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2-Carboxy-6-(quinolin-1-ium-8-yloxy)-benzoate

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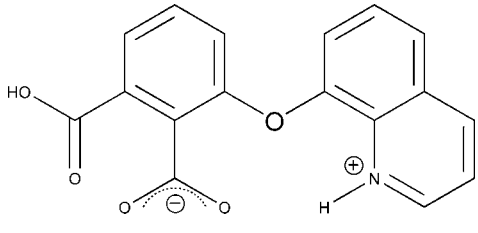
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.058; wR factor = 0.157; data-to-parameter ratio = 14.3.

In the zwitterionic title compound, $C_{17}H_{11}NO_5$, the dihedral angle between the two aromatic rings is 76.90 (7)°. The dihedral angles between the carboxyl groups and the benzene ring are 64.02 (9) and 21.67 (9)°, the larger angle being associated with an intramolecular N—H···$O_{carboxyl}$ hydrogen bond, resulting from proton transfer from the carboxylic acid group to the quinoline N atom and giving an S(9) ring motif. In the crystal, molecules are connected by O—H···O hydrogen bonds into chains extending along the b-axis direction. An overall two-dimensional network structure is formed through π–π interactions between the quinoline rings [minimum ring-centroid separation = 3.6068 (6) Å].

Related literature

For the use of phthalic acid derivatives in the construction of coordination polymers, see: Su *et al.* (2007); Zhang, Su, Li *et al.* (2006). For their potential applications, see: Wang *et al.* (2009); Zhang, Su, Song *et al.* (2006). For graph-set analysis, see: Etter *et al.* (1990).



Experimental

Crystal data

$C_{17}H_{11}NO_5$
M_r = 309.27
Monoclinic, $P2_1/c$
a = 7.7337 (15) Å
b = 11.580 (2) Å
c = 15.260 (3) Å
β = 98.43 (3)°
V = 1351.9 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 293 K
0.47 × 0.45 × 0.10 mm

Data collection

Rigaku Saturn 724 CCD area-detector diffractometer
Absorption correction: numerical (*NUMABS*; Higashi, 2000). T_{min} = 0.948, T_{max} = 0.989
11030 measured reflections
3079 independent reflections
2899 reflections with $I > 2\sigma(I)$
R_{int} = 0.041

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.157
S = 1.27
3079 reflections
216 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2A···O4^{i}	0.93 (4)	1.67 (4)	2.584 (2)	165 (4)
N1—H1A···O5	0.90 (2)	1.67 (2)	2.570 (2)	179 (5)

Symmetry code: (i) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *CrystalClear* (Rigaku, 2007); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZS2185).

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supplementary materials

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2-Carboxy-6-(quinolin-1-ium-8-yloxy)benzoate

Li-Mao Cai, Xin Fang, Mei-Jin Lin, Jin Xie and Jun-Dong Wang

Comment

Phthalic acid derivatives have proved useful as ligands for the construction of coordination polymers which have a number of potential applications (Zhang, Su, Song *et al.*, 2006; Zhang, Su, Li *et al.*, 2006; Su *et al.*, 2007; Wang *et al.*, 2009). As a part of our investigation of the rare earth coordination networks based on these phthalic acid derivatives, we report here the crystal structure of the title compound, the zwitterionic substituted phthalic acid $C_{17}H_{11}NO_5$ (Fig. 1). In this molecule, the carboxylic acid substituent group at C15 has protonated the quinoline N-atom, giving an intramolecular N—H···$O_{carboxyl}$ hydrogen-bonding association [graph set *S*9 (Etter *et al.*, 1990)]. The dihedral angles between the carboxyl groups and the benzene ring are 64.02 (9)° and 21.67 (9)°, the larger angle being associated with the intramolecular hydrogen bond. The molecules are connected by intermolecular carboxylic acid O—H···O hydrogen bonds (Table 1) giving one-dimensional chains which extend along the *b* axial direction and give an overall two-dimensional network structure through π–π interactions between the quinoline rings [minimum ring centroid separation, 3.6068 (6) Å] (Fig. 2).

