—H25⋯Cg58 | 0.93 | 2.86 | 3.744 (2) | 158 |
| C31—H31⋯Cg49 | 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.
and 74.28 (4)$^\circ$, and 48.87 (2) and 89.88 (4)$^\circ$ 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)$^\circ$ compared to angles between the cyanobenzoate and benzene rings of 55.02 (3) and 84.20 (3)$^\circ$.

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.

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 6](image-url)  
Figure 6  
Hirshfeld surface of the title compound mapped over $d_{norm}$, showing the C−H···N interactions.

![Figure 7](image-url)  
Figure 7  
Hirshfeld surface of the title compound mapped over shape-index, showing the C−H···π interactions.
Table 2
Experimental details.

| Parameter                  | Value                  |
|----------------------------|------------------------|
| Chemical formula           | C_{15}H_{32}ClNO_{7}   |
| Mₘ                         | 603.98                 |
| Crystal system, space group| Triclinic, P                 |
| 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 (Å³)                     | 1477.66 (5)            |
| Z                          | 2                      |
| Radiation type             | Mo Kα                  |
| μ (mm⁻¹)                   | 0.18                   |
| Crystal size (mm)          | 0.19 x 0.18 x 0.16     |
| Data collection            | Bruker SMART APEXII CCD |
| Absorption correction     | Multi-scan             |
| T_max, T_min               | 0.966, 0.971           |
| No. of measured, independent and observed reflections | 25466, 5207, 4255 |
| R(F²)                      | 0.038, 0.114, 1.03     |
| (sinθ/λ) max (Å⁻¹)         | 0.595                  |
| Refinement                 |                        |
| R[F² > 2σ(F²)], wR(F²), S  |                        |
| 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 |
| Δρ_max, Δρ_min (e Å⁻³)     | 0.26, -0.35            |

Computer programs: APEX2 and SAINT (Bruker, 2017), SHELXT (Sheldrick, 2015a), SHELXL (Sheldrick, 2015b) 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 acetone. 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; ¹H NMR (500 MHz, CDCl₃) 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—CH₂⁻) ppm; ¹³C NMR (125 MHz, CDCl₃) 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_{15}H_{32}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).

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References

Al-Eryani, W. F. A., Srinivasa, H. T., Jeyaseelan, S., Sadashivaiah, T. & Devarajegowda, H. C. (2011). Acta Cryst. E67, o840.
Bruker (2017). APEX3, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). Acta Cryst. B72, 171–179.
Hartung, H., Stettler, A. & Weissflog, W. (2000). J. Mol. Struct. 526, 31–40.
Ji, Y., Peng, Z., Tong, B., Shi, J., Zhi, J. & Dong, Y. (2017). Dyes Pigments, 139, 664–671.
Kashi, H. K. A., Palakshamurthy, B. S., VinduVahini, M., Srinivasa, H. T. & Devarajegowda, H. C. (2010). Acta Cryst. E66, o2126.
Macrae, C. F., Sovago, I., Cottrell, S. I., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). J. Appl. Cryst. 53, 226–235.
Palakshamurthy, B. S., Srinivasa, H. T., Kumar, V., Sreenivasa, S. & Devarajegowda, H. C. (2012). Acta Cryst. E68, o3382.
Reddy, R. A. & Sadashiva, B. K. (2004). J. Mater. Chem. 14, 310–319.
Sadasiva, B. K., Amaranatha Reddy, R., Pratibha, R. & Madhusudana, N. V. (2002). J. Mater. Chem. 12, 943–950.
Sheldrick, G. M. (2015a). Acta Cryst. A71, 3–8.
Sheldrick, G. M. (2015b). Acta Cryst. C71, 3–8.
Sriram, H. T., Siddagangappa, P. B., Velmurugan, D., Chiecgowda, D. H. & Suresh, H. (2015). Acta Chim. Slov. 62, 768–774.
Spackman, M. A. & Jayatilaka, D. (2009). CrystEngComm, 11, 19–32.
Turner, M. J., MacKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). CrystalExplorer17.5. University of Western Australia. http://hirshfeldsurface.net.
Walba, D. M., Körblová, E., Shao, R., Maclennan, J. E., Link, D. R., Glaser, M. A. & Clark, N. A. (2000). Science, 288, 2181–2184.
Yingchun, J., Zhe, P., Bin, T., Jianbing, S., Junge, Z. & Yuping, D. (2016). Dyes Pigm. 16, S0143–7208.
Crystal structure and Hirshfeld surface analysis of 3-[(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-Cyanophenoxy)carbonyl]phenoxy]carbonyl]phenyl 4-(benzyloxy)-3-chlorobenzoate

