

# Crystal structures and hydrogen bonding in the morpholinium salts of four phenoxyacetic acid analogues

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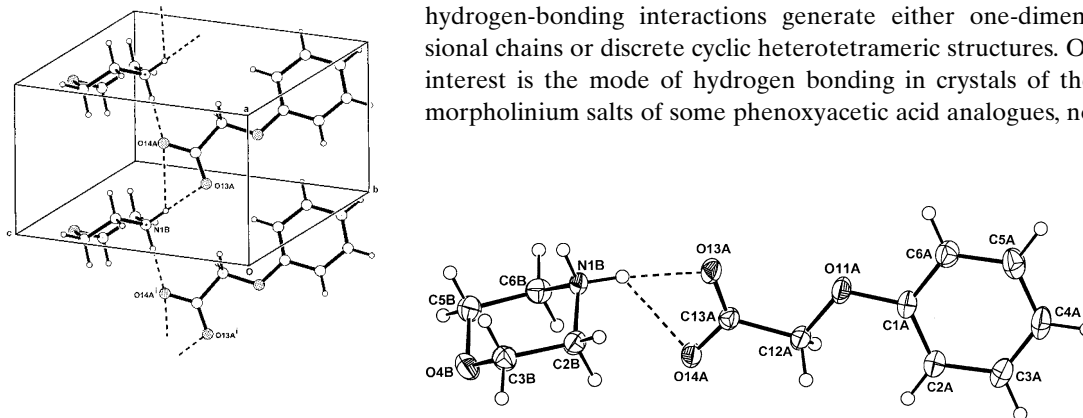
**Supporting information:** this article has supporting information at journals.iucr.org/e

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The anhydrous salts morpholinium (tetrahydro-2-*H*-1,4-oxazin-4-ium) phenoxyacetate, C<sub>4</sub>H<sub>10</sub>NO<sup>+</sup>·C<sub>8</sub>H<sub>7</sub>O<sub>3</sub><sup>-</sup>, (I), morpholinium (4-fluorophenoxy)acetate, C<sub>4</sub>H<sub>10</sub>NO<sup>+</sup>·C<sub>8</sub>H<sub>6</sub>FO<sub>3</sub><sup>-</sup>, (II), and isomeric morpholinium (3,5-dichlorophenoxy)acetate (3,5-D), (III), and morpholinium (2,4-dichlorophenoxy)acetic acid (2,4-D), C<sub>4</sub>H<sub>10</sub>NO<sup>+</sup>·C<sub>8</sub>H<sub>5</sub>Cl<sub>2</sub>O<sub>3</sub><sup>-</sup>, (IV), have been determined and their hydrogen-bonded structures are described. In the crystals of (I), (III) and (IV), one of the the aminium H atoms is involved in a three-centre asymmetric cation–anion N–H···O,O'  $R_1^2(4)$  hydrogen-bonding interaction with the two carboxyl O-atom acceptors of the anion. With the structure of (II), the primary N–H···O interaction is linear. In the structures of (I), (II) and (III), the second N–H···O<sub>carboxyl</sub> hydrogen bond generates one-dimensional chain structures extending in all cases along [100]. With (IV), the ion pairs are linked though inversion-related N–H···O hydrogen bonds [graph set  $R_2^2(8)$ ], giving a cyclic heterotetrameric structure.

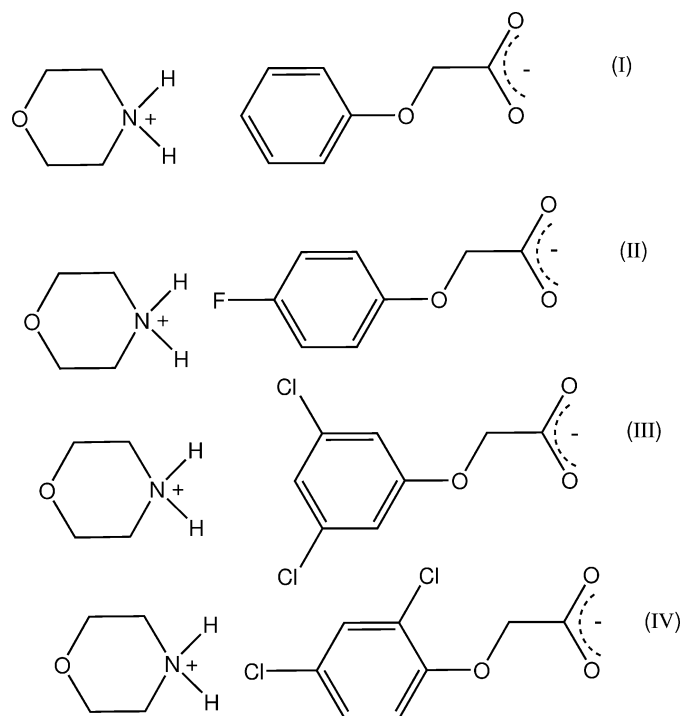
## 1. Chemical context

Morpholine (tetrahydro-2-*H*-1,4-oxazine) is an moderately strong base ( $pK_a = 8.33$ ) and forms salts with a number of organic acids, some having medical applications, *e.g.* the salicylate (retarcyl, depasol), used as an analgesic, an antipyretic and an anti-inflammatory agent (O'Neil, 2001). The crystal structures of a number of these morpholinate compounds have been reported, some examples of salts with substituted benzoic acids being the 4-aminosalicylate (André *et al.*, 2009), and a series of isomeric chloronitrobenzoates (2,4-, 2,5-, 4,2-, 4,3- and 5,2-) (Ishida *et al.*, 2001*a,b,c*). In these, cation–anion hydrogen-bonding interactions generate either one-dimensional chains or discrete cyclic heterotetrameric structures. Of interest is the mode of hydrogen bonding in crystals of the morpholinium salts of some phenoxyacetic acid analogues, no



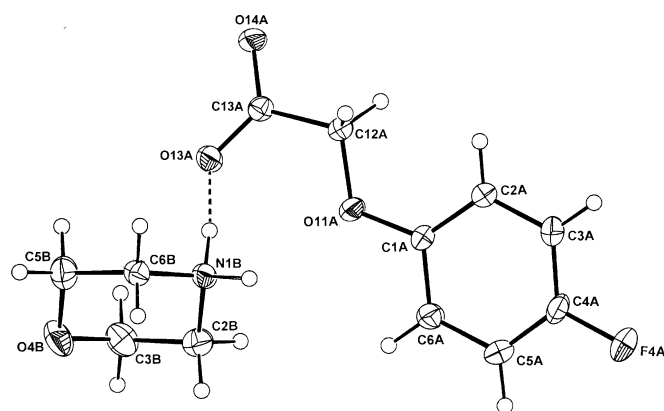
**Figure 1**  
The atom-numbering scheme and the molecular conformation of the morpholinium cation (B) and the phenoxyacetate anion (A) in (I), with displacement ellipsoids drawn at the 40% probability level. The cation–anion hydrogen bonds are shown as dashed lines.

structures of which have been reported previously. The reaction of morpholine with phenoxyacetic acid (PAA), (4-fluorophenoxy)acetic acid (PFPA) and with the two isomeric homologues, (3,5-dichlorophenoxy)acetic acid (3,5-D) and the herbicidally active (2,4-dichlorophenoxy)acetic acid (2,4-D) (Zumdahl, 2010), gave the anhydrous salts (I)–(IV), respectively. Their structures and hydrogen-bonding modes are reported on herein.

