Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

OPEN ACCESS

ISSN 2056-9890

Crystal structure of 3,4-dichloroanilinium hydrogen phthalate

Muhammad Shahid,[a] Muhammad Nawaz Tahir,[b]* Muhammad Salim[a] and Munawar Ali Munawar[a]

[a]Department of Chemistry, University of the Punjab, Lahore, Punjab, Pakistan, and [b]Department of Physics, University of Sargodha, Sargodha, Punjab, Pakistan. *Correspondence e-mail: dmntahir_uos@yahoo.com

Received 9 May 2015; accepted 28 May 2015

Edited by M. Gdaniec, Adam Mickiewicz University, Poland

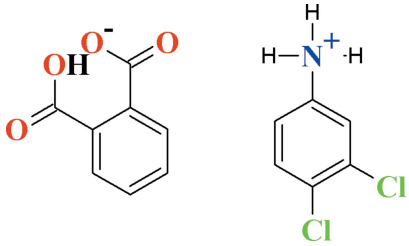
In the title salt, $C_6H_6Cl_2N^+\cdot C_8H_5O_4^-$, the carboxylic acid and carboxylate groups of the anion form dihedral angles of 20.79 (19) and 74.76 (14)°, respectively, with the plane of the benzene ring. In the crystal, molecules are assembled into a two-dimensional polymeric network parallel to (100) *via* N—H···O and O—H···O hydrogen bonds. In addition, within the layer, there are π–π stacking interactions between the benzene rings of the cation and the anion [centroid–centroid distance = 3.6794 (17) Å]. A weak C—H···O interaction is also observed.

Keywords: crystal structure; hydrogen phthalate; hydrogen bonding; π–π stacking interactions.

CCDC reference: 1403731

1. Related literature

For related structures, see: Jagan & Sivakumar (2009, 2011); Kozma *et al.* (1994); Liang *et al.* (2011); Liu (2012).



2. Experimental

2.1. Crystal data

$C_6H_6Cl_2N^+\cdot C_8H_5O_4^-$
M_r = 328.14
Monoclinic, $C2/c$
a = 29.694 (5) Å
b = 7.7536 (13) Å
c = 13.125 (2) Å
β = 98.673 (12)°
V = 2987.3 (9) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.45 mm^{-1}
T = 296 K
0.34 × 0.28 × 0.16 mm

2.2. Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.860, T_{max} = 0.935
11652 measured reflections
3248 independent reflections
1849 reflections with $I > 2\sigma(I)$
R_{int} = 0.051

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.133
S = 1.02
3248 reflections
192 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O4^{i}	0.82	1.77	2.583 (2)	171
N1—H1A···O4	0.89	1.98	2.848 (3)	164
N1—H1B···O3^{ii}	0.89	1.85	2.713 (3)	163
N1—H1C···O3^{i}	0.89	1.90	2.774 (3)	165
C13—H13···O4^{iii}	0.93	2.54	3.328 (4)	143

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON*.

Acknowledgements

The authors acknowledge the provision of funds for the purchase of the diffractometer and encouragement by Dr Muhammad Akram Chaudhary, Vice Chancellor, University of Sargodha, Pakistan.

Supporting information for this paper is available from the IUCr electronic archives (Reference: GK2633).

References

Bruker (2005). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Jagan, R. & Sivakumar, K. (2009). *Acta Cryst.* C**65**, o414–o418.
Jagan, R. & Sivakumar, K. (2011). *Acta Cryst.* C**67**, o373–o377.
Kozma, D., Bocskei, Z., Simon, K. & Fogassy, E. (1994). *J. Chem. Soc. Perkin Trans. 2*, pp. 1883–1886.
Liang, Z. P. (2011). *Acta Cryst.* E**67**, o1430.
Liu, M.-L. (2012). *Acta Cryst.* E**68**, o228.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supporting information

Acta Cryst. (2015). E**71**, o446 [doi:10.1107/S2056989015010300]

