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3-[(*E*)-2-(5,7-Dichloro-8-hydroxyquinolin-2-yl)vinyl]-4-hydroxyphenyl acetate

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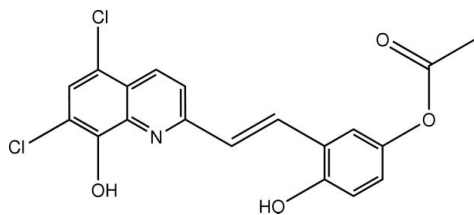
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Key indicators: single-crystal X-ray study; $T = 120$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.043; wR factor = 0.109; data-to-parameter ratio = 14.5.

The two symmetry independent molecules of the title compound, $\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{NO}_4$, show similar conformations with the acetyl group twisted strongly relative to the remaining, virtually flat (r.m.s. deviations = 0.0173 and 0.0065 Å), part of the molecule. The hydroxyl groups of the 8-hydroxyquinoline residues are involved in intramolecular $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds, which, in one case, forms a part of a three-center interaction. Intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds assemble the molecules into a one-dimensional polymeric structure extended along the a axis. The 4-hydroxyphenyl group of one molecule forms an $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond, in which the hydroxyl H atom is disordered, with its inversion center counterpart.

Related literature

For the biological activity and applications of chloroquinolines, see: O'Neill *et al.* (1998); Blauer *et al.* (1998); Egan *et al.* (2000); Zouhiri *et al.* (2000). For the structure of a similar compound, see: Chojnacki *et al.* (2007).



Experimental

Crystal data

$\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{NO}_4$
 $M_r = 390.20$
Triclinic, $P\bar{1}$
 $a = 7.3274$ (15) Å

$b = 10.449$ (2) Å
 $c = 21.550$ (4) Å
 $\alpha = 84.89$ (3)°
 $\beta = 89.50$ (3)°

$\gamma = 87.31$ (3)°
 $V = 1641.6$ (6) Å³
 $Z = 4$
Mo $K\alpha$ radiation

$\mu = 0.42$ mm⁻¹
 $T = 120$ (2) K
 $0.36 \times 0.29 \times 0.11$ mm

Data collection

Oxford Diffraction KM4CCD
 κ -geometry diffractometer
Absorption correction: none
13404 measured reflections

7118 independent reflections
5533 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.109$
 $S = 1.06$
7118 reflections
491 parameters
4 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.54$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.24$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{O1}-\text{H1}\cdots\text{N1}$ | 0.78 (3) | 2.14 (3) | 2.667 (2) | 125 (3) |
| $\text{O2}-\text{H2}\cdots\text{O8}$ | 0.88 (3) | 1.84 (3) | 2.675 (2) | 159 (3) |
| $\text{O5}-\text{H5}\cdots\text{N2}$ | 0.77 (3) | 2.20 (3) | 2.692 (2) | 122 (3) |
| $\text{O5}-\text{H5}\cdots\text{O4}^i$ | 0.77 (3) | 2.38 (3) | 2.990 (2) | 138 (3) |
| $\text{O6}-\text{H6A}\cdots\text{O6}^{ii}$ | 0.829 (19) | 2.12 (3) | 2.892 (3) | 156 (5) |
| $\text{O6}-\text{H6B}\cdots\text{O4}^i$ | 0.844 (10) | 2.445 (11) | 3.130 (3) | 138.9 (18) |

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2178).

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supporting information

Acta Cryst. (2009). E65, o515 [doi:10.1107/S1600536809001950]

3-[(*E*)-2-(5,7-Dichloro-8-hydroxyquinolin-2-yl)vinyl]-4-hydroxyphenyl acetate

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S1. Comment

5,7-Dichloro-2-methylquinolin-8-ol (chlorquinaldol) is a well known antiseptic and generally chloroquinolines are a class of compounds of great interest from a synthetic, theoretical and practical point of view (O'Neill *et al.*, 1998; Blauer *et al.*, 1998; Egan *et al.*, 2000). Styryl derivatives of chloroquinolines have recently attracted special attention due to their antiviral activity (Zouhiri *et al.*, 2000).

The title compound was synthesized in the reaction of 2,5-dihydroxybenzaldehyde with an equimolar quantity of 5,7-dichloro-2-methylquinolin-8-ol in Ac₂O followed by partial hydrolysis in py/H₂O system (Fig. 3).

The molecular structure of title compound is presented in Fig.1. Both molecules from the asymmetric unit exist in an *E* configuration with respect to the ethenyl C=C bond [C10δb C11 = 1.328 (3)Å and C29δb C30 = 1.330 (3) Å]. The dihedral angles between the phenyl and quinoline rings are 5.22 (8)° and 9.80 (8)°.