Experimental

3-Nitropthalonitrile (1.73 g, 10.0 mmol), 8-hydroxyquinoline (1.45 g, 10.0 mmol) and K_2CO_3 (4.14 g, 30.0 mmol) were suspended in dry DMF (20 ml) and stirred at room temperature under a nitrogen atmosphere for 4 h. The reaction mixture was then poured into water (200 ml), and the crude product was separated by filtration and purified by column chromatography on silica gel using CH_2Cl_2 as an eluent. After removal of the solvent by rotary evaporation, 2.25 g of 3-(quinolin-8-yloxy)-phthalonitrile was obtained in a yield of 83%. Under nitrogen, 2.71 g, 10.0 mmol) of this compound and KOH (1.20 g, 30.0 mmol) were suspended in 30 ml of distilled water and refluxed until the solution turned clear. After being cooled to room temperature, the pH of the reaction mixture was slowly adjusted to about 5–6 using HCl (6.0 mol/*L*) with stirring. The solid product was separated by filtration, and then washed successively with water (3 times 30 ml). After drying under vacuum, 2.78 g of final produc was obtained in a yield of 91%. The solid was dissolved in methyl alcohol and the filtered solution was evaporated slowly at room temperature for 5–10 days, giving colorless crystals suitable for X-ray structure analysis.

Refinement

Carboxylic acid H atoms were located in a difference-Fourier analysis and their positional and isotropic displacement parameters were refined. Other H-atoms were placed in geometrically determined positions and were treated as riding, with C—H = 0.93 Å and with U_{iso}(H) = 1.2U_{eq}(C).

Computing details

Data collection: *CrystalClear* (Rigaku, 2007); cell refinement: *CrystalClear* (Rigaku, 2007); data reduction: *CrystalClear* (Rigaku, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for

publication: *SHELXL97* (Sheldrick, 2008).

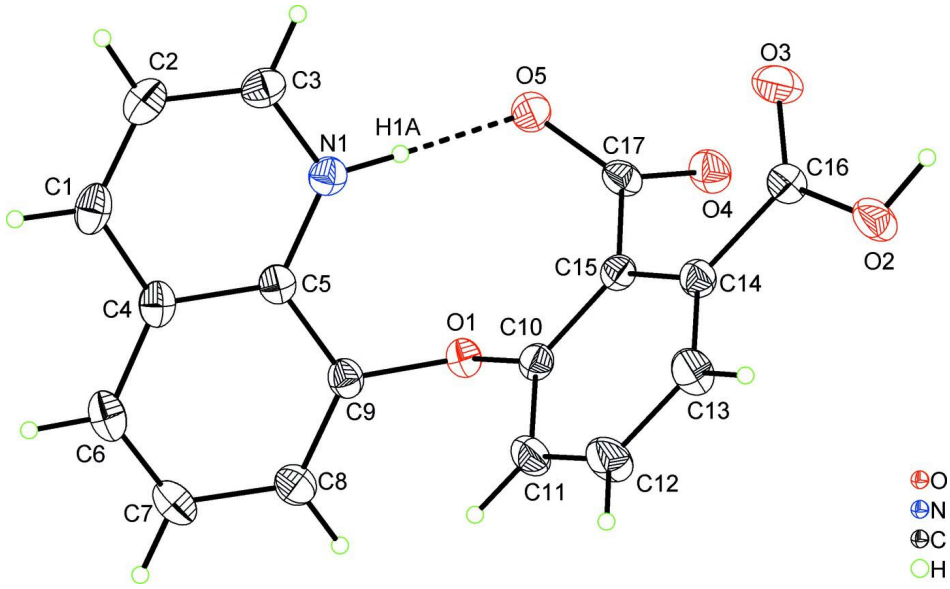

Figure 1

The molecular structure of the title compound, showing the atom-labelling scheme, with the intramolecular hydrogen bond shown as a dashed line. Displacement ellipsoids are drawn at the 30% probability level.