Crystal structure of 3,4-dichloroanilinium hydrogen phthalate

Muhammad Shahid, Muhammad Nawaz Tahir, Muhammad Salim and Munawar Ali Munawar

S1. Comment

The crystal structures of 4-bromoanilinium hydrogen phthalate (Liang, 2011), (*R*,*S*)-*α*-phenylethylammonium hydrogen phthalate (Kozma *et al.*, 1994), 4-chloroanilinium hydrogen phthalate (Jagan & Sivakumar, 2009), 3-hydroxyanilinium hydrogen phthalate (Jagan & Sivakumar, 2009), 2-hydroxyanilinium hydrogen phthalate (Jagan & Sivakumar, 2009), 3-Methylanilinium 2-carboxybenzoate (Liu, 2012) and 4-ethoxyanilinium 2- carboxybenzoate (Jagan & Sivakumar, 2011) have been published which are related to the title compound (I, Fig. 1). (I) is synthesized for the study of co-crystallization.

In (I) the benzene ring A (C2—C7) of the phathalate anion is planar with r.m.s. deviation of 0.0024 Å. The carboxylic B (C1/O1/O2) and carboxylate C (C8/O3/O4) groups are oriented at a dihedral angle of 20.79 (19)° and 74.76 (14)°, respectively, with the parent benzene ring A. The molecules form a two dimensional polymeric network parallel to (100) due to N—H···O and O—H···O hydrogen bonds (Table 1, Fig.2). There exist $\pi\cdots\pi$ interaction between *Cg1*1···*Cg2*1^{i} [i = *x*, *y*, *z*] with centroid-centroid distance of 3.6794 (17) Å, where *Cg1* and *Cg2* are the centroids of the benzene rings A and E (C9—C14). The topology of two-dimensional hydrogen-bond network in the title compound is the same as in 4-chloro-anilinium salt (Jagan & Sivakumar, 2009).

S2. Experimental

Equimolar quantities of phathalic acid (0.831 g, 5 mmol) and 3,4-dichloroaniline (0.810 g, 5 mmol) were refluxed in 20 ml of methanol for 2 h. The solution was kept at room temperature and colorless plates appeared after two days (m.p. 422–423 K).

S3. Refinement

The H atoms were positioned geometrically (C–H = 0.93 Å, N–H = 0.89 Å, O—H = 0.82 Å) and refined as riding with U_{iso}(H) = xU_{eq} (C, N, O), where x = 1.5 for NH_3 and hydroxy and x =1.2 for aromatic H-atoms.

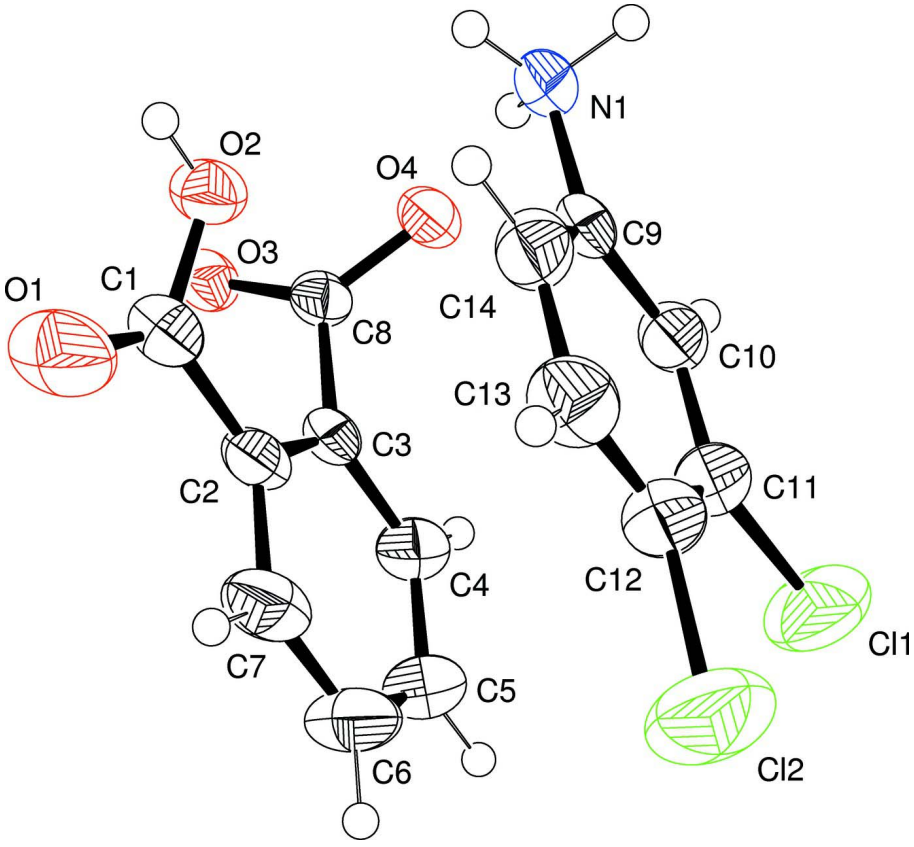


Figure 1

View of the title compound with the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. H-atoms are shown as small circles of arbitrary radii.