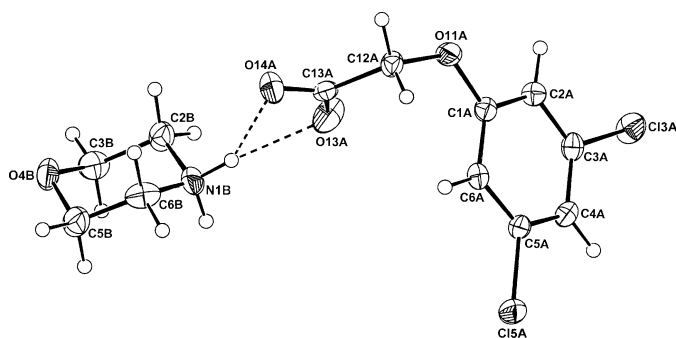


## 2. Structural commentary

The asymmetric units of (I)–(IV) comprise a morpholinium cation (*B*) and a phenoxyacetate anion (*A*) in (I) (Fig. 1), a (4-fluorophenoxy)acetate anion (*A*) in (II) (Fig. 2), a 3,5-dichlorophenoxyacetate anion (*A*) in (III) (Fig. 3) and a (2,4-

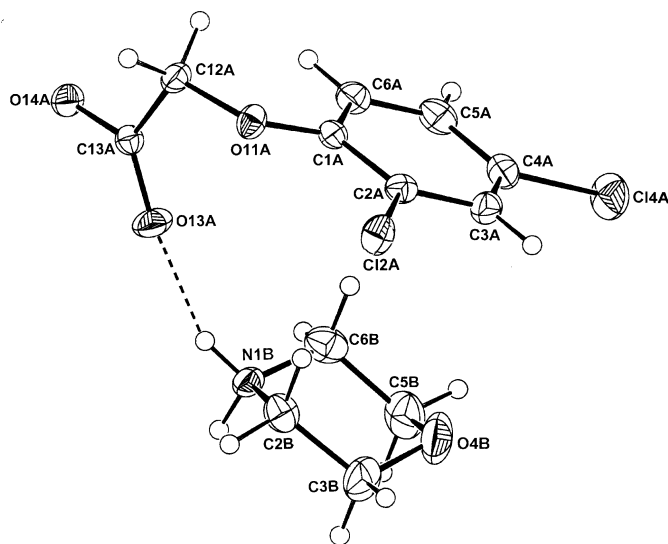


**Figure 2**  
The atom-numbering scheme and the molecular conformation of the morpholinium cation (*B*) and the (4-fluorophenoxy)acetate anion (*A*) in (II), with displacement ellipsoids drawn at the 40% probability level. The cation–anion hydrogen bond is shown as a dashed line.



**Figure 3**  
The atom-numbering scheme and the molecular conformation of the morpholinium cation (*B*) and the 3,5-D anion (*A*) in (III), with displacement ellipsoids drawn at the 40% probability level. The cation–anion hydrogen bonds are shown as dashed lines.

dichlorophenoxy)acetate anion (*A*) in (IV) (Fig. 4). The conformation of the oxoacetate side chains in the anions of (I) and (II) are essentially planar, with the defining torsion angle  $C1A-O11A-C12A-C13A = 176.75(14)$  and  $176.53(14)^\circ$ , respectively. This *antiperiplanar* ( $180 \pm 30^\circ$ ) conformation is similar to those of the parent acids PAA ( $-175.1^\circ$ ; Kennard *et al.*, 1982), PFPA [ $176.0(6)^\circ$ ; Smith *et al.*, 1992] and their proton-transfer salts, *e.g.* the ammonium salts of PAA [ $-177.48(18)^\circ$ ] and PFPA [ $-178.98(17)^\circ$ ] (Smith, 2014). However, with the 3,5-D and 2,4-D salts, the side-chain conformations are both *synclinal* ( $90 \pm 30^\circ$ ) [ $-76.5(2)^\circ$  in (III) and  $72.91(19)^\circ$  in (IV)], similar to that in the parent acid 2,4-D ( $75.2^\circ$ ; Smith *et al.*, 1976), in the tryptaminium salt of 2,4-D [ $81.2(6)^\circ$ ; Smith & Lynch, 2015a] and in the 2:1 salt-adduct of 3,5-D with 4,4'-bipyridine [ $-71.6(3)^\circ$ ; Lynch *et al.*, 2003]. However, in the tryptaminium salt of 3,5-D (Smith & Lynch, 2015b), the ammonium salts of both 2,4-D (Liu *et al.*, 2009) and 3,5-D (Smith, 2014), the *antiperiplanar* conformation is



**Figure 4**  
The atom-numbering scheme and the molecular conformation of the morpholinium cation (*B*) and the 2,4-D anion (*A*) in (IV), with displacement ellipsoids drawn at the 40% probability level. The cation–anion hydrogen bonds are shown as dashed lines.

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

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1 <i>B</i> –H11 <i>B</i> ···O13 <i>A</i>	0.92 (2)	1.83 (2)	2.7366 (18)	169 (2)
N1 <i>B</i> –H11 <i>B</i> ···O14 <i>A</i>	0.92 (2)	2.57 (2)	3.1655 (17)	123 (1)
N1 <i>B</i> –H12 <i>B</i> ···O14 <i>A</i> <sup>i</sup>	0.95 (1)	1.76 (1)	2.7061 (17)	176 (1)
C4 <i>A</i> –H4 <i>A</i> ···O4 <i>B</i> <sup>ii</sup>	0.95	2.59	3.447 (2)	151
C6 <i>B</i> –H62 <i>B</i> ···O13 <i>A</i> <sup>iii</sup>	0.99	2.39	3.148 (2)	133

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

**Table 2**  
Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1 <i>B</i> –H11 <i>B</i> ···O14 <i>A</i> <sup>i</sup>	0.97 (2)	1.76 (2)	2.725 (2)	175 (2)
N1 <i>B</i> –H12 <i>B</i> ···O13 <i>A</i>	0.94 (2)	1.80 (2)	2.718 (2)	165 (2)
C6 <i>B</i> –H61 <i>B</i> ···O14 <i>A</i> <sup>ii</sup>	0.99	2.38	3.188 (2)	138

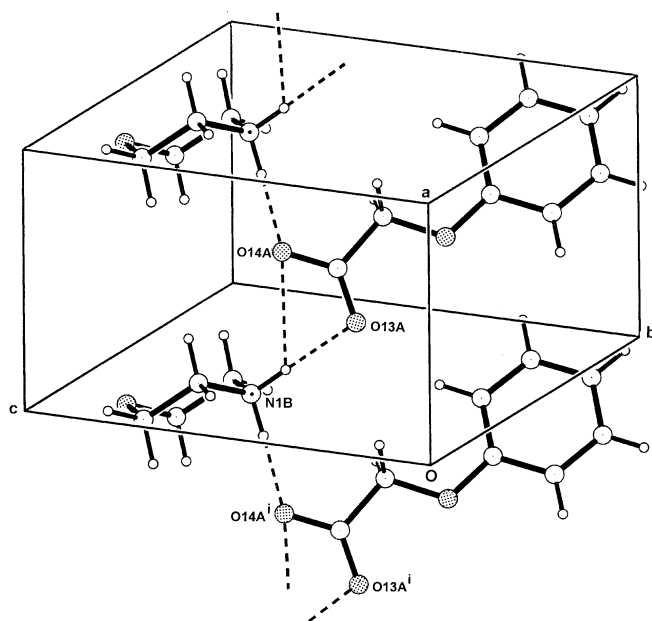
Symmetry codes: (i)  $x + 1, y, z$ ; (ii)  $-x, -y + 2, -z + 1$ .

found [equivalent torsion angles =  $-166.5$  (3),  $172.61$  (8) and  $-171.35$  (15)°, respectively].