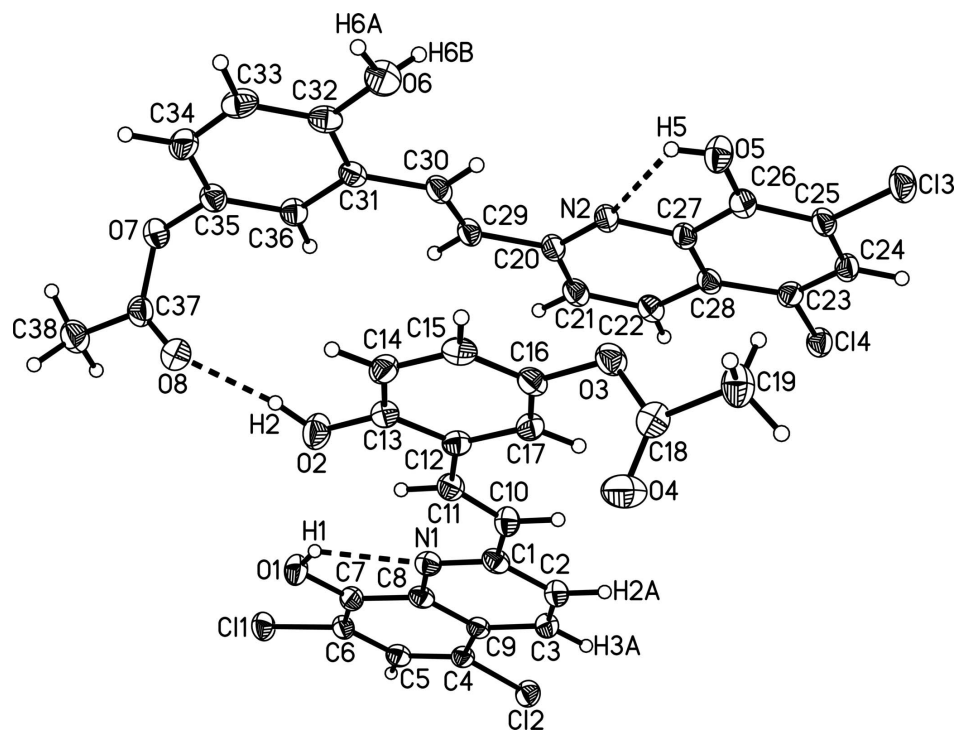
The crystal structure is stabilized by intramolecular and intermolecular hydrogen bonding. Intramolecular O—H...N contacts result in the formation of planar five-membered rings (O1/H1/N1/C8/C7 and O5/H5/N2/C27/C26). The intermolecular interactions O2—H2...O8 and O5—H5...O4ⁱ (symmetry codes: (i) $x + 1, y, z$) assemble molecules into one-dimensional polymeric structure extended along the *a* axis. These assemblies are further joined *via* O6—H6A...O6Aⁱⁱ [symmetry code: (ii) $-x + 2, -y + 1, -z$] hydrogen bonds in which the H atoms are disordered and have 0.5 occupancy (Fig. 2.) An alternative position of the H6A could not be located from a difference Fourier map.

S2. Experimental

To the solution of 5,7-dichloro-2-methylquinolin-8-ol (1.14 g, 5 mmol) in Ac₂O (25 ml) at 303 K, 2,5-dihydroxybenzaldehyde (0.69 g, 5 mmol) was added. The reaction mixture was stirred at 373 K for 16 h. Next, the solvent was evaporated and the py/H₂O system (4:1, 20 ml) was added and the reaction mixture was stirred at 373 K for 3 h. The solvent was evaporated and residue was purified by crystallization using EtOH, THF and finally CH₃CN.

S3. Refinement

Carbon-bound H atoms were included in idealized positions and refined as riding atoms with aromatic and methylene C—H = 0.95 Å, methyl C—H = 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ for aromatic and methylene C—H and $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$ for methyl group. The OH group H atoms H1, H2, H5 were located in a difference Fourier map and fully refined. The O6—H group is disordered. In one site (50% occupancy) it is involved in strong O6—H6A...O6($-x + 2, -y + 1, -z$) hydrogen bonding. H6A was located in a difference Fourier map and in the refinement process the O6—H6A distance was restrained to 0.82 (2) Å and isotropic displacement parameter refined. An alternative position of this H atom (H6B) could not be determined from difference Fourier maps. Position of this H atom was calculated assuming its H-bond interaction with O4 and restrained intramolecular distances O6—H6B 0.85 (1), H30A...H6B 2.20 (1) and C32...H6B 1.83 (1) Å. Isotropic displacement parameter of H6A was refined.

**Figure 1**

Structure of 3-[(*E*)-2-(5,7-dichloro-8-hydroxyquinolin-2-yl)vinyl]-4-hydroxyphenyl acetate showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

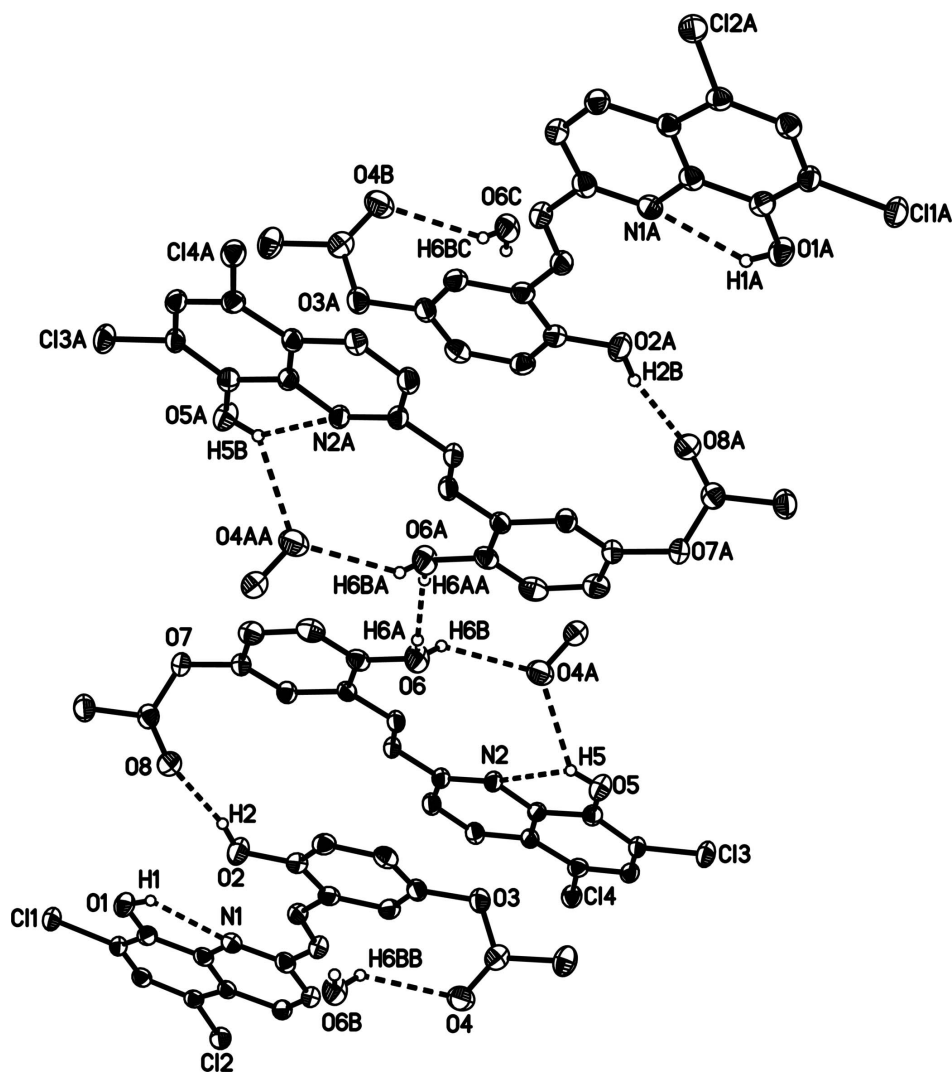


Figure 2

Hydrogen bonds between 3-[(*E*)-2-(5,7-dichloro-8-hydroxyquinolin-2-yl)vinyl]-4-hydroxyphenyl acetate molecules. For clarity, all H atoms, except O—H, have been omitted. Symmetry code for the atoms designated with A: 2 - *x*, 1 - *y*, -*z*.