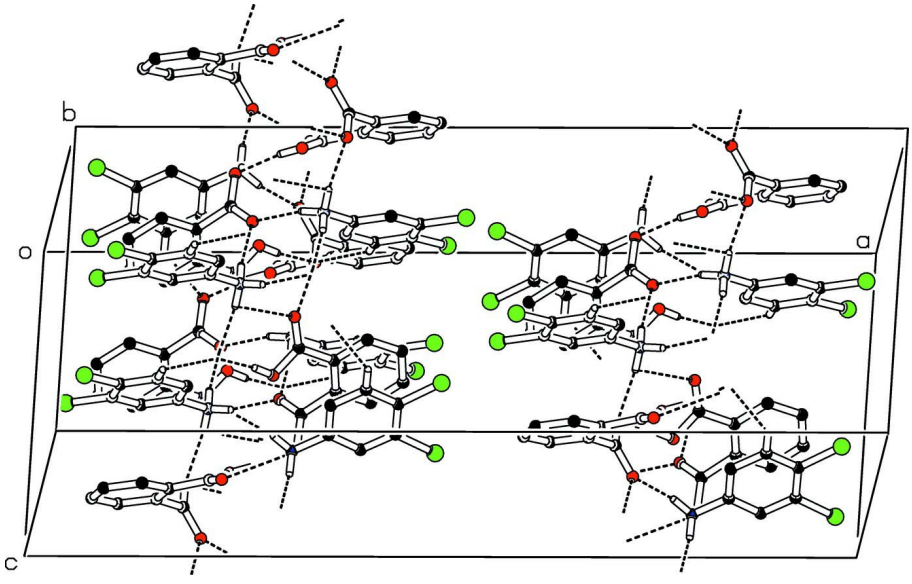


Figure 2

The packing (*PLATON*; Spek, 2009) of two-dimensional (100) polymeric networks.