### 3. Supramolecular features

In the crystals of both (I), (III) and (IV), a primary three-centre  $R_1^2(4)$  N1*B*–H···(O,O')<sub>carboxyl</sub> hydrogen-bonding interaction is present, with the asymmetry in (I) [ $N\cdots O = 2.7366$  (18) and  $3.1655$  (17) Å] and (IV) [ $2.683$  (2) and  $3.115$  (2) Å] being significantly greater than that in (III) [ $2.892$  (3) and  $2.988$  (3) Å] (Tables 1, 3 and 4). With (II), the second N–H···O distance is  $3.241$  (2) Å.

The hydrogen-bonding extensions involving the second aminium H atom of the cation result in different structures in



**Figure 5**  
The one-dimensional hydrogen-bonded polymeric structure of (I) extending along *a*. For symmetry codes, see Table 1.

**Table 3**  
Hydrogen-bond geometry (Å, °) for (III).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1 <i>B</i> –H11 <i>B</i> ···O13 <i>A</i>	0.88 (2)	2.07 (2)	2.892 (3)	156 (2)
N1 <i>B</i> –H11 <i>B</i> ···O14 <i>A</i>	0.88 (2)	2.26 (2)	2.988 (3)	141 (2)
N1 <i>B</i> –H12 <i>B</i> ···O14 <i>A</i> <sup>i</sup>	0.88 (2)	1.87 (2)	2.737 (3)	170 (2)
C12 <i>A</i> –H12 <i>A</i> ···O13 <i>A</i> <sup>ii</sup>	0.99	2.41	3.398 (3)	173

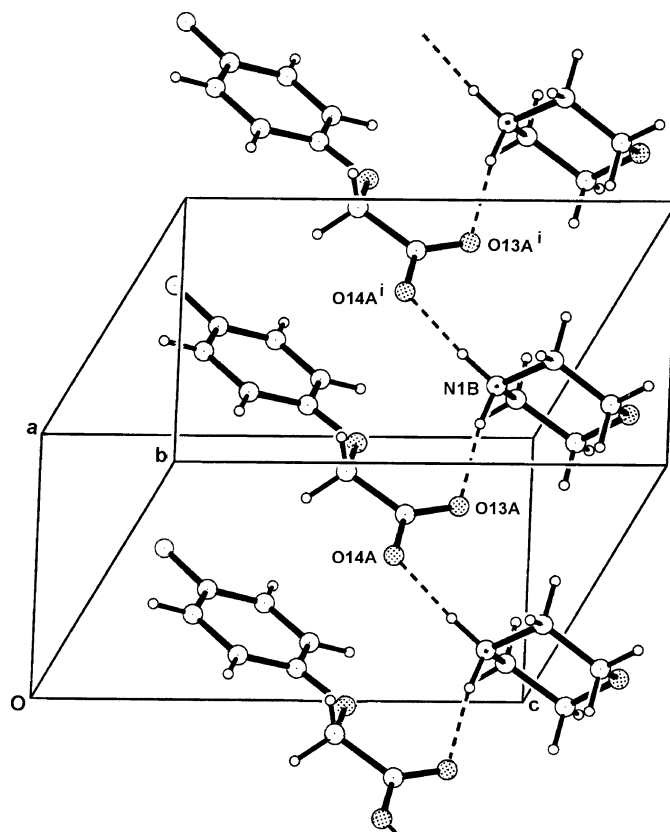
Symmetry codes: (i)  $x - 1, y, z$ ; (ii)  $x + 1, y, z$ .

**Table 4**  
Hydrogen-bond geometry (Å, °) for (IV).

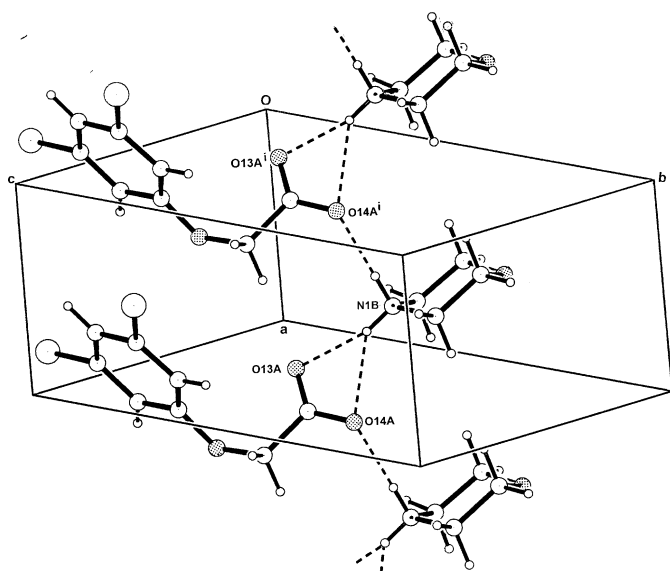
<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1 <i>B</i> –H11 <i>B</i> ···O13 <i>A</i> <sup>i</sup>	0.91 (2)	2.56 (2)	3.115 (2)	120 (1)
N1 <i>B</i> –H11 <i>B</i> ···O14 <i>A</i> <sup>i</sup>	0.91 (2)	1.79 (2)	2.683 (2)	169 (2)
N1 <i>B</i> –H12 <i>B</i> ···O13 <i>A</i>	0.87 (2)	1.92 (2)	2.747 (2)	158 (2)
C12 <i>A</i> –H12 <i>A</i> ···O14 <i>A</i> <sup>ii</sup>	0.99	2.50	3.484 (2)	173
C2 <i>B</i> –H21 <i>B</i> ···O11 <i>A</i> <sup>iii</sup>	0.99	2.57	3.477 (2)	151
C5 <i>B</i> –H52 <i>B</i> ···O4 <i>B</i> <sup>iv</sup>	0.99	2.58	3.489 (3)	153

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

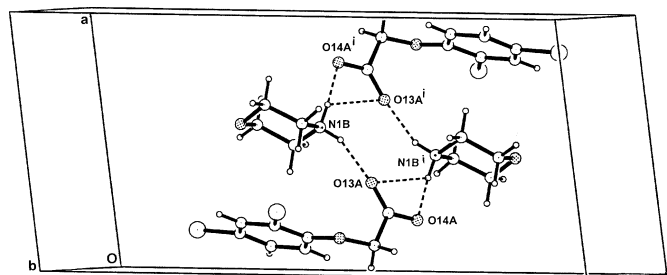
(I)–(III) compared to that in (IV). With (I)–(III), the primary heterodimers are all extended along *a* through an N1*B*–H···O14*A*<sup>i</sup> hydrogen bond (Tables 1–3, respectively), into one-dimensional ribbon structures (Figs. 5–7). These ribbon structures provide further examples of the common hydrogen-



**Figure 6**  
The one-dimensional hydrogen-bonded polymeric structure of (II) extending along *a*. For symmetry codes, see Table 2.