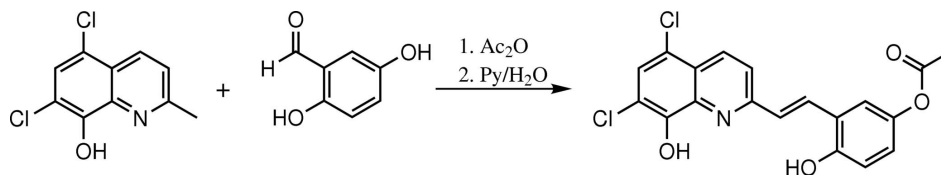


Figure 3

Preparation of the title compound.

3-[(*E*)-2-(5,7-Dichloro-8-hydroxyquinolin-2-yl)vinyl]-4-hydroxyphenyl acetate

Crystal data

$C_{19}H_{13}Cl_2NO_4$

$M_r = 390.20$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 7.3274 (15) \text{ \AA}$

$b = 10.449 (2) \text{ \AA}$

$c = 21.550 (4) \text{ \AA}$
 $\alpha = 84.89 (3)^\circ$
 $\beta = 89.50 (3)^\circ$
 $\gamma = 87.31 (3)^\circ$
 $V = 1641.6 (6) \text{ \AA}^3$
 $Z = 4$
 $F(000) = 800$
 $D_x = 1.579 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 8303 reflections
 $\theta = 2.0\text{--}32.3^\circ$
 $\mu = 0.42 \text{ mm}^{-1}$
 $T = 120 \text{ K}$
 Block, orange
 $0.36 \times 0.29 \times 0.11 \text{ mm}$

Data collection

Oxford Diffraction KM4CCD κ -geometry diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 Detector resolution: 8.1883 pixels mm^{-1}
 ω scans, 0.75 deg width
 13404 measured reflections

7118 independent reflections
 5533 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$
 $\theta_{\text{max}} = 27.0^\circ$, $\theta_{\text{min}} = 4.1^\circ$
 $h = -8 \rightarrow 9$
 $k = -13 \rightarrow 10$
 $l = -27 \rightarrow 27$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.109$
 $S = 1.06$
 7118 reflections
 491 parameters
 4 restraints
 Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0649P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.54 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|-----|--------------|---------------|-------------|----------------------------------|-----------|
| Cl1 | -0.05058 (7) | -0.48122 (4) | 0.39447 (2) | 0.02868 (13) | |
| Cl2 | -0.32326 (7) | -0.14842 (5) | 0.55244 (2) | 0.02702 (13) | |
| Cl3 | 0.51139 (7) | 1.02105 (4) | 0.29549 (2) | 0.02920 (13) | |
| Cl4 | 0.34086 (7) | 0.64476 (4) | 0.46981 (2) | 0.02556 (12) | |
| N1 | -0.0213 (2) | -0.00314 (15) | 0.34122 (7) | 0.0220 (3) | |
| N2 | 0.6083 (2) | 0.55562 (14) | 0.25358 (7) | 0.0206 (3) | |
| O1 | 0.0315 (2) | -0.24598 (15) | 0.31376 (7) | 0.0275 (3) | |
| H1 | 0.059 (4) | -0.177 (3) | 0.3008 (13) | 0.049 (9)* | |
| O2 | 0.2381 (2) | 0.12385 (13) | 0.14624 (7) | 0.0324 (4) | |