Crystal data

C₃₅H₂₂ClNO₇
Mr = 603.98
Triclinic, P₁
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) Å³
Z = 2

F(000) = 624
Prism
Melting point: 445 K

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)
Tmin = 0.966, Tmax = 0.971

25466 measured reflections
5207 independent reflections
4255 reflections with I > 2σ(I)
Rint = 0.024
θmax = 25.0°, θmin = 2.1°
h = −9→9
k = −11→11
l = −23→23

Refinement

Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.038
wR(F²) = 0.114
S = 1.03
5207 reflections

410 parameters
6 restraints
0 constraints
Primary atom site location: structure-invariant direct methods

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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 \( P = (F_o^2 + 2F_c^2)/3 \)

\((\Delta/\sigma)_{\text{max}} = 0.002\)
\(\Delta \rho_{\text{max}} = 0.26 \text{ e Å}^{-3}\)
\(\Delta \rho_{\text{min}} = -0.32 \text{ e Å}^{-3}\)

Extinction correction: SHELXL2018 (Sheldrick, 2015b), \( F_c^* = kF_c[1+0.001xF_c^2\lambda^3/\sin(2\theta)]^{1/4} \)

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 (Å²)

| x     | y     | z     | Uiso*/Ueq |
|-------|-------|-------|-----------|
| 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     | 1.219112     | 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*     |
|       | \(U_{11}\)   | \(U_{22}\)   | \(U_{33}\)   | \(U_{12}\)   | \(U_{13}\)   | \(U_{23}\)   |
|-------|---------------|---------------|---------------|---------------|---------------|---------------|
| O7    | 0.0531 (6)    | 0.0670 (7)    | 0.0505 (6)    | 0.0008 (5)    | 0.0086 (5)    | 0.0023 (5)    |
| O6    | 0.0596 (7)    | 0.0465 (6)    | 0.0544 (6)    | 0.0017 (5)    | 0.0134 (5)    | 0.0011 (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)   |

**Atomic displacement parameters \((\text{Å}^2)\)**
Geometric parameters (Å, °)

| Bond          | Length (Å) | Angle (°) |
|---------------|------------|-----------|
| O7—C26        | 1.3545 (19) | C1—C6     | 1.385 (2) |
| O6—C22        | 1.3591 (19) | C1—C7     | 1.476 (2) |
| O6—C3         | 1.4086 (17) | C8—C13    | 1.370 (3) |
| O6—C1         | 1.3563 (19) | C13—C12   | 1.382 (2) |
| O2—C8         | 1.396 (2)   | C13—H13   | 0.9300    |
| O2—C8         | 1.396 (2)   | C12—C11   | 1.386 (2) |
| O2—C8         | 1.396 (2)   | C12—H12   | 0.9300    |
| O2—C8         | 1.396 (2)   | C11—C10   | 1.385 (2) |
| O2—C8         | 1.396 (2)   | C11—C14   | 1.477 (2) |
| O2—C8         | 1.396 (2)   | C15—C20   | 1.363 (3) |