**Figure 7**  
The one-dimensional hydrogen-bonded polymeric structure of (III) extending along *a*. For symmetry codes, see Table 3



**Figure 8**  
The cyclic hydrogen-bonded heterotetramer structure of (IV). For symmetry codes, see Table 4.

bonded structure type found among the anhydrous aromatic morpholinium benzoate salts, *e.g.* with salicylic acid (Smith & Lynch, 2015*b*) and with 2-chloro-4-nitrobenzoic acid (Ishida *et al.*, 2001*a*). In both of these examples, helical chains extend along  $2_1$ screw axes in the crystals. Present also in structures of (I)–(IV) are minor weak inter-unit C–H...O interactions: in (I), C4A–H...O4B<sup>ii</sup> (Table 1); in (II), C4A–H...O4B<sup>ii</sup>;

**Table 5**  
Experimental details.

	(I)	(II)	(III)	(IV)
<b>Crystal data</b>				
Chemical formula	C <sub>4</sub> H <sub>10</sub> NO <sup>+</sup> ·C <sub>8</sub> H <sub>7</sub> O <sub>3</sub> <sup>−</sup>	C <sub>4</sub> H <sub>10</sub> NO <sup>+</sup> ·C <sub>8</sub> H <sub>6</sub> FO <sub>3</sub> <sup>−</sup>	C <sub>4</sub> H <sub>10</sub> NO <sup>+</sup> ·C <sub>8</sub> H <sub>5</sub> Cl <sub>2</sub> O <sub>3</sub> <sup>−</sup>	C <sub>4</sub> H <sub>10</sub> NO <sup>+</sup> ·C <sub>8</sub> H <sub>5</sub> Cl <sub>2</sub> O <sub>3</sub> <sup>−</sup>
<i>M<sub>r</sub></i>	239.27	257.26	308.15	308.15
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>
Temperature (K)	200	200	200	200
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.7079 (5), 9.7735 (9), 11.3586 (10)	5.7997 (5), 10.2605 (10), 10.4836 (11)	5.1733 (4), 11.3751 (10), 11.7808 (10)	9.3657 (5), 7.1702 (3), 21.1340 (11)
$\alpha$ , $\beta$ , $\gamma$ (°)	78.277 (7), 86.171 (7), 77.512 (7)	88.388 (8), 82.792 (8), 80.325 (8)	86.904 (7), 85.106 (7), 77.936 (7)	90, 97.981 (5), 90
<i>V</i> (Å <sup>3</sup> )	605.58 (10)	610.11 (10)	675.01 (10)	1405.48 (12)
<i>Z</i>	2	2	2	4
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>−1</sup> )	0.10	0.11	0.49	0.47
Crystal size (mm)	0.50 × 0.15 × 0.04	0.50 × 0.25 × 0.05	0.50 × 0.13 × 0.10	0.35 × 0.35 × 0.12
<b>Data collection</b>				
Diffractometer	Oxford Diffraction Gemini-S CCD detector	Oxford Diffraction Gemini-S CCD detector	Oxford Diffraction Gemini-S CCD detector	Oxford Diffraction Gemini-S CCD detector
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Agilent, 2014)	Multi-scan ( <i>CrysAlis PRO</i> ; Agilent, 2014)	Multi-scan ( <i>CrysAlis PRO</i> ; Agilent, 2014)	Multi-scan ( <i>CrysAlis PRO</i> ; Agilent, 2014)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.860, 0.980	0.488, 0.980	0.903, 0.989	0.933, 0.980
No. of measured, independent and observed reflections	4172, 2370, 1765 [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	4984, 2394, 1743 [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	5616, 2646, 2096 [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	6400, 2754, 2273 [ <i>I</i> 2 $\sigma$ ( <i>I</i> )]
<i>R</i> <sub>int</sub>	0.033	0.033	0.027	0.026
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>−1</sup> )	0.617	0.617	0.617	0.617
<b>Refinement</b>				
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.048, 0.113, 1.02	0.046, 0.116, 1.04	0.039, 0.091, 1.03	0.038, 0.091, 1.04
No. of reflections	2370	2394	2646	2754
No. of parameters	154	169	178	178
No. of restraints	0	2	2	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>−3</sup> )	0.16, −0.17	0.19, −0.20	0.24, −0.26	0.28, −0.26

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SIR92* (Altomare *et al.*, 1993), *SHELXS97* and *SHELXL97* (Sheldrick, 2008) within *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

C6B—H···O13A<sup>iii</sup> (Table 2): in (III), Cl2A—H···O13A<sup>ii</sup> (Table 3).

In the crystal of (IV), the second N1B—H···O14A<sup>i</sup> hydrogen bond generates a centrosymmetric heterotetrameric ring structure [graph set  $R_4^2(8)$ ] (Fig. 8). For symmetry code (i), see Table 4. This cyclic system typifies the second structure type also found in a number of examples of morpholinium salts with ring-substituted benzoic acids, *e.g.* in the 2-chloro-5-nitro-, 4-chloro-2-nitro-, 4-chloro-3-nitro- and 5-chloro-2-nitrobenzoate series (Ishida *et al.*, 2001*a,b,c*) and in the 4-aminosalicylate (André *et al.*, 2009).

Only weak inter-unit C—H···O interactions to carboxyl or phenoxy O-atom acceptors are present in (IV) (Table 4), while no  $\pi$ - $\pi$  interactions are found in any of the structures.

#### 4. Synthesis and crystallization

The title compounds (I)–(IV) were prepared by the dropwise addition of morpholine at room temperature to solutions of phenoxyacetic acid (150 mg), (4-fluorophenoxy)acetic acid (170 mg), (2,4-dichlorophenoxy)acetic acid or (2,4-dichlorophenoxy)acetic acid (220 mg), respectively, in 15 ml of ethanol. Room-temperature evaporation of the solutions gave either colourless plates of (III) or needles of (IV) from which specimens were cleaved for the X-ray analyses. For (I) and (II), the same preparative procedure was employed using phenoxyacetic acid or (4-fluorophenoxy)acetic acid but the final oils which resulted after solvent evaporation were redissolved in ethanol, finally giving thin colourless fragile plates of compounds (I) and (II) from which specimens were cleaved for the X-ray analyses.

#### 5. Refinement details

Crystal data, data collection and structure refinement details are given in Table 5. H atoms were placed in calculated positions (aromatic C—H = 0.95 Å or methylene C—H = 0.99 Å) and were allowed to ride in the refinements, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The aminium H atoms were located in

difference Fourier analyses and were allowed to refine with distance restraints [ $\text{N—H} = 0.90(2) \text{ \AA}$ ] and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ .

#### Acknowledgements

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## supporting information

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## Crystal structures and hydrogen bonding in the morpholinium salts of four phenoxyacetic acid analogues

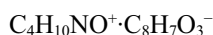
Graham Smith and Daniel E. Lynch

### Computing details

For all compounds, data collection: *CrysAlis PRO* (Agilent, 2014); cell refinement: *CrysAlis PRO* (Agilent, 2014); data reduction: *CrysAlis PRO* (Agilent, 2014). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008) for (I), (II); *SIR92* (Altomare *et al.*, 1993) for (III), (IV). For all compounds, program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) within *WinGX* (Farrugia, 2012); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON* (Spek, 2009).

### (I) Tetrahydro-2H-1,4-oxazin-4-ium phenoxyacetate

#### Crystal data



$$M_r = 239.27$$

Triclinic,  $P\bar{1}$

Hall symbol: -P 1

$$a = 5.7079 (5) \text{ \AA}$$

$$b = 9.7735 (9) \text{ \AA}$$

$$c = 11.3586 (10) \text{ \AA}$$

$$\alpha = 78.277 (7)^\circ$$

$$\beta = 86.171 (7)^\circ$$

$$\gamma = 77.512 (7)^\circ$$

$$V = 605.58 (10) \text{ \AA}^3$$

$$Z = 2$$

$$F(000) = 256$$

$$D_x = 1.312 \text{ Mg m}^{-3}$$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1029 reflections

$$\theta = 3.9\text{--}28.5^\circ$$

$$\mu = 0.10 \text{ mm}^{-1}$$

$$T = 200 \text{ K}$$

Plate, colourless

$$0.50 \times 0.15 \times 0.04 \text{ mm}$$

#### Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer

Radiation source: Enhance (Mo) X-ray source

Graphite monochromator

Detector resolution: 16.077 pixels  $\text{mm}^{-1}$

$\omega$  scans

Absorption correction: multi-scan

(*CrysAlis PRO*; Agilent, 2014)

$$T_{\min} = 0.860, T_{\max} = 0.980$$

4172 measured reflections

2370 independent reflections

1765 reflections with  $I > 2\sigma(I)$

$$R_{\text{int}} = 0.033$$

$$\theta_{\max} = 26.0^\circ, \theta_{\min} = 3.1^\circ$$

$$h = -7 \rightarrow 6$$

$$k = -12 \rightarrow 12$$

$$l = -13 \rightarrow 13$$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.048$$

$$wR(F^2) = 0.113$$

$$S = 1.02$$

2370 reflections

154 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 atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0456P)^2]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.16 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.17 \text{ e } \text{\AA}^{-3}$

