Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

4-Amino-2-chlorobenzoic acid

Muneeb Hayat Khan,[a] Islam Ullah Khan[a] and Mehmet Akkurt[b]*

[a]Materials Chemistry Laboratory, Department of Chemistry, GC University, Lahore 54000, Pakistan, and [b]Department of Physics, Faculty of Sciences, Erciyes University, 38039 Kayseri, Turkey
Correspondence e-mail: akkurt@erciyes.edu.tr

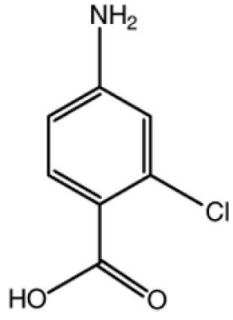
Received 25 July 2011; accepted 30 July 2011

Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.029; wR factor = 0.077; data-to-parameter ratio = 10.5.

The title compound, $C_7H_6ClNO_2$, crystallizes with two roughly planar molecules in the asymmetric unit (r.m.s. deviations = 0.073 and 0.074 Å). The amine H atoms of the two molecules have opposite orientations. In the crystal, molecules are linked into dimers by pairs of O—H···O hydrogen bonds, generating $R_2^2(8)$ loops. N—H···N and N—H···Cl hydrogen bonds link the dimers into a three-dimensional network. The crystal studied was found to be a racemic twin.

Related literature

For an isomer (2-amino-4-chlorobenzoic acid) of the title compound, see: Farag *et al.* (2011). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_7H_6ClNO_2$
M_r = 171.58
Monoclinic, $P2_1$
a = 3.9595 (2) Å
b = 22.6656 (11) Å
c = 8.0285 (4) Å
β = 104.257 (2)°
V = 698.32 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.49 mm^{-1}
T = 296 K
0.28 × 0.13 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer
3009 measured reflections
2295 independent reflections
2197 reflections with $I > 2\sigma(I)$
R_{int} = 0.011

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.077
S = 1.07
2295 reflections
218 parameters
7 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Absolute structure: Flack (1983), 514 Freidel pairs
Flack parameter: 0.50 (6)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H*O1*···O4^{i}	0.82 (3)	1.84 (3)	2.650 (3)	171 (3)
N1—H*N2*···N2	0.86 (3)	2.60 (3)	3.375 (4)	150 (3)
O3—H*O3*···O2^{ii}	0.81 (3)	1.84 (3)	2.650 (3)	173 (3)
N2—H*N3*···Cl2^{iii}	0.86 (3)	2.81 (3)	3.374 (2)	125 (2)
N2—H*N4*···N1^{iv}	0.86 (3)	2.47 (3)	3.302 (4)	163 (2)

Symmetry codes: (i) $-x, y-\frac{1}{2}, -z+1$; (ii) $-x, y+\frac{1}{2}, -z+1$; (iii) $x, y, z+1$; (iv) $x+1, y, z$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); 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* (Farrugia, 1999) and *PLATON* (Spek, 2009).

The authors are grateful to the Higher Education Commission (HEC), Pakistan, for providing funds for the single-crystal XRD facilities at GC University, Lahore.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB6334).

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farag, A. M., Teoh, S. G., Osman, H., Yeap, C. S. & Fun, H.-K. (2011). *Acta Cryst.* E**67**, o37.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supporting information

Acta Cryst. (2011). E**67**, o2247 [doi:10.1107/S1600536811030728]

4-Amino-2-chlorobenzoic acid

Muneeb Hayat Khan, Islam Ullah Khan and Mehmet Akkurt

S1. Comment

The title compound, (I), is used as a starting material for the synthesis of various sulphonamides.

As shown in Fig. 1, the asymmetric unit of the title compound contains two independent molecules. Both have the bond lengths and angles as expected for a molecule of this kind (Farag *et al.*, 2011).

The amine H atoms of the two molecules have opposite orientations. In the crystal, the molecules form dimers *via* intermolecular O—H···O hydrogen bonds, forming a graph-set motif $R^2_2(8)$ (Bernstein *et al.*, 1995; Table 1, Fig. 2). Furthermore, C—H···O, N—H···N and N—H···Cl interactions stabilize the crystal structure.

S2. Experimental

To a 100-ml round bottom flask equipped with a reflux condenser, was placed 0.5 g (2.486 mmol) of 2-chloro-4-amino benzoic acid and 0.447 g m of granulated tin. Then, 30 ml of concentrated HCl in was added in six intervals (5 ml each time with cooling in ice). The reaction is highly exothermic and the reaction mixture is keept under control by keeping it in ice water. When all the HCl was added and the temprature of the reaction mixture was stable, the round bottom flask was placed on water bath for 90 min under reflux.