**supporting information**
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—C21 1.441 (2)
C35—C30 0.9300  C27—C28 1.370 (2)
C35—C33 1.349 (3)  C27—Cl 1.7284 (15)
C30—C31 1.363 (3)  C28—H28 0.9300
C30—C29 1.495 (2)  C9—C10 1.376 (3)
C29—H29A 0.9700  C9—H9 0.9300
C29—H29B 0.9700  C31—C32 1.376 (3)
C26—C25 1.384 (2)  C31—H31 0.9300
C26—C27 1.388 (2)  C32—H32 0.9300
C25—C24 1.379 (2)  C33—C34 119.68 (19)
C25—H25 0.9300  C33—C34—C35 120.33 (19)
C24—C23 1.376 (2)  C33—C34—H34 119.8
C24—H24 0.9300  C35—C34—H35 120.1
C23—C28 1.390 (2)  C34—C35—C36 118.56 (17)
C23—C22 1.471 (2)  C34—C35—H35 120.1
C3—C2 1.369 (2)  C31—C32—C33 119.9
C3—C4 1.373 (2)  C31—C32—H32 120.5
C2—C1 1.392 (2)  C32—C33—C34 119.68 (19)
C2—H2 0.944 (18)  C32—C33—H33 120.3
C6—C5 1.378 (2)  C33—C34—C35 120.33 (19)
C5—C4 1.380 (2)  C33—C34—H34 120.1
C4—H4 0.929 (18)  C35—C34—H35 120.1
C31—C30 118.25 (13)  C35—C34—H35 120.1
C31—C30—C35 119.8  O3—C34—O4 122.49 (15)
C31—C30—C29 120.2  O3—C34—C11 125.25 (16)
C31—C30—C35 120.2  O4—C34—C11 112.3 (15)
C31—C30—C35 120.2  C20—C15—C16 122.31 (16)
C31—C30—C29 120.2  C20—C15—O4 117.50 (16)
C31—C30—C35 120.2  C16—C15—O4 120.08 (16)
C31—C30—C35 120.2  C20—C15—H15 120.08 (16)
C31—C30—C29 120.2  C15—C20—H20 120.7
C31—C30—C35 120.2  C15—C20—C19 118.63 (16)
C31—C30—C35 120.2  C19—C20—H20 120.7
C31—C30—C29 120.2  O3—C14—O4 122.22 (15)
C31—C30—C35 120.2  O3—C14—C11 124.49 (15)
C31—C30—C35 120.2  O4—C14—C11 112.3 (15)
C31—C30—C29 120.2  C20—C15—C16 122.31 (16)
C31—C30—C35 120.2  C20—C15—O4 117.50 (16)
C31—C30—C35 120.2  C16—C15—O4 120.08 (16)
C31—C30—C29 120.2  C20—C15—H15 120.08 (16)
C31—C30—C35 120.2  C15—C20—H20 120.7
C31—C30—C35 120.2  C15—C20—C19 118.63 (16)
C31—C30—C29 120.2  C19—C20—H20 120.7
C31—C30—C35 120.2  O3—C14—O4 122.22 (15)
C31—C30—C35 120.2  O3—C14—C11 124.49 (15)
C31—C30—C29 120.2  O4—C14—C11 112.3 (15)
C31—C30—C35 120.2  C20—C15—C16 122.31 (16)
C31—C30—C35 120.2  C20—C15—O4 117.50 (16)
C31—C30—C29 120.2  C16—C15—O4 120.08 (16)
C31—C30—C35 120.2  C20—C15—H15 120.08 (16)
C31—C30—C35 120.2  C15—C20—H20 120.7
C31—C30—C35 120.2  C15—C20—C19 118.63 (16)
C31—C30—C29 120.2  C19—C20—H20 120.7
C31—C30—C35 120.2  O3—C14—O4 122.22 (15)
C31—C30—C35 120.2  O3—C14—C11 124.49 (15)
C31—C30—C29 120.2  O4—C14—C11 112.3 (15)
C31—C30—C35 120.2  C20—C15—C16 122.31 (16)
C31—C30—C35 120.2  C20—C15—O4 117.50 (16)
C31—C30—C29 120.2  C16—C15—O4 120.08 (16)
C31—C30—C35 120.2  C20—C15—H15 120.08 (16)
C31—C30—C35 120.2  C15—C20—H20 120.7
C31—C30—C35 120.2  C15—C20—C19 118.63 (16)
C31—C30—C29 120.2  C19—C20—H20 120.7
C31—C30—C35 120.2  O3—C14—O4 122.22 (15)
C31—C30—C35 120.2  O3—C14—C11 124.49 (15)
C31—C30—C29 120.2  O4—C14—C11 112.3 (15)
| Bond          | Angle (°) ± Standard Deviation |
|--------------|-------------------------------|
| O7—C26—C27  | 117.23 (13)                   |
| C25—C26—C27 | 118.10 (14)                   |
| C24—C25—C26 | 120.76 (15)                   |
| C24—C25—H25 | 119.6                         |
| C26—C25—H25 | 119.6                         |
| C23—C24—C25 | 120.81 (14)                   |
| C23—C24—H24 | 119.6                         |
| C25—C24—H24 | 119.6                         |
| C24—C23—C28 | 118.75 (14)                   |
| C24—C23—C22 | 122.69 (14)                   |
| C28—C23—C22 | 118.56 (14)                   |
| O5—C22—O6   | 122.68 (14)                   |
| O5—C22—C23  | 125.70 (14)                   |
| O6—C22—C23  | 111.61 (13)                   |
| C2—C3—C4    | 122.09 (14)                   |
| C4—C3—O6    | 117.58 (14)                   |
| C2—C3—O6    | 120.24 (14)                   |
| C2—C3—O6    | 117.58 (14)                   |
| C4—C3—O6    | 120.24 (14)                   |
| C3—C2—C1    | 118.53 (15)                   |
| C3—C2—H2    | 120.9 (11)                    |
| C1—C2—H2    | 120.5 (11)                    |
| C6—C1—C2    | 119.99 (14)                   |
| C6—C1—C7    | 117.75 (14)                   |
| C2—C1—C7    | 122.20 (14)                   |
| O1—C7—O2    | 122.12 (14)                   |
| C13—C8—C9   | 121.82 (16)                   |
| C13—C8—O2   | 118.33 (17)                   |
| C9—C8—O2    | 119.73 (16)                   |
| C8—C13—C12  | 118.98 (17)                   |
| C32—C33—C34—C35 | 0.5 (4) |
| C33—C34—C35—C30 | −1.6 (3) |
| C34—C35—C30—C31 | 1.5 (3) |
| C34—C35—C30—C29 | 176.40 (17) |
| C26—O7—C29—C30 | −179.10 (15) |
| C31—C30—C29—O7 | −92.2 (2) |
| C35—C30—C29—O7 | 93.0 (2) |
| C29—O7—C26—C25 | −3.6 (3) |
| C29—O7—C26—C27 | 175.84 (15) |