*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 esds are taken into account in the estimation of distances, angles and torsion angles

**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  $F^2 > 2\text{sigma}(F^2)$  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 ( $\text{\AA}^2$ )*

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O11A	0.3926 (2)	0.81847 (13)	0.38178 (10)	0.0374 (4)
O13A	0.11992 (19)	0.65034 (13)	0.51716 (10)	0.0358 (4)
O14A	0.41444 (19)	0.54699 (13)	0.64451 (10)	0.0323 (4)
C1A	0.5198 (3)	0.91643 (18)	0.32122 (15)	0.0303 (5)
C2A	0.7157 (3)	0.94974 (19)	0.36542 (16)	0.0346 (6)
C3A	0.8267 (3)	1.0526 (2)	0.29642 (17)	0.0415 (7)
C4A	0.7481 (4)	1.1208 (2)	0.18324 (18)	0.0449 (7)
C5A	0.5549 (4)	1.0854 (2)	0.13875 (17)	0.0432 (7)
C6A	0.4402 (3)	0.98450 (19)	0.20676 (16)	0.0365 (6)
C12A	0.4895 (3)	0.73323 (18)	0.49189 (14)	0.0288 (5)
C13A	0.3264 (3)	0.63578 (18)	0.55411 (14)	0.0268 (5)
O4B	-0.1545 (2)	0.39037 (15)	0.94974 (10)	0.0445 (5)
N1B	-0.1183 (2)	0.50356 (15)	0.70035 (12)	0.0270 (4)
C2B	-0.1277 (3)	0.59359 (19)	0.79155 (14)	0.0322 (6)
C3B	-0.2632 (3)	0.5347 (2)	0.90159 (15)	0.0386 (6)
C5B	-0.1515 (4)	0.3030 (2)	0.86300 (16)	0.0410 (7)
C6B	-0.0136 (3)	0.35172 (19)	0.75076 (15)	0.0349 (6)
H2A	0.77390	0.90240	0.44270	0.0420*
H3A	0.95950	1.07660	0.32770	0.0500*
H4A	0.82570	1.19120	0.13660	0.0540*
H5A	0.50030	1.13090	0.06040	0.0520*
H6A	0.30650	0.96140	0.17550	0.0440*
H11A	0.51320	0.79650	0.54600	0.0350*
H12A	0.64820	0.67470	0.47530	0.0350*
H11B	-0.032 (3)	0.5424 (18)	0.6353 (13)	0.0320*
H12B	-0.280 (2)	0.5164 (19)	0.6782 (13)	0.0320*
H21B	-0.20870	0.69300	0.75840	0.0390*
H22B	0.03720	0.59430	0.81310	0.0390*
H31B	-0.26710	0.59360	0.96330	0.0460*
H32B	-0.43070	0.53980	0.88040	0.0460*
H51B	-0.31840	0.30590	0.84220	0.0490*

H52B	-0.07770	0.20290	0.89820	0.0490*
H61B	0.15700	0.34140	0.76960	0.0420*
H62B	-0.02120	0.29200	0.69100	0.0420*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O11A	0.0348 (7)	0.0363 (8)	0.0397 (7)	-0.0186 (6)	-0.0046 (5)	0.0088 (6)
O13A	0.0252 (7)	0.0472 (9)	0.0342 (7)	-0.0162 (6)	-0.0014 (5)	0.0031 (6)
O14A	0.0270 (6)	0.0366 (8)	0.0316 (7)	-0.0121 (6)	-0.0004 (5)	0.0030 (6)
C1A	0.0299 (9)	0.0232 (9)	0.0364 (10)	-0.0081 (8)	0.0070 (8)	-0.0021 (8)
C2A	0.0351 (10)	0.0320 (11)	0.0373 (10)	-0.0128 (8)	0.0028 (8)	-0.0028 (8)
C3A	0.0387 (11)	0.0391 (12)	0.0509 (12)	-0.0201 (9)	0.0074 (9)	-0.0086 (10)
C4A	0.0515 (12)	0.0360 (12)	0.0487 (12)	-0.0222 (10)	0.0140 (10)	-0.0025 (10)
C5A	0.0545 (12)	0.0326 (11)	0.0387 (11)	-0.0117 (10)	0.0037 (9)	0.0030 (9)
C6A	0.0378 (10)	0.0307 (11)	0.0405 (10)	-0.0105 (9)	-0.0012 (8)	-0.0018 (8)
C12A	0.0255 (9)	0.0281 (10)	0.0328 (9)	-0.0101 (8)	0.0001 (7)	-0.0012 (8)
C13A	0.0257 (9)	0.0290 (10)	0.0273 (9)	-0.0093 (8)	0.0044 (7)	-0.0071 (8)
O4B	0.0641 (9)	0.0436 (9)	0.0267 (7)	-0.0196 (7)	-0.0014 (6)	0.0001 (6)
N1B	0.0239 (7)	0.0331 (9)	0.0247 (7)	-0.0120 (7)	0.0021 (6)	-0.0015 (6)
C2B	0.0333 (10)	0.0317 (10)	0.0342 (10)	-0.0119 (8)	0.0013 (8)	-0.0073 (8)
C3B	0.0458 (11)	0.0422 (12)	0.0295 (10)	-0.0137 (9)	0.0061 (8)	-0.0083 (9)
C5B	0.0577 (13)	0.0309 (11)	0.0363 (10)	-0.0180 (9)	-0.0055 (9)	-0.0003 (8)
C6B	0.0366 (10)	0.0313 (11)	0.0356 (10)	-0.0045 (8)	-0.0037 (8)	-0.0057 (8)

*Geometric parameters (Å, °)*

O11A—C1A	1.372 (2)	C2A—H2A	0.9500
O11A—C12A	1.426 (2)	C3A—H3A	0.9500
O13A—C13A	1.247 (2)	C4A—H4A	0.9500
O14A—C13A	1.256 (2)	C5A—H5A	0.9500
O4B—C5B	1.426 (2)	C6A—H6A	0.9500
O4B—C3B	1.424 (2)	C12A—H11A	0.9900
N1B—C6B	1.485 (2)	C12A—H12A	0.9900
N1B—C2B	1.481 (2)	C2B—C3B	1.504 (2)
N1B—H12B	0.948 (12)	C5B—C6B	1.501 (3)
N1B—H11B	0.923 (16)	C2B—H21B	0.9900
C1A—C6A	1.391 (2)	C2B—H22B	0.9900
C1A—C2A	1.381 (2)	C3B—H31B	0.9900
C2A—C3A	1.384 (3)	C3B—H32B	0.9900
C3A—C4A	1.378 (3)	C5B—H51B	0.9900
C4A—C5A	1.379 (3)	C5B—H52B	0.9900
C5A—C6A	1.378 (3)	C6B—H61B	0.9900
C12A—C13A	1.515 (2)	C6B—H62B	0.9900
C1A—O11A—C12A	116.65 (13)	C13A—C12A—H11A	109.00
C3B—O4B—C5B	110.28 (13)	O11A—C12A—H11A	109.00
C2B—N1B—C6B	110.91 (13)	C13A—C12A—H12A	109.00