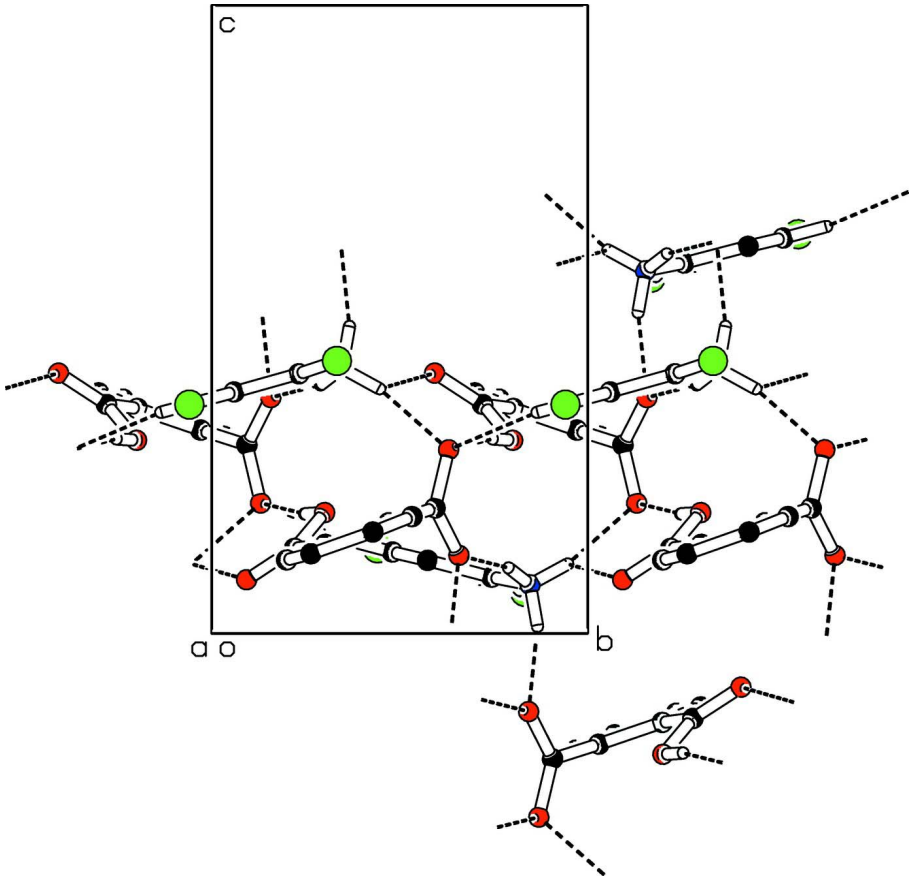


Figure 3

Hydrogen bonds within (100) layer.

3,4-Dichloroanilinium 2-carboxybenzoate

Crystal data

$C_6H_6Cl_2N^+·C_8H_5O_4^-$
M_r = 328.14
Monoclinic, *C*2/*c*
a = 29.694 (5) Å
b = 7.7536 (13) Å
c = 13.125 (2) Å
β = 98.673 (12)°
V = 2987.3 (9) Å^3
Z = 8
F(000) = 1344
D_x = 1.459 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 1849 reflections
θ = 2.8–27.0°
μ = 0.45 mm^{-1}
T = 296 K
Plate, colorless
0.34 × 0.28 × 0.16 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 7.80 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.860, T_{max} = 0.935
11652 measured reflections
3248 independent reflections
1849 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 27.0°, θ_{min} = 2.8°
h = −37→37
k = −9→9
l = −15→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.133$
$S = 1.02$
3248 reflections
192 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0503P)^2 + 2.3478P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.21968 (8)	0.5928 (3)	0.41451 (18)	0.0727 (7)
O2	0.23502 (6)	0.8002 (2)	0.30759 (13)	0.0427 (5)
H2	0.2590	0.7471	0.3096	0.064*
O3	0.21509 (6)	1.1573 (2)	0.37561 (12)	0.0417 (5)
O4	0.19151 (5)	1.1301 (2)	0.20757 (12)	0.0377 (4)
C1	0.20865 (9)	0.7204 (4)	0.3646 (2)	0.0416 (7)
C2	0.16278 (8)	0.8021 (4)	0.35827 (18)	0.0379 (6)
C3	0.15350 (8)	0.9708 (4)	0.32373 (16)	0.0340 (6)
C4	0.10931 (9)	1.0324 (4)	0.3140 (2)	0.0476 (7)
H4	0.1029	1.1443	0.2907	0.057*
C5	0.07466 (10)	0.9285 (5)	0.3386 (2)	0.0575 (9)
H5	0.0451	0.9709	0.3316	0.069*
C6	0.08358 (10)	0.7643 (5)	0.3731 (2)	0.0654 (10)
H6	0.0601	0.6957	0.3900	0.078*
C7	0.12732 (10)	0.6995 (4)	0.3830 (2)	0.0533 (8)
H7	0.1332	0.5872	0.4063	0.064*
C8	0.18979 (8)	1.0937 (3)	0.30026 (18)	0.0324 (6)
Cl1	0.03331 (3)	0.83295 (14)	0.06616 (8)	0.0831 (4)
Cl2	0.04230 (3)	0.44073 (16)	0.13559 (9)	0.0970 (4)
N1	0.20521 (7)	0.8466 (3)	0.07778 (14)	0.0374 (5)
H1A	0.2041	0.9466	0.1106	0.056*
H1B	0.2057	0.8662	0.0111	0.056*
H1C	0.2303	0.7895	0.1043	0.056*
C9	0.16540 (8)	0.7446 (4)	0.08969 (16)	0.0334 (6)
C10	0.12353 (8)	0.8247 (4)	0.07404 (18)	0.0396 (6)