| Bond          | Angle (°) ± Standard Deviation |
|--------------|-------------------------------|
| C18—C19—H19  | 119.9                         |
| C19—C18—C17  | 120.04 (16)                   |
| C19—C18—C21  | 118.90 (17)                   |
| C17—C18—C21  | 121.06 (16)                   |
| N1—C21—C18   | 177.7 (2)                     |
| C28—C27—C1   | 119.84 (12)                   |
| C28—C27—Cl   | 118.91 (12)                   |
| C27—C28—C26  | 120.32 (14)                   |
| C27—C28—H28  | 119.8                         |
| C23—C28—Cl   | 119.8                         |
| C8—C9—C10    | 119.15 (17)                   |
| C8—C9—H9     | 120.4                         |
| C10—C9—C11   | 120.26 (18)                   |
| C9—C10—H10   | 119.9                         |
| C11—C10—H10  | 119.9                         |
| C16—C17—C18  | 119.79 (16)                   |
| C16—C17—H17  | 120.1                         |
| C18—C17—H17  | 120.1                         |
| C15—C16—C17  | 119.01 (17)                   |
| C15—C16—H16  | 120.5                         |
| C15—C16—H16  | 120.5                         |
| C17—C16—H16  | 120.5                         |
| C5—C6—C1     | 120.23 (15)                   |
| C5—C6—H6     | 120.9 (11)                    |
| C1—C6—H6     | 118.8 (11)                    |
| C6—C5—C4     | 119.93 (15)                   |
| C6—C5—H5     | 120.0                         |
| C3—C4—C5     | 119.21 (15)                   |
| C3—C4—H5     | 120.0                         |
| C3—C4—H4     | 119.5 (11)                    |
| C5—C4—H4     | 121.3 (11)                    |
| C30—C31—C32  | 121.0 (2)                     |
| C30—C31—H31  | 119.5                         |
| C32—C31—H31  | 119.5                         |
| C33—C32—C31  | 120.6 (2)                     |
| C33—C32—H32  | 119.7                         |
| C31—C32—H32  | 119.7                         |
| C15—O4—C14—C11 | 170.88 (14) |
| C10—C11—C14—O3 | −7.1 (3) |
| C12—C11—C14—O3 | 170.25 (19) |
| C10—C11—C14—O4 | 174.84 (15) |
| C12—C11—C14—O4 | −7.8 (2) |
| C10—C11—C14—O4 | 174.84 (15) |
| C12—C11—C14—O4 | −7.8 (2) |
| C14—O4—C15—C20 | −98.2 (2) |
| 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)
C26—C25—C24—C23 0.1 (3) C25—C26—C27—C28 1.3 (3)
C28—C23—C22—O5 -6.0 (3) O7—C26—C27—C28 0.5 (2)
C24—C23—C22—O6 -7.2 (2) C25—C26—C27—C28 179.98 (14)
C28—C23—C22—O6 172.84 (14) C27—C28—C23—C22 -1.0 (3)
C24—C23—C22—O6 -7.2 (2) C1—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) C19—C18—C17—C16 -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) C13—C8—C9—C10 -175.92 (16)
C6—C1—C7—O2 177.76 (14) O4—C15—C16—C17 175.92 (16)
C2—C1—C7—O2 -5.1 (2) O4—C15—C16—C17 175.92 (16)
C6—C1—C7—O2 -5.1 (2) O4—C15—C16—C17 175.92 (16)
C7—O2—C8—C13 -5.1 (2) C2—C1—C6—C5 -0.3 (2)
C7—O2—C8—C13 -99.95 (19) C19—C18—C17—C16 177.48 (15)
C12—H12···O4 0.93 2.42 2.733 (2) 100
C24—H24···O6 0.93 2.40 2.721 (2) 100
C17—H17···N1i 0.93 2.62 3.504 (3) 158
|        | d (Å) | r (Å) | D (Å)     | θ (°) |
|--------|-------|-------|-----------|-------|
| C25—H25⋯Cg5\textsuperscript{i} | 0.93  | 2.86  | 3.744 (2) | 158   |
| C31—H31⋯Cg4\textsuperscript{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.