| | | | | | |
|------|--------------|---------------|--------------|-------------|------|
| H2 | 0.306 (4) | 0.101 (3) | 0.1151 (13) | 0.051 (8)* | |
| O3 | 0.22826 (19) | 0.64374 (13) | 0.17441 (7) | 0.0272 (3) | |
| O4 | -0.0706 (2) | 0.66859 (14) | 0.15324 (8) | 0.0415 (4) | |
| O5 | 0.6377 (2) | 0.80890 (14) | 0.22189 (7) | 0.0280 (3) | |
| H5 | 0.671 (4) | 0.746 (3) | 0.2085 (13) | 0.054 (9)* | |
| O6 | 0.8761 (2) | 0.47684 (14) | 0.05196 (8) | 0.0320 (3) | |
| H6B | 0.936 (2) | 0.4981 (17) | 0.0825 (5) | 0.11 (3)* | 0.50 |
| H6A | 0.918 (7) | 0.495 (5) | 0.0166 (13) | 0.057 (18)* | 0.50 |
| O7 | 0.74929 (18) | -0.04271 (12) | 0.07725 (6) | 0.0263 (3) | |
| O8 | 0.44540 (19) | -0.00398 (14) | 0.06726 (7) | 0.0315 (3) | |
| C1 | -0.0496 (3) | 0.11986 (18) | 0.35315 (9) | 0.0229 (4) | |
| C2 | -0.1381 (3) | 0.15372 (18) | 0.40825 (9) | 0.0245 (4) | |
| H2A | -0.1588 | 0.2419 | 0.4150 | 0.029* | |
| C3 | -0.1942 (3) | 0.06119 (18) | 0.45183 (9) | 0.0229 (4) | |
| H3A | -0.2528 | 0.0846 | 0.4889 | 0.027* | |
| C4 | -0.2139 (2) | -0.17651 (18) | 0.48241 (9) | 0.0206 (4) | |
| C5 | -0.1781 (2) | -0.30041 (18) | 0.46866 (9) | 0.0220 (4) | |
| H5A | -0.2092 | -0.3702 | 0.4975 | 0.026* | |
| C6 | -0.0950 (3) | -0.32370 (18) | 0.41148 (9) | 0.0226 (4) | |
| C7 | -0.0468 (3) | -0.22522 (18) | 0.36942 (9) | 0.0220 (4) | |
| C8 | -0.0785 (2) | -0.09591 (18) | 0.38460 (9) | 0.0211 (4) | |
| C9 | -0.1646 (2) | -0.07036 (17) | 0.44149 (9) | 0.0193 (4) | |
| C10 | 0.0138 (3) | 0.22128 (18) | 0.30779 (9) | 0.0240 (4) | |
| H10A | -0.0067 | 0.3081 | 0.3169 | 0.029* | |
| C11 | 0.0983 (3) | 0.19915 (18) | 0.25467 (9) | 0.0233 (4) | |
| H11A | 0.1183 | 0.1116 | 0.2467 | 0.028* | |
| C12 | 0.1638 (2) | 0.29527 (18) | 0.20718 (9) | 0.0216 (4) | |
| C13 | 0.2360 (3) | 0.25260 (18) | 0.15143 (9) | 0.0235 (4) | |
| C14 | 0.2986 (3) | 0.33822 (19) | 0.10404 (9) | 0.0244 (4) | |
| H14A | 0.3448 | 0.3075 | 0.0665 | 0.029* | |
| C15 | 0.2936 (3) | 0.46913 (19) | 0.11148 (9) | 0.0250 (4) | |
| H15A | 0.3372 | 0.5287 | 0.0795 | 0.030* | |
| C16 | 0.2238 (3) | 0.51087 (18) | 0.16657 (9) | 0.0233 (4) | |
| C17 | 0.1590 (3) | 0.42768 (18) | 0.21369 (9) | 0.0235 (4) | |
| H17A | 0.1109 | 0.4598 | 0.2506 | 0.028* | |
| C18 | 0.0700 (3) | 0.71436 (18) | 0.16649 (9) | 0.0260 (4) | |
| C19 | 0.0972 (3) | 0.85296 (19) | 0.17313 (10) | 0.0330 (5) | |
| H19A | -0.0143 | 0.8924 | 0.1900 | 0.050* | |
| H19B | 0.1246 | 0.8969 | 0.1322 | 0.050* | |
| H19C | 0.1992 | 0.8607 | 0.2015 | 0.050* | |
| C20 | 0.5942 (2) | 0.42938 (17) | 0.26808 (9) | 0.0207 (4) | |
| C21 | 0.5229 (3) | 0.38022 (18) | 0.32605 (9) | 0.0238 (4) | |
| H21A | 0.5151 | 0.2900 | 0.3351 | 0.029* | |
| C22 | 0.4651 (3) | 0.46163 (17) | 0.36918 (9) | 0.0231 (4) | |
| H22A | 0.4176 | 0.4284 | 0.4082 | 0.028* | |
| C23 | 0.4206 (3) | 0.69136 (18) | 0.39503 (9) | 0.0214 (4) | |
| C24 | 0.4301 (2) | 0.81905 (18) | 0.37680 (9) | 0.0218 (4) | |
| H24A | 0.3893 | 0.8814 | 0.4039 | 0.026* | |