TLC check after 90 min showed completion of reaction. Reaction mixtures was treated with 60% NaOH solution followed by the addition of NaCl solution and extration with di-ethyl ether.

Diethyl ether was evaporated on rotary evaporator and reddish brown precipates of the required product were obtained. This was recrystallized in methanol to yield reddish brown prisms of (I).

S3. Refinement

The H atoms of the NH_2 and OH groups in the title compound were located in a difference map and refined with the distance restraint N——H = 0.86 (1) and O——H = 0.82 (1) Å; their U_{iso} values were constrained to be $1.5U_{eq}$ of the carrier atom for hydroxyl H atoms and $1.2U_{eq}$ for amine H atoms. The remaining aromatic H atoms were positioned geometrically with C—H = 0.93 Å, and refined using a riding model, with U_{iso}(H) = $1.2U_{eq}$(C). The crystal studied was a racemic twin [Flack parameter = 0.50 (6)].

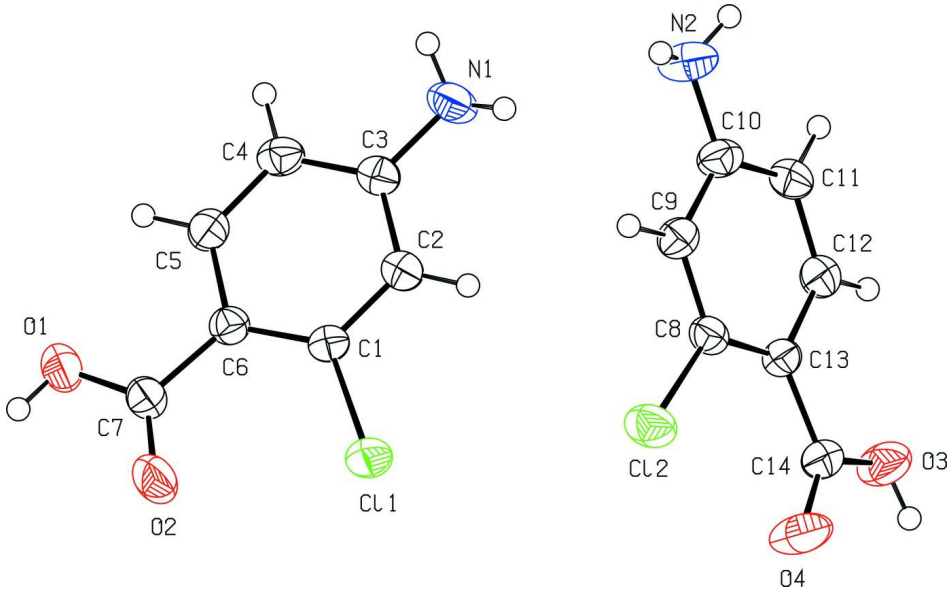


Figure 1

The molecule of the title compound, with displacement ellipsoids for non-H atoms drawn at the 50% probability level.