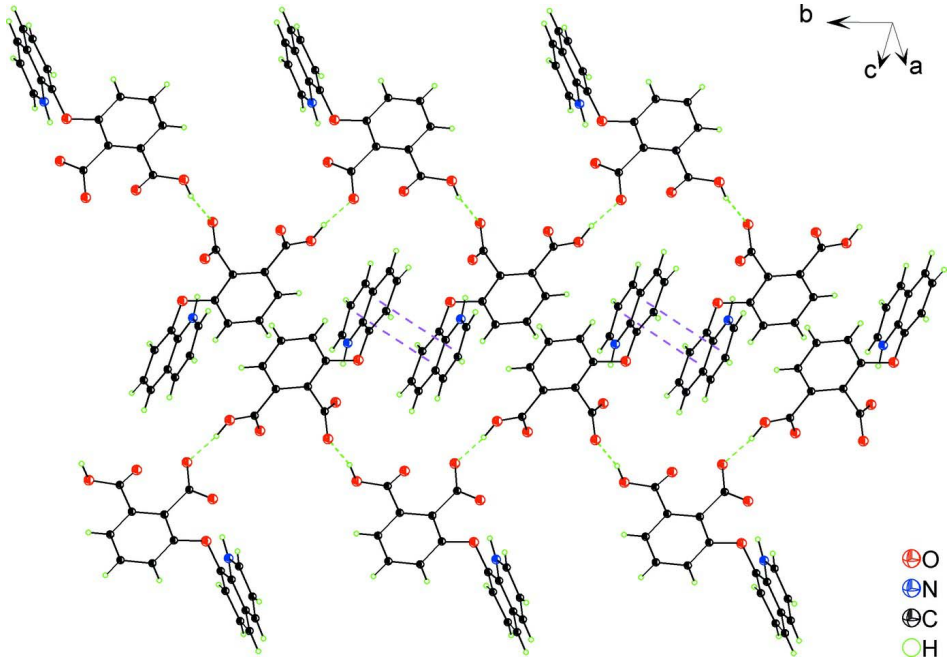

Figure 2

The two-dimensional supramolecular structure formed through hydrogen-bonds and π–π stacking interactions. Hydrogen bonds are shown with green dashed lines and π–π stacking interactions are shown by blue dashed lines.

2-Carboxy-6-(quinolin-1-ium-8-yloxy)benzoate

Crystal data

$C_{17}H_{11}NO_5$
$M_r = 309.27$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 7.7337$ (15) Å
$b = 11.580$ (2) Å
$c = 15.260$ (3) Å
$\beta = 98.43$ (3)°
$V = 1351.9$ (5) Å^3
$Z = 4$
$F(000) = 640$
$D_x = 1.520$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4908 reflections
$\theta = 3.2$–27.6°
$\mu = 0.11$ mm^{-1}
$T = 293$ K
Plate, colourless
0.47 × 0.45 × 0.10 mm

Data collection

Rigaku Saturn 724 CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: numerical (*NUMABS*; Higashi, 2000).
$T_{min} = 0.948$, $T_{max} = 0.989$
11030 measured reflections
3079 independent reflections
2899 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 27.6°$, $\theta_{min} = 3.2°$
$h = -9 \rightarrow 10$
$k = -14 \rightarrow 14$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.157$
$S = 1.27$
3079 reflections
216 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0659P)^2 + 0.6417P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-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.

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 $F^2 > 2$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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O4	0.50110 (19)	0.69917 (13)	0.20095 (9)	0.0243 (3)
O1	0.25866 (17)	0.79156 (12)	−0.00275 (9)	0.0188 (3)
O5	0.2260 (2)	0.76160 (13)	0.18306 (9)	0.0256 (4)
N1	−0.0436 (2)	0.81385 (14)	0.07072 (11)	0.0193 (4)