C6B—N1B—H11B	113.4 (11)	O11A—C12A—H12A	109.00
C2B—N1B—H12B	104.8 (10)	H11A—C12A—H12A	108.00
H11B—N1B—H12B	109.0 (14)	N1B—C2B—C3B	109.23 (14)
C2B—N1B—H11B	106.3 (10)	O4B—C3B—C2B	111.23 (14)
C6B—N1B—H12B	111.9 (11)	O4B—C5B—C6B	111.72 (16)
O11A—C1A—C6A	115.56 (15)	N1B—C6B—C5B	109.35 (14)
C2A—C1A—C6A	119.48 (16)	N1B—C2B—H21B	110.00
O11A—C1A—C2A	124.96 (15)	N1B—C2B—H22B	110.00
C1A—C2A—C3A	119.58 (16)	C3B—C2B—H21B	110.00
C2A—C3A—C4A	121.20 (18)	C3B—C2B—H22B	110.00
C3A—C4A—C5A	118.97 (19)	H21B—C2B—H22B	108.00
C4A—C5A—C6A	120.65 (18)	O4B—C3B—H31B	109.00
C1A—C6A—C5A	120.10 (17)	O4B—C3B—H32B	109.00
O11A—C12A—C13A	111.82 (14)	C2B—C3B—H31B	109.00
O13A—C13A—O14A	125.13 (16)	C2B—C3B—H32B	109.00
O13A—C13A—C12A	120.24 (14)	H31B—C3B—H32B	108.00
O14A—C13A—C12A	114.59 (15)	O4B—C5B—H51B	109.00
C3A—C2A—H2A	120.00	O4B—C5B—H52B	109.00
C1A—C2A—H2A	120.00	C6B—C5B—H51B	109.00
C4A—C3A—H3A	119.00	C6B—C5B—H52B	109.00
C2A—C3A—H3A	119.00	H51B—C5B—H52B	108.00
C5A—C4A—H4A	121.00	N1B—C6B—H61B	110.00
C3A—C4A—H4A	121.00	N1B—C6B—H62B	110.00
C4A—C5A—H5A	120.00	C5B—C6B—H61B	110.00
C6A—C5A—H5A	120.00	C5B—C6B—H62B	110.00
C5A—C6A—H6A	120.00	H61B—C6B—H62B	108.00
C1A—C6A—H6A	120.00		
C12A—O11A—C1A—C2A	-8.1 (2)	O11A—C1A—C2A—C3A	-178.84 (17)
C12A—O11A—C1A—C6A	171.64 (15)	C1A—C2A—C3A—C4A	-1.2 (3)
C1A—O11A—C12A—C13A	176.53 (14)	C2A—C3A—C4A—C5A	0.1 (3)
C5B—O4B—C3B—C2B	-60.23 (18)	C3A—C4A—C5A—C6A	0.7 (3)
C3B—O4B—C5B—C6B	59.8 (2)	C4A—C5A—C6A—C1A	-0.4 (3)
C6B—N1B—C2B—C3B	-55.34 (17)	O11A—C12A—C13A—O14A	172.45 (14)
C2B—N1B—C6B—C5B	54.74 (18)	O11A—C12A—C13A—O13A	-9.8 (2)
C6A—C1A—C2A—C3A	1.5 (3)	N1B—C2B—C3B—O4B	58.00 (18)
O11A—C1A—C6A—C5A	179.61 (16)	O4B—C5B—C6B—N1B	-56.8 (2)
C2A—C1A—C6A—C5A	-0.7 (3)		

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1B—H11B $\cdots$ O13A	0.92 (2)	1.83 (2)	2.7366 (18)	169 (2)
N1B—H11B $\cdots$ O14A	0.92 (2)	2.57 (2)	3.1655 (17)	123 (1)
N1B—H12B $\cdots$ O14A <sup>i</sup>	0.95 (1)	1.76 (1)	2.7061 (17)	176 (1)

C4A—H4A···O4B <sup>ii</sup>	0.95	2.59	3.447 (2)	151
C6B—H62B···O13A <sup>iii</sup>	0.99	2.39	3.148 (2)	133

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

## (II) Tetrahydro-2H-1,4-oxazin-4-ium (4-fluorophenoxy)acetate

### Crystal data

$C_4H_{10}NO^+ \cdot C_8H_6FO_3^-$

$M_r = 257.26$

Triclinic,  $P\bar{1}$

Hall symbol:  $-P\ 1$

$a = 5.7997$  (5) Å

$b = 10.2605$  (10) Å

$c = 10.4836$  (11) Å

$\alpha = 88.388$  (8)°

$\beta = 82.792$  (8)°

$\gamma = 80.325$  (8)°

$V = 610.11$  (10) Å<sup>3</sup>

$Z = 2$

$F(000) = 272$

$D_x = 1.400$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 1163 reflections

$\theta = 4.0$ – $28.4$ °

$\mu = 0.11$  mm<sup>-1</sup>

$T = 200$  K

Plate, colourless

$0.50 \times 0.25 \times 0.05$  mm

### Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 16.077 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2014)

$T_{\min} = 0.488$ ,  $T_{\max} = 0.980$

4984 measured reflections

2394 independent reflections

1743 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\max} = 26.0$ °,  $\theta_{\min} = 3.6$ °

$h = -7$ → $6$

$k = -10$ → $12$

$l = -12$ → $12$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.046$

$wR(F^2) = 0.116$

$S = 1.04$

2394 reflections

169 parameters

2 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

$w = 1/[\sigma^2(F_o^2) + (0.046P)^2 + 0.0267P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.19$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.20$  e Å<sup>-3</sup>

### 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 esds are taken into account in the estimation of distances, angles and torsion angles

**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 ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
F4A	1.10905 (19)	0.50899 (12)	0.11938 (12)	0.0518 (4)
O11A	0.3317 (2)	0.71651 (12)	0.44716 (12)	0.0328 (4)
O13A	-0.0039 (2)	0.82589 (13)	0.62958 (12)	0.0331 (4)
O14A	-0.2493 (2)	0.88910 (13)	0.48447 (12)	0.0350 (4)
C1A	0.5169 (3)	0.66778 (16)	0.35718 (18)	0.0255 (6)
C2A	0.5357 (3)	0.69979 (18)	0.22788 (18)	0.0300 (6)
C3A	0.7372 (3)	0.64655 (19)	0.14698 (19)	0.0357 (6)
C4A	0.9096 (3)	0.56021 (18)	0.1981 (2)	0.0331 (6)
C5A	0.8925 (3)	0.52405 (18)	0.3247 (2)	0.0333 (6)
C6A	0.6948 (3)	0.57908 (18)	0.40512 (19)	0.0308 (6)
C12A	0.1408 (3)	0.80714 (17)	0.40429 (17)	0.0263 (6)
C13A	-0.0514 (3)	0.84287 (16)	0.51649 (18)	0.0249 (6)
O4B	0.3300 (2)	0.84416 (14)	0.96211 (13)	0.0458 (5)
N1B	0.4282 (3)	0.85297 (15)	0.68920 (15)	0.0288 (5)
C2B	0.4898 (3)	0.72899 (19)	0.76326 (19)	0.0357 (7)
C3B	0.3244 (4)	0.7319 (2)	0.8863 (2)	0.0415 (7)
C5B	0.2614 (4)	0.9620 (2)	0.8921 (2)	0.0425 (7)
C6B	0.4214 (3)	0.96981 (18)	0.76981 (19)	0.0329 (6)
H2A	0.41190	0.75780	0.19420	0.0360*
H3A	0.75460	0.66960	0.05830	0.0430*
H5A	1.01350	0.46260	0.35680	0.0400*
H6A	0.68030	0.55610	0.49380	0.0370*
H11A	0.07620	0.76630	0.33510	0.0320*
H12A	0.19810	0.88810	0.36920	0.0320*
H11B	0.541 (3)	0.861 (2)	0.6143 (17)	0.0500*
H12B	0.283 (3)	0.855 (2)	0.6580 (19)	0.0500*
H21B	0.47750	0.65180	0.71140	0.0430*
H22B	0.65420	0.72040	0.78310	0.0430*
H31B	0.36880	0.65030	0.93650	0.0500*
H32B	0.16190	0.73360	0.86570	0.0500*
H51B	0.26350	1.03940	0.94600	0.0510*
H52B	0.09820	0.96510	0.87220	0.0510*
H61B	0.36500	1.05120	0.72200	0.0390*
H62B	0.58220	0.97440	0.78970	0.0390*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
F4A	0.0376 (7)	0.0649 (8)	0.0429 (8)	0.0137 (6)	0.0067 (6)	-0.0140 (6)
O11A	0.0251 (6)	0.0409 (8)	0.0265 (8)	0.0079 (5)	0.0010 (5)	0.0031 (6)
O13A	0.0230 (6)	0.0513 (8)	0.0237 (8)	-0.0042 (6)	-0.0012 (6)	0.0015 (6)
O14A	0.0216 (7)	0.0497 (8)	0.0300 (8)	0.0041 (6)	-0.0036 (6)	0.0026 (6)
C1A	0.0231 (9)	0.0256 (9)	0.0259 (11)	-0.0003 (7)	-0.0003 (8)	-0.0031 (8)
C2A	0.0297 (10)	0.0304 (10)	0.0270 (11)	0.0040 (8)	-0.0045 (8)	-0.0024 (8)
C3A	0.0379 (11)	0.0405 (11)	0.0244 (11)	0.0025 (9)	0.0015 (9)	-0.0043 (9)