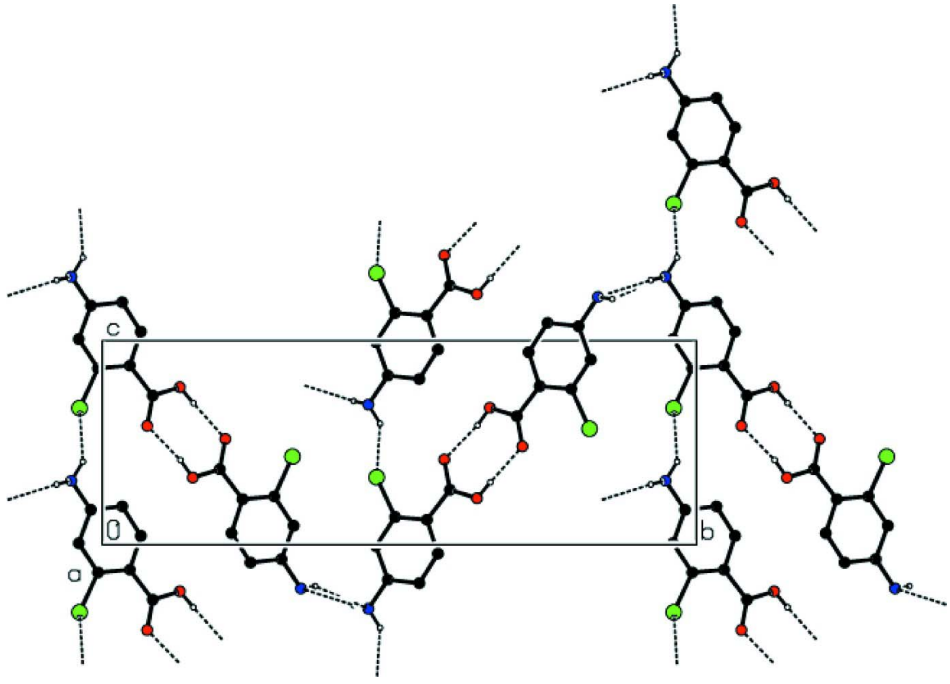


Figure 2

Partial view of the dimers by two O—H···O hydrogen bonds and the packing in the crystal. Hydrogen atoms that not involved in the hydrogen-bonding (dashed lines) have been omitted for clarity.

4-Amino-2-chlorobenzoic acid

Crystal data

$C_7H_6ClNO_2$
$M_r = 171.58$
Monoclinic, $P2_1$
Hall symbol: P 2yb
$a = 3.9595$ (2) Å
$b = 22.6656$ (11) Å
$c = 8.0285$ (4) Å
$\beta = 104.257$ (2)°
$V = 698.32$ (6) Å^3
$Z = 4$
$F(000) = 352$
$D_x = 1.632$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3211 reflections
$\theta = 2.8$–$28.3°$
$\mu = 0.49$ mm^{-1}
$T = 296$ K
Prism, reddish brown
0.28 × 0.13 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed tube
Graphite monochromator
φ and ω scans
3009 measured reflections
2295 independent reflections
2197 reflections with $I > 2\sigma(I)$
$R_{int} = 0.011$
$\theta_{max} = 28.3°$, $\theta_{min} = 2.8°$
$h = -5 \rightarrow 5$
$k = -18 \rightarrow 30$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.077$
$S = 1.07$
2295 reflections
218 parameters
7 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
$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 0.092P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}
Absolute structure: Flack (1983), 514 Freidel pairs
Absolute structure parameter: 0.50 (6)

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses 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 observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs *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}
Cl1	0.23950 (15)	0.81998 (3)	0.56801 (6)	0.0427 (2)
O1	−0.2726 (5)	0.65233 (9)	0.6710 (2)	0.0502 (6)
O2	−0.0913 (6)	0.70711 (10)	0.4820 (2)	0.0577 (7)