O3	0.3439 (2)	0.47845 (13)	0.24357 (10)	0.0323 (4)
O2	0.4250 (2)	0.33268 (13)	0.16305 (10)	0.0299 (4)
C1	−0.3499 (3)	0.89691 (17)	−0.02677 (15)	0.0238 (4)
H1	−0.4540	0.9225	−0.0593	0.029*
C2	−0.3460 (3)	0.86376 (18)	0.05908 (15)	0.0247 (4)
H2	−0.4464	0.8680	0.0859	0.030*
C3	−0.1888 (3)	0.82314 (17)	0.10662 (14)	0.0225 (4)
H3	−0.1864	0.8019	0.1656	0.027*
C4	−0.1965 (3)	0.89267 (17)	−0.06673 (14)	0.0210 (4)
C5	−0.0436 (2)	0.84770 (16)	−0.01521 (12)	0.0182 (4)
C6	−0.1882 (3)	0.93173 (18)	−0.15387 (14)	0.0253 (5)
H6	−0.2878	0.9605	−0.1886	0.030*
C7	−0.0340 (3)	0.92718 (19)	−0.18686 (14)	0.0259 (5)
H7	−0.0286	0.9559	−0.2433	0.031*
C8	0.1181 (3)	0.87963 (18)	−0.13695 (13)	0.0221 (4)
H8	0.2218	0.8761	−0.1609	0.027*
C9	0.1119 (2)	0.83900 (16)	−0.05353 (13)	0.0188 (4)
C10	0.2595 (2)	0.67061 (16)	−0.00022 (13)	0.0179 (4)
C11	0.2268 (3)	0.60626 (19)	−0.07763 (13)	0.0252 (5)
H11	0.1961	0.6424	−0.1321	0.030*
C12	0.2408 (3)	0.4877 (2)	−0.07202 (14)	0.0303 (5)
H12	0.2187	0.4433	−0.1232	0.036*
C13	0.2875 (3)	0.43417 (18)	0.00914 (14)	0.0262 (5)
H13	0.2971	0.3542	0.0120	0.031*
C14	0.3200 (3)	0.49906 (17)	0.08628 (13)	0.0194 (4)
C15	0.3055 (2)	0.61968 (17)	0.08224 (12)	0.0172 (4)
C16	0.3644 (3)	0.43696 (17)	0.17291 (13)	0.0197 (4)
C17	0.3492 (3)	0.69741 (16)	0.16191 (12)	0.0191 (4)
H2A	0.447 (5)	0.295 (4)	0.218 (3)	0.085 (13)*
H1A	0.052 (4)	0.794 (4)	0.110 (2)	0.102 (15)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O4	0.0257 (8)	0.0249 (8)	0.0204 (7)	−0.0003 (6)	−0.0027 (6)	−0.0041 (6)
O1	0.0191 (7)	0.0175 (7)	0.0193 (7)	0.0007 (5)	0.0012 (5)	0.0013 (5)
O5	0.0315 (8)	0.0255 (8)	0.0193 (7)	0.0092 (6)	0.0017 (6)	−0.0038 (6)
N1	0.0204 (8)	0.0174 (8)	0.0201 (8)	−0.0001 (6)	0.0026 (6)	−0.0020 (6)
O3	0.0535 (11)	0.0249 (8)	0.0204 (8)	0.0080 (7)	0.0113 (7)	0.0022 (6)
O2	0.0490 (10)	0.0205 (8)	0.0193 (8)	0.0094 (7)	0.0020 (7)	0.0021 (6)
C1	0.0200 (9)	0.0159 (9)	0.0342 (12)	0.0013 (7)	−0.0005 (8)	−0.0048 (8)
C2	0.0204 (10)	0.0214 (10)	0.0329 (11)	−0.0009 (8)	0.0063 (8)	−0.0050 (8)
C3	0.0259 (10)	0.0188 (10)	0.0236 (10)	−0.0015 (8)	0.0063 (8)	−0.0044 (8)
C4	0.0198 (9)	0.0151 (9)	0.0268 (10)	−0.0004 (7)	−0.0011 (8)	−0.0015 (7)
C5	0.0195 (9)	0.0150 (9)	0.0194 (9)	−0.0010 (7)	0.0004 (7)	−0.0020 (7)
C6	0.0259 (11)	0.0196 (10)	0.0278 (11)	0.0001 (8)	−0.0045 (8)	0.0030 (8)
C7	0.0306 (11)	0.0252 (11)	0.0204 (10)	−0.0024 (9)	−0.0014 (8)	0.0057 (8)
C8	0.0243 (10)	0.0201 (10)	0.0219 (10)	−0.0021 (8)	0.0033 (8)	0.0021 (7)
C9	0.0200 (9)	0.0164 (9)	0.0191 (9)	0.0006 (7)	−0.0001 (7)	−0.0003 (7)
C10	0.0176 (9)	0.0173 (9)	0.0191 (9)	0.0017 (7)	0.0031 (7)	−0.0001 (7)