| | | | | |
|------|------------|---------------|--------------|------------|
| C25 | 0.5008 (3) | 0.85796 (17) | 0.31761 (9) | 0.0217 (4) |
| C26 | 0.5643 (3) | 0.77065 (18) | 0.27752 (9) | 0.0216 (4) |
| C27 | 0.5491 (2) | 0.63696 (17) | 0.29608 (9) | 0.0201 (4) |
| C28 | 0.4767 (2) | 0.59576 (17) | 0.35519 (9) | 0.0200 (4) |
| C29 | 0.6498 (3) | 0.34132 (17) | 0.22142 (9) | 0.0218 (4) |
| H29A | 0.6386 | 0.2518 | 0.2319 | 0.026* |
| C30 | 0.7150 (3) | 0.37867 (17) | 0.16535 (9) | 0.0218 (4) |
| H30A | 0.7306 | 0.4682 | 0.1563 | 0.026* |
| C31 | 0.7652 (2) | 0.29585 (17) | 0.11613 (9) | 0.0203 (4) |
| C32 | 0.8451 (3) | 0.34769 (18) | 0.06051 (9) | 0.0236 (4) |
| C33 | 0.8925 (3) | 0.2713 (2) | 0.01282 (9) | 0.0280 (4) |
| H33A | 0.9492 | 0.3082 | -0.0239 | 0.034* |
| C34 | 0.8578 (3) | 0.1428 (2) | 0.01846 (9) | 0.0273 (4) |
| H34A | 0.8884 | 0.0905 | -0.0143 | 0.033* |
| C35 | 0.7775 (3) | 0.09090 (18) | 0.07278 (9) | 0.0228 (4) |
| C36 | 0.7329 (3) | 0.16355 (17) | 0.12123 (9) | 0.0214 (4) |
| H36A | 0.6802 | 0.1245 | 0.1582 | 0.026* |
| C37 | 0.5759 (3) | -0.07926 (19) | 0.07142 (9) | 0.0255 (4) |
| C38 | 0.5673 (3) | -0.22131 (19) | 0.06933 (10) | 0.0319 (5) |
| H38A | 0.4973 | -0.2393 | 0.0328 | 0.048* |
| H38B | 0.5076 | -0.2582 | 0.1072 | 0.048* |
| H38C | 0.6914 | -0.2597 | 0.0666 | 0.048* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|---------------|--------------|---------------|
| Cl1 | 0.0327 (3) | 0.0194 (2) | 0.0345 (3) | 0.00009 (19) | -0.0010 (2) | -0.0062 (2) |
| Cl2 | 0.0297 (3) | 0.0280 (3) | 0.0239 (2) | -0.00402 (19) | 0.0061 (2) | -0.00418 (19) |
| Cl3 | 0.0367 (3) | 0.0158 (2) | 0.0351 (3) | 0.00011 (19) | 0.0011 (2) | -0.00306 (19) |
| Cl4 | 0.0294 (3) | 0.0246 (2) | 0.0233 (2) | -0.00214 (19) | 0.00264 (19) | -0.00533 (19) |
| N1 | 0.0209 (8) | 0.0239 (8) | 0.0211 (8) | -0.0022 (6) | -0.0006 (6) | -0.0014 (7) |
| N2 | 0.0215 (8) | 0.0182 (8) | 0.0226 (8) | -0.0004 (6) | -0.0022 (6) | -0.0050 (6) |
| O1 | 0.0350 (8) | 0.0255 (8) | 0.0227 (7) | -0.0010 (6) | 0.0048 (6) | -0.0061 (6) |
| O2 | 0.0409 (9) | 0.0216 (7) | 0.0352 (9) | -0.0023 (6) | 0.0108 (7) | -0.0060 (6) |
| O3 | 0.0281 (8) | 0.0195 (7) | 0.0340 (8) | -0.0028 (6) | -0.0025 (6) | -0.0016 (6) |
| O4 | 0.0271 (8) | 0.0254 (8) | 0.0696 (12) | -0.0013 (6) | -0.0025 (8) | 0.0090 (8) |
| O5 | 0.0378 (9) | 0.0210 (7) | 0.0246 (8) | 0.0022 (6) | 0.0043 (6) | -0.0016 (6) |
| O6 | 0.0404 (9) | 0.0219 (7) | 0.0326 (9) | -0.0061 (6) | 0.0069 (7) | 0.0053 (7) |
| O7 | 0.0277 (8) | 0.0197 (7) | 0.0324 (8) | -0.0024 (5) | 0.0017 (6) | -0.0075 (6) |
| O8 | 0.0297 (8) | 0.0319 (8) | 0.0341 (8) | -0.0020 (6) | 0.0042 (6) | -0.0092 (7) |
| C1 | 0.0215 (10) | 0.0228 (10) | 0.0244 (10) | -0.0022 (7) | -0.0056 (8) | -0.0006 (8) |
| C2 | 0.0242 (10) | 0.0206 (10) | 0.0293 (11) | -0.0007 (8) | -0.0001 (8) | -0.0058 (8) |
| C3 | 0.0219 (10) | 0.0246 (10) | 0.0228 (10) | -0.0006 (7) | -0.0009 (8) | -0.0059 (8) |
| C4 | 0.0177 (9) | 0.0252 (10) | 0.0191 (9) | -0.0012 (7) | -0.0009 (7) | -0.0039 (8) |
| C5 | 0.0203 (10) | 0.0226 (10) | 0.0230 (10) | -0.0019 (7) | -0.0030 (8) | -0.0004 (8) |
| C6 | 0.0216 (10) | 0.0196 (9) | 0.0273 (10) | -0.0002 (7) | -0.0030 (8) | -0.0065 (8) |
| C7 | 0.0208 (10) | 0.0254 (10) | 0.0203 (9) | 0.0005 (7) | -0.0030 (8) | -0.0051 (8) |
| C8 | 0.0176 (9) | 0.0230 (9) | 0.0226 (10) | -0.0013 (7) | -0.0049 (7) | -0.0010 (8) |

| | | | | | | |
|-----|-------------|-------------|-------------|-------------|-------------|-------------|
| C9 | 0.0172 (9) | 0.0216 (9) | 0.0195 (9) | -0.0022 (7) | -0.0020 (7) | -0.0030 (7) |
| C10 | 0.0282 (11) | 0.0193 (9) | 0.0245 (10) | 0.0001 (8) | 0.0006 (8) | -0.0030 (8) |
| C11 | 0.0224 (10) | 0.0199 (9) | 0.0273 (10) | 0.0001 (7) | -0.0023 (8) | -0.0020 (8) |
| C12 | 0.0176 (9) | 0.0231 (9) | 0.0238 (10) | -0.0003 (7) | -0.0011 (8) | -0.0007 (8) |
| C13 | 0.0204 (10) | 0.0239 (10) | 0.0265 (10) | -0.0007 (7) | -0.0003 (8) | -0.0045 (8) |
| C14 | 0.0225 (10) | 0.0286 (10) | 0.0223 (10) | -0.0003 (8) | 0.0027 (8) | -0.0044 (8) |
| C15 | 0.0215 (10) | 0.0275 (10) | 0.0253 (10) | -0.0043 (8) | -0.0009 (8) | 0.0029 (8) |
| C16 | 0.0220 (10) | 0.0190 (9) | 0.0290 (10) | -0.0026 (7) | -0.0040 (8) | -0.0015 (8) |
| C17 | 0.0200 (10) | 0.0247 (10) | 0.0260 (10) | 0.0010 (7) | -0.0014 (8) | -0.0049 (8) |
| C18 | 0.0320 (12) | 0.0230 (10) | 0.0216 (10) | 0.0009 (8) | 0.0033 (8) | 0.0048 (8) |
| C19 | 0.0467 (14) | 0.0242 (11) | 0.0276 (11) | 0.0005 (9) | 0.0020 (10) | -0.0005 (9) |
| C20 | 0.0207 (10) | 0.0185 (9) | 0.0238 (10) | -0.0008 (7) | -0.0029 (8) | -0.0056 (8) |
| C21 | 0.0252 (10) | 0.0179 (9) | 0.0286 (10) | -0.0026 (7) | -0.0034 (8) | -0.0019 (8) |
| C22 | 0.0246 (10) | 0.0197 (9) | 0.0252 (10) | -0.0033 (7) | -0.0020 (8) | -0.0017 (8) |
| C23 | 0.0190 (9) | 0.0247 (10) | 0.0211 (9) | 0.0003 (7) | -0.0010 (7) | -0.0052 (8) |
| C24 | 0.0207 (10) | 0.0213 (9) | 0.0242 (10) | 0.0015 (7) | -0.0041 (8) | -0.0080 (8) |
| C25 | 0.0219 (10) | 0.0146 (8) | 0.0290 (10) | -0.0008 (7) | -0.0029 (8) | -0.0035 (8) |
| C26 | 0.0218 (10) | 0.0196 (9) | 0.0235 (10) | 0.0006 (7) | -0.0045 (8) | -0.0024 (8) |
| C27 | 0.0176 (9) | 0.0195 (9) | 0.0238 (10) | 0.0008 (7) | -0.0052 (7) | -0.0059 (8) |
| C28 | 0.0185 (9) | 0.0191 (9) | 0.0229 (10) | -0.0007 (7) | -0.0051 (7) | -0.0048 (7) |
| C29 | 0.0228 (10) | 0.0155 (9) | 0.0277 (10) | -0.0013 (7) | -0.0016 (8) | -0.0049 (8) |
| C30 | 0.0232 (10) | 0.0159 (9) | 0.0267 (10) | -0.0028 (7) | -0.0021 (8) | -0.0031 (8) |
| C31 | 0.0177 (9) | 0.0183 (9) | 0.0250 (10) | -0.0019 (7) | -0.0030 (7) | -0.0015 (8) |
| C32 | 0.0206 (10) | 0.0231 (10) | 0.0261 (10) | -0.0032 (7) | -0.0012 (8) | 0.0042 (8) |
| C33 | 0.0253 (11) | 0.0363 (11) | 0.0214 (10) | -0.0038 (8) | 0.0034 (8) | 0.0040 (9) |
| C34 | 0.0262 (11) | 0.0360 (11) | 0.0206 (10) | -0.0022 (8) | 0.0019 (8) | -0.0071 (9) |
| C35 | 0.0233 (10) | 0.0191 (9) | 0.0261 (10) | -0.0019 (7) | -0.0006 (8) | -0.0033 (8) |
| C36 | 0.0242 (10) | 0.0191 (9) | 0.0206 (9) | -0.0030 (7) | 0.0016 (8) | 0.0000 (7) |
| C37 | 0.0299 (11) | 0.0274 (10) | 0.0203 (10) | -0.0044 (8) | 0.0017 (8) | -0.0066 (8) |
| C38 | 0.0366 (12) | 0.0263 (11) | 0.0342 (12) | -0.0066 (9) | 0.0011 (9) | -0.0077 (9) |