H10	0.1211	0.9403	0.0551	0.047*
C11	0.08537 (9)	0.7318 (4)	0.0867 (2)	0.0496 (8)
C12	0.08933 (9)	0.5597 (5)	0.1155 (2)	0.0530 (8)
C13	0.13137 (10)	0.4807 (4)	0.1296 (2)	0.0526 (8)
H13	0.1339	0.3649	0.1480	0.063*
C14	0.16975 (9)	0.5740 (4)	0.1163 (2)	0.0440 (7)
H14	0.1982	0.5214	0.1253	0.053*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0725 (15)	0.0638 (16)	0.0883 (17)	0.0207 (12)	0.0337 (12)	0.0404 (14)
O2	0.0415 (10)	0.0463 (12)	0.0432 (10)	0.0097 (9)	0.0159 (9)	0.0077 (9)
O3	0.0421 (10)	0.0544 (13)	0.0293 (9)	−0.0072 (9)	0.0077 (8)	−0.0073 (9)
O4	0.0425 (10)	0.0423 (12)	0.0297 (9)	−0.0029 (8)	0.0099 (7)	0.0012 (8)
C1	0.0494 (16)	0.0422 (18)	0.0352 (14)	0.0016 (14)	0.0130 (12)	0.0024 (13)
C2	0.0431 (15)	0.0443 (17)	0.0289 (13)	−0.0027 (13)	0.0134 (11)	0.0022 (12)
C3	0.0350 (13)	0.0466 (18)	0.0215 (12)	−0.0019 (12)	0.0081 (10)	−0.0032 (11)
C4	0.0389 (15)	0.060 (2)	0.0461 (16)	0.0032 (14)	0.0129 (12)	0.0022 (14)
C5	0.0377 (16)	0.079 (3)	0.0589 (19)	−0.0002 (16)	0.0161 (14)	0.0029 (18)
C6	0.0465 (18)	0.087 (3)	0.067 (2)	−0.0160 (19)	0.0239 (15)	0.001 (2)
C7	0.0604 (19)	0.054 (2)	0.0493 (17)	−0.0114 (16)	0.0211 (14)	0.0061 (15)
C8	0.0333 (13)	0.0358 (15)	0.0297 (13)	0.0046 (11)	0.0103 (10)	−0.0041 (11)
Cl1	0.0388 (4)	0.1064 (9)	0.1041 (7)	0.0154 (5)	0.0106 (4)	0.0168 (6)
Cl2	0.0625 (6)	0.1052 (9)	0.1236 (9)	−0.0304 (6)	0.0149 (5)	0.0246 (7)
N1	0.0389 (12)	0.0462 (15)	0.0275 (10)	0.0019 (10)	0.0061 (9)	−0.0017 (10)
C9	0.0376 (14)	0.0429 (17)	0.0205 (11)	−0.0011 (12)	0.0069 (10)	−0.0035 (11)
C10	0.0409 (15)	0.0439 (18)	0.0344 (13)	0.0058 (13)	0.0074 (11)	0.0020 (12)
C11	0.0374 (15)	0.067 (2)	0.0450 (16)	0.0050 (15)	0.0073 (12)	0.0014 (15)
C12	0.0451 (17)	0.065 (2)	0.0493 (17)	−0.0126 (16)	0.0076 (13)	0.0005 (16)
C13	0.060 (2)	0.0458 (19)	0.0521 (17)	−0.0053 (16)	0.0104 (14)	0.0020 (15)
C14	0.0440 (16)	0.0467 (19)	0.0412 (15)	0.0064 (14)	0.0057 (12)	−0.0002 (13)

Geometric parameters (Å, º)

O1—C1	1.204 (3)	C7—H7	0.9300
O2—C1	1.316 (3)	Cl1—C11	1.718 (3)
O2—H2	0.8200	Cl2—C12	1.726 (3)
O3—C8	1.250 (3)	N1—C9	1.450 (3)
O4—C8	1.257 (3)	N1—H1A	0.8900
C1—C2	1.493 (4)	N1—H1B	0.8900
C2—C7	1.396 (4)	N1—H1C	0.8900
C2—C3	1.398 (4)	C9—C14	1.369 (4)
C3—C4	1.384 (3)	C9—C10	1.377 (3)
C3—C8	1.505 (3)	C10—C11	1.374 (4)
C4—C5	1.383 (4)	C10—H10	0.9300
C4—H4	0.9300	C11—C12	1.388 (5)
C5—C6	1.364 (5)	C12—C13	1.378 (4)