C11	0.0313 (11)	0.0267 (11)	0.0160 (9)	0.0061 (9)	−0.0016 (8)	−0.0002 (8)
C12	0.0451 (13)	0.0255 (11)	0.0179 (10)	0.0053 (10)	−0.0039 (9)	−0.0066 (8)
C13	0.0357 (12)	0.0180 (10)	0.0226 (10)	0.0024 (8)	−0.0031 (9)	−0.0036 (8)
C14	0.0206 (9)	0.0187 (10)	0.0183 (9)	0.0015 (7)	0.0010 (7)	−0.0008 (7)
C15	0.0161 (8)	0.0178 (9)	0.0177 (9)	0.0003 (7)	0.0025 (7)	−0.0012 (7)
C16	0.0221 (9)	0.0166 (9)	0.0201 (10)	−0.0022 (7)	0.0019 (7)	−0.0001 (7)
C17	0.0257 (10)	0.0158 (9)	0.0154 (9)	−0.0011 (7)	0.0024 (7)	0.0011 (7)

Geometric parameters (Å, º)

O4—C17	1.237 (2)	C5—C9	1.416 (3)
O1—C9	1.390 (2)	C6—C7	1.361 (3)
O1—C10	1.401 (2)	C6—H6	0.9300
O5—C17	1.286 (2)	C7—C8	1.416 (3)
N1—C3	1.324 (3)	C7—H7	0.9300
N1—C5	1.369 (3)	C8—C9	1.365 (3)
N1—H1A	0.904 (19)	C8—H8	0.9300
O3—C16	1.212 (2)	C10—C15	1.388 (3)
O2—C16	1.312 (2)	C10—C11	1.388 (3)
O2—H2A	0.93 (4)	C11—C12	1.379 (3)
C1—C2	1.361 (3)	C11—H11	0.9300
C1—C4	1.412 (3)	C12—C13	1.385 (3)
C1—H1	0.9300	C12—H12	0.9300
C2—C3	1.403 (3)	C13—C14	1.388 (3)
C2—H2	0.9300	C13—H13	0.9300
C3—H3	0.9300	C14—C15	1.402 (3)
C4—C6	1.415 (3)	C14—C16	1.500 (3)
C4—C5	1.420 (3)	C15—C17	1.511 (3)
C9—O1—C10	114.24 (14)	C7—C8—H8	120.1
C3—N1—C5	119.49 (18)	C8—C9—O1	121.25 (18)
C3—N1—H1A	114 (3)	C8—C9—C5	120.59 (18)
C5—N1—H1A	126 (3)	O1—C9—C5	118.12 (17)
C16—O2—H2A	110 (3)	C15—C10—C11	122.27 (18)
C2—C1—C4	120.31 (19)	C15—C10—O1	116.70 (16)
C2—C1—H1	119.8	C11—C10—O1	120.90 (17)
C4—C1—H1	119.8	C12—C11—C10	118.60 (19)
C1—C2—C3	119.16 (19)	C12—C11—H11	120.7
C1—C2—H2	120.4	C10—C11—H11	120.7
C3—C2—H2	120.4	C11—C12—C13	120.61 (19)
N1—C3—C2	122.5 (2)	C11—C12—H12	119.7
N1—C3—H3	118.8	C13—C12—H12	119.7
C2—C3—H3	118.8	C12—C13—C14	120.5 (2)
C1—C4—C6	123.50 (19)	C12—C13—H13	119.8
C1—C4—C5	117.26 (19)	C14—C13—H13	119.8
C6—C4—C5	119.23 (19)	C13—C14—C15	119.92 (18)
N1—C5—C9	119.65 (17)	C13—C14—C16	118.52 (18)
N1—C5—C4	121.24 (18)	C15—C14—C16	121.53 (17)
C9—C5—C4	119.11 (18)	C10—C15—C14	118.12 (17)
C7—C6—C4	119.90 (19)	C10—C15—C17	118.28 (17)