Geometric parameters (Å, °)

| | | | |
|---------|-------------|----------|-----------|
| C11—C6 | 1.7334 (19) | C13—C14 | 1.386 (3) |
| C12—C4 | 1.744 (2) | C14—C15 | 1.390 (3) |
| C13—C25 | 1.7334 (19) | C14—H14A | 0.9500 |
| C14—C23 | 1.745 (2) | C15—C16 | 1.386 (3) |
| N1—C1 | 1.339 (2) | C15—H15A | 0.9500 |
| N1—C8 | 1.364 (2) | C16—C17 | 1.373 (3) |
| N2—C20 | 1.337 (2) | C17—H17A | 0.9500 |
| N2—C27 | 1.359 (2) | C18—C19 | 1.491 (3) |
| O1—C7 | 1.356 (2) | C19—H19A | 0.9800 |
| O1—H1 | 0.78 (3) | C19—H19B | 0.9800 |
| O2—C13 | 1.359 (2) | C19—H19C | 0.9800 |
| O2—H2 | 0.88 (3) | C20—C21 | 1.413 (3) |
| O3—C18 | 1.349 (2) | C20—C29 | 1.465 (3) |
| O3—C16 | 1.415 (2) | C21—C22 | 1.366 (3) |
| O4—C18 | 1.203 (2) | C21—H21A | 0.9500 |

| | | | |
|------------|-------------|---------------|-------------|
| O5—C26 | 1.345 (2) | C22—C28 | 1.414 (3) |
| O5—H5 | 0.77 (3) | C22—H22A | 0.9500 |
| O6—C32 | 1.375 (2) | C23—C24 | 1.362 (3) |
| O6—H6B | 0.844 (10) | C23—C28 | 1.418 (3) |
| O6—H6A | 0.829 (19) | C24—C25 | 1.406 (3) |
| O7—C37 | 1.354 (2) | C24—H24A | 0.9500 |
| O7—C35 | 1.416 (2) | C25—C26 | 1.374 (3) |
| O8—C37 | 1.208 (2) | C26—C27 | 1.428 (3) |
| C1—C2 | 1.413 (3) | C27—C28 | 1.415 (3) |
| C1—C10 | 1.466 (3) | C29—C30 | 1.328 (3) |
| C2—C3 | 1.362 (3) | C29—H29A | 0.9500 |
| C2—H2A | 0.9500 | C30—C31 | 1.461 (3) |
| C3—C9 | 1.418 (3) | C30—H30A | 0.9500 |
| C3—H3A | 0.9500 | C31—C32 | 1.405 (3) |
| C4—C5 | 1.367 (3) | C31—C36 | 1.408 (2) |
| C4—C9 | 1.413 (3) | C32—C33 | 1.389 (3) |
| C5—C6 | 1.405 (3) | C33—C34 | 1.373 (3) |
| C5—H5A | 0.9500 | C33—H33A | 0.9500 |
| C6—C7 | 1.366 (3) | C34—C35 | 1.384 (3) |
| C7—C8 | 1.426 (3) | C34—H34A | 0.9500 |
| C8—C9 | 1.414 (3) | C35—C36 | 1.373 (3) |
| C10—C11 | 1.330 (3) | C36—H36A | 0.9500 |
| C10—H10A | 0.9500 | C37—C38 | 1.493 (3) |
| C11—C12 | 1.463 (3) | C38—H38A | 0.9800 |
| C11—H11A | 0.9500 | C38—H38B | 0.9800 |
| C12—C17 | 1.402 (3) | C38—H38C | 0.9800 |
| C12—C13 | 1.409 (3) | | |
| | | | |
| C1—N1—C8 | 117.82 (16) | C18—C19—H19B | 109.5 |
| C20—N2—C27 | 118.02 (16) | H19A—C19—H19B | 109.5 |
| C7—O1—H1 | 103 (2) | C18—C19—H19C | 109.5 |
| C13—O2—H2 | 112.3 (18) | H19A—C19—H19C | 109.5 |
| C18—O3—C16 | 117.18 (15) | H19B—C19—H19C | 109.5 |
| C26—O5—H5 | 104 (2) | N2—C20—C21 | 121.72 (17) |
| C32—O6—H6B | 109.3 (12) | N2—C20—C29 | 118.39 (17) |
| C32—O6—H6A | 110 (4) | C21—C20—C29 | 119.87 (17) |
| H6B—O6—H6A | 118 (4) | C22—C21—C20 | 120.43 (17) |
| C37—O7—C35 | 117.40 (15) | C22—C21—H21A | 119.8 |
| N1—C1—C2 | 121.63 (18) | C20—C21—H21A | 119.8 |
| N1—C1—C10 | 118.84 (17) | C21—C22—C28 | 119.35 (18) |
| C2—C1—C10 | 119.52 (17) | C21—C22—H22A | 120.3 |
| C3—C2—C1 | 120.62 (18) | C28—C22—H22A | 120.3 |
| C3—C2—H2A | 119.7 | C24—C23—C28 | 121.65 (18) |
| C1—C2—H2A | 119.7 | C24—C23—C14 | 118.94 (15) |
| C2—C3—C9 | 119.60 (18) | C28—C23—C14 | 119.40 (14) |
| C2—C3—H3A | 120.2 | C23—C24—C25 | 119.58 (17) |
| C9—C3—H3A | 120.2 | C23—C24—H24A | 120.2 |
| C5—C4—C9 | 121.84 (18) | C25—C24—H24A | 120.2 |