C5—H5	0.9300	C13—C14	1.383 (4)
C6—C7	1.380 (4)	C13—H13	0.9300
C6—H6	0.9300	C14—H14	0.9300
C1—O2—H2	109.5	C9—N1—H1A	109.5
O1—C1—O2	124.0 (3)	C9—N1—H1B	109.5
O1—C1—C2	123.3 (2)	H1A—N1—H1B	109.5
O2—C1—C2	112.6 (2)	C9—N1—H1C	109.5
C7—C2—C3	119.3 (3)	H1A—N1—H1C	109.5
C7—C2—C1	117.3 (3)	H1B—N1—H1C	109.5
C3—C2—C1	123.2 (2)	C14—C9—C10	121.5 (2)
C4—C3—C2	119.4 (2)	C14—C9—N1	120.5 (2)
C4—C3—C8	117.4 (3)	C10—C9—N1	118.1 (2)
C2—C3—C8	123.1 (2)	C11—C10—C9	119.2 (3)
C5—C4—C3	120.4 (3)	C11—C10—H10	120.4
C5—C4—H4	119.8	C9—C10—H10	120.4
C3—C4—H4	119.8	C10—C11—C12	120.0 (3)
C6—C5—C4	120.5 (3)	C10—C11—Cl1	118.7 (3)
C6—C5—H5	119.8	C12—C11—Cl1	121.3 (2)
C4—C5—H5	119.8	C13—C12—C11	120.1 (3)
C5—C6—C7	120.3 (3)	C13—C12—Cl2	118.7 (3)
C5—C6—H6	119.9	C11—C12—Cl2	121.2 (2)
C7—C6—H6	119.9	C12—C13—C14	119.9 (3)
C6—C7—C2	120.2 (3)	C12—C13—H13	120.1
C6—C7—H7	119.9	C14—C13—H13	120.1
C2—C7—H7	119.9	C9—C14—C13	119.3 (3)
O3—C8—O4	124.7 (2)	C9—C14—H14	120.3
O3—C8—C3	116.8 (2)	C13—C14—H14	120.3
O4—C8—C3	118.4 (2)		
O1—C1—C2—C7	−20.8 (4)	C2—C3—C8—O3	−74.5 (3)
O2—C1—C2—C7	157.5 (2)	C4—C3—C8—O4	−74.4 (3)
O1—C1—C2—C3	162.9 (3)	C2—C3—C8—O4	108.1 (3)
O2—C1—C2—C3	−18.9 (4)	C14—C9—C10—C11	0.8 (4)
C7—C2—C3—C4	−0.5 (4)	N1—C9—C10—C11	−178.8 (2)
C1—C2—C3—C4	175.8 (2)	C9—C10—C11—C12	0.4 (4)
C7—C2—C3—C8	176.9 (2)	C9—C10—C11—Cl1	−179.63 (18)
C1—C2—C3—C8	−6.8 (4)	C10—C11—C12—C13	−1.3 (4)
C2—C3—C4—C5	0.3 (4)	Cl1—C11—C12—C13	178.8 (2)
C8—C3—C4—C5	−177.2 (2)	C10—C11—C12—Cl2	178.2 (2)
C3—C4—C5—C6	0.2 (4)	Cl1—C11—C12—Cl2	−1.8 (4)
C4—C5—C6—C7	−0.5 (5)	C11—C12—C13—C14	0.9 (4)
C5—C6—C7—C2	0.3 (5)	Cl2—C12—C13—C14	−178.6 (2)
C3—C2—C7—C6	0.2 (4)	C10—C9—C14—C13	−1.2 (4)
C1—C2—C7—C6	−176.3 (3)	N1—C9—C14—C13	178.5 (2)
C4—C3—C8—O3	102.9 (3)	C12—C13—C14—C9	0.3 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O4^{i}	0.82	1.77	2.583 (2)	171
N1—H1*A*···O4	0.89	1.98	2.848 (3)	164
N1—H1*B*···O3^{ii}	0.89	1.85	2.713 (3)	163
N1—H1*C*···O3^{i}	0.89	1.90	2.774 (3)	165
C13—H13···O4^{iii}	0.93	2.54	3.328 (4)	143

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