N1	0.5447 (5)	0.83421 (11)	1.2139 (3)	0.0431 (7)
C1	0.2193 (5)	0.78948 (10)	0.7631 (3)	0.0277 (5)
C2	0.3803 (5)	0.82200 (12)	0.9065 (3)	0.0316 (5)
C3	0.3834 (5)	0.80158 (10)	1.0704 (3)	0.0306 (6)
C4	0.2106 (6)	0.74934 (11)	1.0871 (3)	0.0349 (6)
C5	0.0515 (6)	0.71758 (11)	0.9432 (3)	0.0338 (6)
C6	0.0508 (5)	0.73617 (10)	0.7767 (3)	0.0294 (6)
C7	−0.1085 (5)	0.69776 (11)	0.6301 (3)	0.0341 (6)
Cl2	0.80948 (15)	0.96180 (3)	0.66956 (7)	0.0442 (2)
O3	0.3027 (6)	1.13060 (8)	0.7718 (2)	0.0511 (6)
O4	0.4834 (7)	1.07555 (10)	0.5823 (2)	0.0581 (7)
N2	1.1098 (6)	0.94780 (12)	1.3131 (3)	0.0491 (8)
C8	0.7883 (5)	0.99282 (10)	0.8643 (3)	0.0293 (5)
C9	0.9466 (5)	0.96044 (12)	1.0074 (3)	0.0321 (5)
C10	0.9516 (5)	0.98080 (11)	1.1714 (3)	0.0349 (6)
C11	0.7808 (6)	1.03355 (12)	1.1881 (3)	0.0356 (6)
C12	0.6218 (6)	1.06497 (11)	1.0437 (3)	0.0347 (6)
C13	0.6238 (5)	1.04643 (10)	0.8776 (3)	0.0295 (6)
C14	0.4640 (5)	1.08498 (11)	0.7309 (3)	0.0336 (6)
HO1	−0.335 (8)	0.6315 (13)	0.585 (3)	0.0640*
H2	0.48700	0.85770	0.89330	0.0380*
HN1	0.607 (7)	0.8126 (13)	1.303 (3)	0.0510*
HN2	0.707 (6)	0.8583 (11)	1.203 (4)	0.0510*
H4	0.20270	0.73590	1.19550	0.0420*
H5	−0.05990	0.68240	0.95690	0.0410*
HO3	0.220 (8)	1.1532 (14)	0.694 (4)	0.0660*
HN3	1.163 (7)	0.9675 (13)	1.407 (3)	0.0530*
HN4	1.262 (6)	0.9232 (11)	1.296 (4)	0.0530*
H9	1.05120	0.92460	0.99420	0.0390*
H11	0.77480	1.04740	1.29640	0.0430*
H12	0.50820	1.09990	1.05690	0.0420*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0554 (3)	0.0449 (3)	0.0274 (2)	−0.0095 (3)	0.0097 (2)	0.0044 (2)
O1	0.0723 (11)	0.0413 (11)	0.0365 (9)	−0.0205 (9)	0.0123 (8)	−0.0066 (8)
O2	0.0901 (14)	0.0528 (12)	0.0312 (8)	−0.0299 (11)	0.0170 (9)	−0.0109 (9)
N1	0.0473 (10)	0.0514 (15)	0.0276 (9)	−0.0042 (9)	0.0033 (8)	−0.0061 (9)
C1	0.0280 (8)	0.0302 (11)	0.0252 (9)	0.0023 (8)	0.0073 (7)	0.0022 (8)
C2	0.0313 (8)	0.0335 (11)	0.0290 (9)	0.0005 (9)	0.0058 (7)	−0.0018 (10)
C3	0.0292 (8)	0.0340 (12)	0.0281 (9)	0.0038 (8)	0.0061 (7)	−0.0020 (8)
C4	0.0407 (10)	0.0384 (13)	0.0267 (10)	0.0060 (9)	0.0103 (9)	0.0025 (9)
C5	0.0384 (10)	0.0301 (12)	0.0332 (11)	−0.0001 (9)	0.0097 (8)	0.0019 (9)
C6	0.0316 (9)	0.0288 (11)	0.0274 (10)	0.0026 (8)	0.0068 (7)	0.0004 (8)
C7	0.0355 (9)	0.0323 (12)	0.0328 (11)	−0.0013 (8)	0.0053 (8)	−0.0034 (9)
Cl2	0.0540 (3)	0.0475 (3)	0.0305 (3)	0.0080 (3)	0.0091 (2)	−0.0060 (3)
O3	0.0750 (12)	0.0388 (11)	0.0384 (9)	0.0208 (10)	0.0121 (8)	0.0072 (9)

O4	0.0890 (14)	0.0535 (12)	0.0324 (9)	0.0303 (11)	0.0163 (9)	0.0112 (9)
N2	0.0545 (11)	0.0603 (17)	0.0320 (10)	0.0120 (11)	0.0095 (9)	0.0132 (11)
C8	0.0304 (8)	0.0325 (11)	0.0253 (9)	−0.0041 (8)	0.0073 (7)	−0.0026 (9)
C9	0.0319 (8)	0.0304 (10)	0.0335 (9)	0.0030 (9)	0.0072 (7)	0.0026 (10)
C10	0.0322 (9)	0.0419 (13)	0.0298 (10)	−0.0042 (9)	0.0062 (8)	0.0083 (9)
C11	0.0419 (10)	0.0379 (13)	0.0266 (10)	−0.0022 (9)	0.0077 (9)	−0.0037 (9)
C12	0.0421 (10)	0.0308 (11)	0.0314 (10)	−0.0001 (9)	0.0094 (8)	−0.0029 (9)
C13	0.0310 (9)	0.0290 (11)	0.0278 (10)	−0.0019 (8)	0.0057 (8)	0.0033 (8)
C14	0.0391 (10)	0.0322 (12)	0.0291 (10)	0.0004 (9)	0.0078 (8)	0.0039 (9)

Geometric parameters (Å, º)