| | | | |
|--------------|-------------|----------------|-------------|
| C5—C4—C12 | 119.16 (15) | C26—C25—C24 | 121.94 (17) |
| C9—C4—C12 | 119.00 (14) | C26—C25—C13 | 119.34 (15) |
| C4—C5—C6 | 119.44 (18) | C24—C25—C13 | 118.70 (14) |
| C4—C5—H5A | 120.3 | O5—C26—C25 | 121.47 (17) |
| C6—C5—H5A | 120.3 | O5—C26—C27 | 120.29 (17) |
| C7—C6—C5 | 121.55 (17) | C25—C26—C27 | 118.25 (18) |
| C7—C6—C11 | 119.40 (15) | N2—C27—C28 | 123.85 (17) |
| C5—C6—C11 | 119.05 (15) | N2—C27—C26 | 115.49 (17) |
| O1—C7—C6 | 122.30 (17) | C28—C27—C26 | 120.66 (17) |
| O1—C7—C8 | 118.63 (18) | C22—C28—C27 | 116.62 (17) |
| C6—C7—C8 | 119.06 (18) | C22—C28—C23 | 125.54 (18) |
| N1—C8—C9 | 124.12 (17) | C27—C28—C23 | 117.83 (17) |
| N1—C8—C7 | 115.63 (17) | C30—C29—C20 | 124.17 (17) |
| C9—C8—C7 | 120.25 (18) | C30—C29—H29A | 117.9 |
| C4—C9—C8 | 117.80 (17) | C20—C29—H29A | 117.9 |
| C4—C9—C3 | 126.01 (18) | C29—C30—C31 | 126.50 (17) |
| C8—C9—C3 | 116.19 (18) | C29—C30—H30A | 116.7 |
| C11—C10—C1 | 123.99 (18) | C31—C30—H30A | 116.7 |
| C11—C10—H10A | 118.0 | C32—C31—C36 | 117.29 (17) |
| C1—C10—H10A | 118.0 | C32—C31—C30 | 120.27 (16) |
| C10—C11—C12 | 126.92 (18) | C36—C31—C30 | 122.42 (17) |
| C10—C11—H11A | 116.5 | O6—C32—C33 | 118.40 (17) |
| C12—C11—H11A | 116.5 | O6—C32—C31 | 120.19 (18) |
| C17—C12—C13 | 117.82 (18) | C33—C32—C31 | 121.41 (17) |
| C17—C12—C11 | 123.98 (18) | C34—C33—C32 | 120.34 (18) |
| C13—C12—C11 | 118.20 (17) | C34—C33—H33A | 119.8 |
| O2—C13—C14 | 121.97 (18) | C32—C33—H33A | 119.8 |
| O2—C13—C12 | 116.57 (18) | C33—C34—C35 | 118.78 (19) |
| C14—C13—C12 | 121.45 (17) | C33—C34—H34A | 120.6 |
| C13—C14—C15 | 119.90 (18) | C35—C34—H34A | 120.6 |
| C13—C14—H14A | 120.0 | C36—C35—C34 | 122.11 (18) |
| C15—C14—H14A | 120.0 | C36—C35—O7 | 121.07 (17) |
| C16—C15—C14 | 118.57 (18) | C34—C35—O7 | 116.78 (17) |
| C16—C15—H15A | 120.7 | C35—C36—C31 | 120.05 (18) |
| C14—C15—H15A | 120.7 | C35—C36—H36A | 120.0 |
| C17—C16—C15 | 122.35 (18) | C31—C36—H36A | 120.0 |
| C17—C16—O3 | 119.97 (17) | O8—C37—O7 | 123.06 (18) |
| C15—C16—O3 | 117.62 (17) | O8—C37—C38 | 124.83 (19) |
| C16—C17—C12 | 119.90 (18) | O7—C37—C38 | 112.10 (17) |
| C16—C17—H17A | 120.1 | C37—C38—H38A | 109.5 |
| C12—C17—H17A | 120.1 | C37—C38—H38B | 109.5 |
| O4—C18—O3 | 122.59 (18) | H38A—C38—H38B | 109.5 |
| O4—C18—C19 | 126.15 (19) | C37—C38—H38C | 109.5 |
| O3—C18—C19 | 111.19 (18) | H38A—C38—H38C | 109.5 |
| C18—C19—H19A | 109.5 | H38B—C38—H38C | 109.5 |
| C8—N1—C1—C2 | -1.0 (3) | C27—N2—C20—C21 | -1.0 (3) |
| C8—N1—C1—C10 | 178.83 (16) | C27—N2—C20—C29 | 177.25 (16) |