C7—C6—H6	120.1	C14—C15—C17	123.46 (17)
C4—C6—H6	120.1	O3—C16—O2	124.23 (19)
C6—C7—C8	121.31 (19)	O3—C16—C14	123.45 (18)
C6—C7—H7	119.3	O2—C16—C14	112.32 (17)
C8—C7—H7	119.3	O4—C17—O5	123.76 (18)
C9—C8—C7	119.73 (19)	O4—C17—C15	118.82 (17)
C9—C8—H8	120.1	O5—C17—C15	117.37 (17)

C4—C1—C2—C3	−1.3 (3)	C9—O1—C10—C11	49.8 (2)
C5—N1—C3—C2	1.8 (3)	C15—C10—C11—C12	−0.1 (3)
C1—C2—C3—N1	−1.1 (3)	O1—C10—C11—C12	175.68 (19)
C2—C1—C4—C6	−176.32 (19)	C10—C11—C12—C13	−0.3 (4)
C2—C1—C4—C5	3.0 (3)	C11—C12—C13—C14	0.3 (4)
C3—N1—C5—C9	179.36 (18)	C12—C13—C14—C15	0.0 (3)
C3—N1—C5—C4	0.0 (3)	C12—C13—C14—C16	178.0 (2)
C1—C4—C5—N1	−2.3 (3)	C11—C10—C15—C14	0.4 (3)
C6—C4—C5—N1	176.99 (18)	O1—C10—C15—C14	−175.46 (16)
C1—C4—C5—C9	178.31 (17)	C11—C10—C15—C17	176.33 (18)
C6—C4—C5—C9	−2.4 (3)	O1—C10—C15—C17	0.4 (3)
C1—C4—C6—C7	178.45 (19)	C13—C14—C15—C10	−0.4 (3)
C5—C4—C6—C7	−0.8 (3)	C16—C14—C15—C10	−178.36 (17)
C4—C6—C7—C8	2.6 (3)	C13—C14—C15—C17	−176.09 (19)
C6—C7—C8—C9	−1.0 (3)	C16—C14—C15—C17	6.0 (3)
C7—C8—C9—O1	179.88 (18)	C13—C14—C16—O3	−157.0 (2)
C7—C8—C9—C5	−2.3 (3)	C15—C14—C16—O3	20.9 (3)
C10—O1—C9—C8	−101.6 (2)	C13—C14—C16—O2	22.0 (3)
C10—O1—C9—C5	80.5 (2)	C15—C14—C16—O2	−160.01 (18)
N1—C5—C9—C8	−175.44 (18)	C10—C15—C17—O4	−112.9 (2)
C4—C5—C9—C8	3.9 (3)	C14—C15—C17—O4	62.7 (3)
N1—C5—C9—O1	2.5 (3)	C10—C15—C17—O5	64.5 (2)
C4—C5—C9—O1	−178.14 (16)	C14—C15—C17—O5	−119.8 (2)
C9—O1—C10—C15	−134.25 (17)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*A*···O4^{i}	0.93 (4)	1.67 (4)	2.584 (2)	165 (4)
N1—H1*A*···O5	0.90 (2)	1.67 (2)	2.570 (2)	179 (5)

Symmetry code: (i) −*x*+1, *y*−1/2, −*z*+1/2.