C4A	0.0265 (10)	0.0342 (10)	0.0346 (13)	0.0025 (8)	0.0039 (8)	-0.0122 (9)
C5A	0.0253 (9)	0.0337 (10)	0.0383 (13)	0.0040 (8)	-0.0053 (9)	-0.0006 (9)
C6A	0.0287 (10)	0.0344 (10)	0.0275 (11)	-0.0018 (8)	-0.0018 (8)	0.0043 (9)
C12A	0.0237 (9)	0.0273 (9)	0.0259 (11)	0.0011 (7)	-0.0022 (8)	0.0005 (8)
C13A	0.0224 (9)	0.0261 (9)	0.0266 (11)	-0.0053 (7)	-0.0023 (8)	-0.0003 (8)
O4B	0.0628 (10)	0.0521 (9)	0.0227 (8)	-0.0119 (7)	-0.0039 (7)	0.0049 (7)
N1B	0.0222 (8)	0.0415 (9)	0.0217 (9)	-0.0032 (7)	-0.0014 (7)	0.0008 (7)
C2B	0.0345 (10)	0.0336 (11)	0.0384 (13)	-0.0030 (8)	-0.0062 (9)	0.0006 (9)
C3B	0.0494 (13)	0.0433 (12)	0.0339 (13)	-0.0160 (10)	-0.0043 (10)	0.0084 (10)
C5B	0.0488 (12)	0.0450 (13)	0.0300 (13)	-0.0015 (10)	0.0015 (10)	-0.0025 (10)
C6B	0.0337 (10)	0.0346 (11)	0.0298 (12)	-0.0034 (8)	-0.0057 (9)	0.0034 (9)

*Geometric parameters (Å, °)*

F4A—C4A	1.370 (2)	C12A—C13A	1.523 (3)
O11A—C1A	1.373 (2)	C2A—H2A	0.9500
O11A—C12A	1.431 (2)	C3A—H3A	0.9500
O13A—C13A	1.251 (2)	C5A—H5A	0.9500
O14A—C13A	1.249 (2)	C6A—H6A	0.9500
O4B—C5B	1.422 (2)	C12A—H11A	0.9900
O4B—C3B	1.425 (2)	C12A—H12A	0.9900
N1B—C6B	1.478 (2)	C2B—C3B	1.506 (3)
N1B—C2B	1.487 (2)	C5B—C6B	1.494 (3)
N1B—H12B	0.938 (18)	C2B—H21B	0.9900
N1B—H11B	0.968 (18)	C2B—H22B	0.9900
C1A—C6A	1.391 (3)	C3B—H31B	0.9900
C1A—C2A	1.381 (3)	C3B—H32B	0.9900
C2A—C3A	1.395 (3)	C5B—H51B	0.9900
C3A—C4A	1.372 (3)	C5B—H52B	0.9900
C4A—C5A	1.364 (3)	C6B—H61B	0.9900
C5A—C6A	1.382 (3)	C6B—H62B	0.9900
C1A—O11A—C12A	117.83 (14)	C13A—C12A—H11A	110.00
C3B—O4B—C5B	109.82 (15)	O11A—C12A—H11A	110.00
C2B—N1B—C6B	110.58 (15)	C13A—C12A—H12A	110.00
C6B—N1B—H11B	106.7 (12)	O11A—C12A—H12A	110.00
C2B—N1B—H12B	110.3 (12)	H11A—C12A—H12A	108.00
H11B—N1B—H12B	105.8 (16)	N1B—C2B—C3B	109.48 (16)
C2B—N1B—H11B	112.8 (12)	O4B—C3B—C2B	111.75 (17)
C6B—N1B—H12B	110.5 (12)	O4B—C5B—C6B	111.70 (17)
O11A—C1A—C6A	114.80 (16)	N1B—C6B—C5B	110.52 (15)
C2A—C1A—C6A	119.88 (17)	N1B—C2B—H21B	110.00
O11A—C1A—C2A	125.33 (16)	N1B—C2B—H22B	110.00
C1A—C2A—C3A	119.71 (17)	C3B—C2B—H21B	110.00
C2A—C3A—C4A	118.64 (18)	C3B—C2B—H22B	110.00
C3A—C4A—C5A	122.83 (18)	H21B—C2B—H22B	108.00
F4A—C4A—C5A	118.33 (16)	O4B—C3B—H31B	109.00
F4A—C4A—C3A	118.84 (18)	O4B—C3B—H32B	109.00

C4A—C5A—C6A	118.38 (17)	C2B—C3B—H31B	109.00
C1A—C6A—C5A	120.53 (18)	C2B—C3B—H32B	109.00
O11A—C12A—C13A	109.56 (14)	H31B—C3B—H32B	108.00
O13A—C13A—O14A	125.43 (17)	O4B—C5B—H51B	109.00
O14A—C13A—C12A	114.50 (16)	O4B—C5B—H52B	109.00
O13A—C13A—C12A	120.06 (15)	C6B—C5B—H51B	109.00
C3A—C2A—H2A	120.00	C6B—C5B—H52B	109.00
C1A—C2A—H2A	120.00	H51B—C5B—H52B	108.00
C4A—C3A—H3A	121.00	N1B—C6B—H61B	110.00
C2A—C3A—H3A	121.00	N1B—C6B—H62B	110.00
C4A—C5A—H5A	121.00	C5B—C6B—H61B	110.00
C6A—C5A—H5A	121.00	C5B—C6B—H62B	110.00
C5A—C6A—H6A	120.00	H61B—C6B—H62B	108.00
C1A—C6A—H6A	120.00		
C12A—O11A—C1A—C2A	0.5 (2)	C1A—C2A—C3A—C4A	1.8 (3)
C12A—O11A—C1A—C6A	-179.26 (15)	C2A—C3A—C4A—F4A	-179.19 (16)
C1A—O11A—C12A—C13A	176.75 (14)	C2A—C3A—C4A—C5A	0.0 (3)
C3B—O4B—C5B—C6B	-59.8 (2)	C3A—C4A—C5A—C6A	-1.4 (3)
C5B—O4B—C3B—C2B	60.3 (2)	F4A—C4A—C5A—C6A	177.88 (16)
C6B—N1B—C2B—C3B	53.5 (2)	C4A—C5A—C6A—C1A	0.8 (3)
C2B—N1B—C6B—C5B	-53.7 (2)	O11A—C12A—C13A—O14A	-160.39 (14)
C6A—C1A—C2A—C3A	-2.3 (3)	O11A—C12A—C13A—O13A	20.1 (2)
O11A—C1A—C2A—C3A	177.92 (16)	N1B—C2B—C3B—O4B	-57.4 (2)
C2A—C1A—C6A—C5A	1.0 (3)	O4B—C5B—C6B—N1B	57.1 (2)
O11A—C1A—C6A—C5A	-179.22 (16)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1B—H11B...O14A <sup>i</sup>	0.97 (2)	1.76 (2)	2.725 (2)	175 (2)
N1B—H12B...O13A	0.94 (2)	1.80 (2)	2.718 (2)	165 (2)
C6B—H61B...O14A <sup>ii</sup>	0.99	2.38	3.188 (2)	138