Cl1—C1	1.732 (2)	C3—C4	1.390 (3)
Cl2—C8	1.735 (2)	C4—C5	1.375 (3)
O1—C7	1.302 (3)	C5—C6	1.401 (3)
O2—C7	1.226 (3)	C6—C7	1.475 (3)
O1—HO1	0.82 (3)	C2—H2	0.9300
O3—C14	1.299 (3)	C4—H4	0.9300
O4—C14	1.233 (3)	C5—H5	0.9300
O3—HO3	0.81 (3)	C8—C9	1.377 (3)
N1—C3	1.386 (3)	C8—C13	1.395 (3)
N1—HN1	0.85 (3)	C9—C10	1.391 (3)
N1—HN2	0.86 (3)	C10—C11	1.396 (4)
N2—C10	1.377 (3)	C11—C12	1.374 (3)
N2—HN4	0.86 (3)	C12—C13	1.400 (3)
N2—HN3	0.86 (3)	C13—C14	1.478 (3)
C1—C6	1.398 (3)	C9—H9	0.9300
C1—C2	1.383 (3)	C11—H11	0.9300
C2—C3	1.392 (3)	C12—H12	0.9300
C7—O1—HO1	108 (2)	C5—C4—H4	120.00
C14—O3—HO3	116 (2)	C3—C4—H4	120.00
C3—N1—HN1	111.7 (19)	C4—C5—H5	119.00
HN1—N1—HN2	112 (3)	C6—C5—H5	119.00
C3—N1—HN2	117 (2)	C9—C8—C13	121.7 (2)
C10—N2—HN4	115 (2)	Cl2—C8—C9	115.01 (18)
HN3—N2—HN4	117 (3)	Cl2—C8—C13	123.30 (18)
C10—N2—HN3	114.0 (19)	C8—C9—C10	120.7 (2)
Cl1—C1—C2	115.19 (18)	N2—C10—C11	121.2 (2)
Cl1—C1—C6	123.03 (18)	C9—C10—C11	118.7 (2)
C2—C1—C6	121.8 (2)	N2—C10—C9	120.0 (2)
C1—C2—C3	120.3 (2)	C10—C11—C12	119.7 (2)
C2—C3—C4	119.0 (2)	C11—C12—C13	122.6 (2)
N1—C3—C4	120.8 (2)	C8—C13—C12	116.5 (2)
N1—C3—C2	120.2 (2)	C8—C13—C14	124.8 (2)
C3—C4—C5	120.0 (2)	C12—C13—C14	118.7 (2)
C4—C5—C6	122.5 (2)	O3—C14—C13	114.2 (2)
C5—C6—C7	118.9 (2)	O4—C14—C13	123.5 (2)

C1—C6—C7	124.5 (2)	O3—C14—O4	122.3 (2)
C1—C6—C5	116.5 (2)	C8—C9—H9	120.00
O2—C7—C6	123.8 (2)	C10—C9—H9	120.00
O1—C7—C6	114.0 (2)	C10—C11—H11	120.00
O1—C7—O2	122.1 (2)	C12—C11—H11	120.00
C1—C2—H2	120.00	C11—C12—H12	119.00
C3—C2—H2	120.00	C13—C12—H12	119.00

Cl1—C1—C2—C3	−179.44 (17)	Cl2—C8—C9—C10	179.22 (17)
C6—C1—C2—C3	1.1 (3)	C13—C8—C9—C10	−0.9 (3)
Cl1—C1—C6—C5	−179.00 (17)	Cl2—C8—C13—C12	178.57 (17)
Cl1—C1—C6—C7	4.2 (3)	Cl2—C8—C13—C14	−3.3 (3)
C2—C1—C6—C5	0.4 (3)	C9—C8—C13—C12	−1.3 (3)
C2—C1—C6—C7	−176.4 (2)	C9—C8—C13—C14	176.8 (2)
C1—C2—C3—N1	−180.0 (2)	C8—C9—C10—N2	179.8 (2)
C1—C2—C3—C4	−2.5 (3)	C8—C9—C10—C11	2.6 (3)
N1—C3—C4—C5	179.9 (2)	N2—C10—C11—C12	−179.2 (2)
C2—C3—C4—C5	2.5 (3)	C9—C10—C11—C12	−2.0 (3)
C3—C4—C5—C6	−1.0 (4)	C10—C11—C12—C13	−0.2 (4)
C4—C5—C6—C1	−0.5 (3)	C11—C12—C13—C8	1.9 (3)
C4—C5—C6—C7	176.5 (2)	C11—C12—C13—C14	−176.4 (2)
C1—C6—C7—O1	−175.4 (2)	C8—C13—C14—O3	175.1 (2)
C1—C6—C7—O2	4.4 (4)	C8—C13—C14—O4	−5.7 (4)
C5—C6—C7—O1	7.8 (3)	C12—C13—C14—O3	−6.8 (3)
C5—C6—C7—O2	−172.3 (2)	C12—C13—C14—O4	172.4 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H*O*1···O4^{i}	0.82 (3)	1.84 (3)	2.650 (3)	171 (3)
N1—H*N*2···N2	0.86 (3)	2.60 (3)	3.375 (4)	150 (3)
O3—H*O*3···O2^{ii}	0.81 (3)	1.84 (3)	2.650 (3)	173 (3)
N2—H*N*3···Cl2^{iii}	0.86 (3)	2.81 (3)	3.374 (2)	125 (2)
N2—H*N*4···N1^{iv}	0.86 (3)	2.47 (3)	3.302 (4)	163 (2)

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