| | | | |
|-----------------|--------------|-----------------|--------------|
| N1—C1—C2—C3 | 1.4 (3) | N2—C20—C21—C22 | 0.3 (3) |
| C10—C1—C2—C3 | -178.34 (18) | C29—C20—C21—C22 | -177.92 (17) |
| C1—C2—C3—C9 | -0.5 (3) | C20—C21—C22—C28 | 0.2 (3) |
| C9—C4—C5—C6 | -2.0 (3) | C28—C23—C24—C25 | -1.4 (3) |
| C12—C4—C5—C6 | 178.09 (14) | C14—C23—C24—C25 | 177.52 (14) |
| C4—C5—C6—C7 | 0.8 (3) | C23—C24—C25—C26 | -1.2 (3) |
| C4—C5—C6—C11 | -179.90 (14) | C23—C24—C25—C13 | 179.99 (14) |
| C5—C6—C7—O1 | -179.23 (17) | C24—C25—C26—O5 | -177.55 (17) |
| C11—C6—C7—O1 | 1.5 (3) | C13—C25—C26—O5 | 1.3 (3) |
| C5—C6—C7—C8 | 1.3 (3) | C24—C25—C26—C27 | 3.0 (3) |
| C11—C6—C7—C8 | -178.01 (14) | C13—C25—C26—C27 | -178.21 (14) |
| C1—N1—C8—C9 | -0.4 (3) | C20—N2—C27—C28 | 1.2 (3) |
| C1—N1—C8—C7 | 179.42 (17) | C20—N2—C27—C26 | -178.79 (16) |
| O1—C7—C8—N1 | -1.6 (3) | O5—C26—C27—N2 | -1.7 (3) |
| C6—C7—C8—N1 | 177.91 (17) | C25—C26—C27—N2 | 177.76 (16) |
| O1—C7—C8—C9 | 178.25 (16) | O5—C26—C27—C28 | 178.26 (17) |
| C6—C7—C8—C9 | -2.2 (3) | C25—C26—C27—C28 | -2.3 (3) |
| C5—C4—C9—C8 | 1.0 (3) | C21—C22—C28—C27 | 0.0 (3) |
| C12—C4—C9—C8 | -179.07 (13) | C21—C22—C28—C23 | 179.39 (18) |
| C5—C4—C9—C3 | -179.37 (18) | N2—C27—C28—C22 | -0.7 (3) |
| C12—C4—C9—C3 | 0.6 (3) | C26—C27—C28—C22 | 179.30 (16) |
| N1—C8—C9—C4 | -179.03 (16) | N2—C27—C28—C23 | 179.81 (17) |
| C7—C8—C9—C4 | 1.1 (3) | C26—C27—C28—C23 | -0.2 (3) |
| N1—C8—C9—C3 | 1.3 (3) | C24—C23—C28—C22 | -177.38 (18) |
| C7—C8—C9—C3 | -178.55 (17) | C14—C23—C28—C22 | 3.7 (3) |
| C2—C3—C9—C4 | 179.58 (18) | C24—C23—C28—C27 | 2.0 (3) |
| C2—C3—C9—C8 | -0.8 (3) | C14—C23—C28—C27 | -176.89 (13) |
| N1—C1—C10—C11 | 0.2 (3) | N2—C20—C29—C30 | 0.4 (3) |
| C2—C1—C10—C11 | -179.98 (18) | C21—C20—C29—C30 | 178.71 (18) |
| C1—C10—C11—C12 | 179.48 (18) | C20—C29—C30—C31 | -177.19 (17) |
| C10—C11—C12—C17 | 5.4 (3) | C29—C30—C31—C32 | -175.38 (19) |
| C10—C11—C12—C13 | -174.54 (19) | C29—C30—C31—C36 | 6.1 (3) |
| C17—C12—C13—O2 | -179.68 (17) | C36—C31—C32—O6 | 178.42 (17) |
| C11—C12—C13—O2 | 0.3 (3) | C30—C31—C32—O6 | -0.2 (3) |
| C17—C12—C13—C14 | -0.7 (3) | C36—C31—C32—C33 | -0.8 (3) |
| C11—C12—C13—C14 | 179.21 (17) | C30—C31—C32—C33 | -179.41 (18) |
| O2—C13—C14—C15 | 180.00 (18) | O6—C32—C33—C34 | -177.64 (18) |
| C12—C13—C14—C15 | 1.1 (3) | C31—C32—C33—C34 | 1.6 (3) |
| C13—C14—C15—C16 | -0.6 (3) | C32—C33—C34—C35 | -0.9 (3) |
| C14—C15—C16—C17 | -0.3 (3) | C33—C34—C35—C36 | -0.5 (3) |
| C14—C15—C16—O3 | 177.00 (16) | C33—C34—C35—O7 | -178.19 (17) |
| C18—O3—C16—C17 | -79.5 (2) | C37—O7—C35—C36 | 76.0 (2) |
| C18—O3—C16—C15 | 103.1 (2) | C37—O7—C35—C34 | -106.3 (2) |
| C15—C16—C17—C12 | 0.6 (3) | C34—C35—C36—C31 | 1.3 (3) |
| O3—C16—C17—C12 | -176.57 (16) | O7—C35—C36—C31 | 178.87 (16) |
| C13—C12—C17—C16 | -0.1 (3) | C32—C31—C36—C35 | -0.6 (3) |
| C11—C12—C17—C16 | 179.92 (18) | C30—C31—C36—C35 | 177.95 (17) |
| C16—O3—C18—O4 | -0.1 (3) | C35—O7—C37—O8 | -5.6 (3) |

C16—O3—C18—C19

-177.25 (17)

C35—O7—C37—C38

173.12 (16)

Hydrogen-bond geometry (Å, °)

| <i>D—H...A</i> | <i>D—H</i> | <i>H...A</i> | <i>D...A</i> | <i>D—H...A</i> |
|---------------------------|------------|--------------|--------------|----------------|
| O1—H1...N1 | 0.78 (3) | 2.14 (3) | 2.667 (2) | 125 (3) |
| O2—H2...O8 | 0.88 (3) | 1.84 (3) | 2.675 (2) | 159 (3) |
| O5—H5...N2 | 0.77 (3) | 2.20 (3) | 2.692 (2) | 122 (3) |
| O5—H5...O4 ⁱ | 0.77 (3) | 2.38 (3) | 2.990 (2) | 138 (3) |
| O6—H6A...O6 ⁱⁱ | 0.83 (2) | 2.12 (3) | 2.892 (3) | 156 (5) |
| O6—H6B...O4 ⁱ | 0.84 (1) | 2.45 (1) | 3.130 (3) | 139 (2) |

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