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

(III) Tetrahydro-2*H*-1,4-oxazin-4-ium (3,5-dichlorophenoxy)acetate

Crystal data

$C_4H_{10}NO^+ \cdot C_8H_5Cl_2O_3^-$

$M_r = 308.15$

Triclinic,  $P\bar{1}$

Hall symbol: -P 1

$a = 5.1733$  (4) Å

$b = 11.3751$  (10) Å

$c = 11.7808$  (10) Å

$\alpha = 86.904$  (7)°

$\beta = 85.106$  (7)°

$\gamma = 77.936$  (7)°

$V = 675.01$  (10) Å<sup>3</sup>

$Z = 2$

$F(000) = 320$

$D_x = 1.516$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 1520 reflections

$\theta = 3.7$ – $27.8$ °

$\mu = 0.49$  mm<sup>-1</sup>

$T = 200$  K

Needle, colourless

$0.50 \times 0.13 \times 0.10$  mm

*Data collection*Oxford Diffraction Gemini-S CCD-detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 16.077 pixels mm<sup>-1</sup> $\omega$  scansAbsorption correction: multi-scan  
(CrysAlis PRO; Agilent, 2014) $T_{\min} = 0.903$ ,  $T_{\max} = 0.989$ 

5616 measured reflections

2646 independent reflections

2096 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.027$  $\theta_{\max} = 26.0^\circ$ ,  $\theta_{\min} = 3.5^\circ$  $h = -6 \rightarrow 6$  $k = -14 \rightarrow 12$  $l = -14 \rightarrow 14$ *Refinement*Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.039$  $wR(F^2) = 0.091$  $S = 1.03$ 

2646 reflections

178 parameters

2 restraints

Primary atom site location: structure-invariant  
direct methodsSecondary atom site location: difference Fourier  
mapHydrogen site location: inferred from  
neighbouring sitesH atoms treated by a mixture of independent  
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0328P)^2 + 0.273P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = 0.001$  $\Delta\rho_{\max} = 0.24 \text{ e } \text{\AA}^{-3}$  $\Delta\rho_{\min} = -0.26 \text{ e } \text{\AA}^{-3}$ *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 esds are taken into account in the estimation of distances, angles and torsion angles**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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl3A	0.43721 (11)	0.33427 (5)	1.07395 (5)	0.0409 (2)
Cl5A	0.87160 (12)	-0.05932 (5)	0.83964 (5)	0.0423 (2)
O11A	1.2226 (3)	0.31888 (13)	0.77458 (13)	0.0356 (5)
O13A	0.8276 (3)	0.47790 (19)	0.67505 (15)	0.0575 (7)
O14A	1.0229 (3)	0.63014 (15)	0.69348 (14)	0.0476 (6)
C1A	1.0356 (4)	0.26801 (19)	0.83573 (17)	0.0271 (6)
C2A	0.8470 (4)	0.32703 (19)	0.91505 (17)	0.0281 (6)
C3A	0.6719 (4)	0.26282 (19)	0.97100 (17)	0.0279 (6)
C4A	0.6730 (4)	0.14542 (19)	0.94986 (17)	0.0307 (7)
C5A	0.8641 (4)	0.08971 (19)	0.87030 (18)	0.0303 (7)
C6A	1.0479 (4)	0.14815 (19)	0.81392 (18)	0.0300 (7)
C12A	1.2129 (4)	0.44437 (19)	0.77898 (19)	0.0306 (7)
C13A	1.0030 (4)	0.5221 (2)	0.70886 (18)	0.0335 (7)
O4B	0.3249 (3)	0.88990 (15)	0.45028 (14)	0.0502 (6)
N1B	0.4795 (4)	0.70096 (19)	0.61100 (17)	0.0416 (7)
C2B	0.5070 (5)	0.6814 (2)	0.48655 (19)	0.0395 (8)

C3B	0.3059 (4)	0.7719 (2)	0.4277 (2)	0.0418 (8)
C5B	0.4761 (4)	0.8273 (2)	0.6354 (2)	0.0415 (8)
C6B	0.2754 (5)	0.9090 (2)	0.5686 (2)	0.0466 (8)
H2A	0.83820	0.40890	0.93060	0.0340*
H4A	0.54740	0.10420	0.98840	0.0370*
H6A	1.18090	0.10720	0.76100	0.0360*
H12A	1.38860	0.46070	0.75130	0.0370*
H13A	1.17790	0.46790	0.85940	0.0370*
H11B	0.607 (4)	0.648 (2)	0.641 (2)	0.0560*
H12B	0.332 (4)	0.684 (2)	0.644 (2)	0.0560*
H21B	0.48270	0.59940	0.47290	0.0470*
H22B	0.68720	0.68820	0.45520	0.0470*
H31B	0.33260	0.76060	0.34450	0.0500*
H32B	0.12620	0.75950	0.45370	0.0500*
H51B	0.65360	0.84550	0.61490	0.0500*
H52B	0.43210	0.84010	0.71790	0.0500*
H61B	0.09660	0.89510	0.59410	0.0560*
H62B	0.27880	0.99360	0.58300	0.0560*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C13A	0.0453 (3)	0.0386 (3)	0.0341 (3)	-0.0032 (3)	0.0093 (2)	-0.0012 (2)
C15A	0.0563 (4)	0.0308 (3)	0.0431 (3)	-0.0179 (3)	0.0037 (3)	-0.0068 (2)
O11A	0.0296 (8)	0.0266 (8)	0.0495 (10)	-0.0083 (6)	0.0073 (7)	0.0017 (7)
O13A	0.0363 (10)	0.0903 (15)	0.0527 (11)	-0.0302 (10)	-0.0208 (8)	0.0323 (10)
O14A	0.0523 (10)	0.0345 (10)	0.0491 (10)	0.0042 (8)	-0.0036 (8)	0.0083 (8)
C1A	0.0251 (10)	0.0283 (11)	0.0291 (11)	-0.0076 (9)	-0.0058 (9)	0.0029 (9)
C2A	0.0310 (11)	0.0228 (11)	0.0310 (11)	-0.0054 (9)	-0.0070 (9)	0.0017 (9)
C3A	0.0291 (11)	0.0308 (12)	0.0226 (10)	-0.0040 (9)	-0.0026 (8)	0.0026 (9)
C4A	0.0329 (12)	0.0330 (12)	0.0274 (11)	-0.0113 (9)	-0.0018 (9)	0.0046 (9)
C5A	0.0375 (12)	0.0256 (11)	0.0296 (11)	-0.0085 (9)	-0.0083 (9)	0.0008 (9)
C6A	0.0296 (11)	0.0303 (12)	0.0292 (11)	-0.0048 (9)	-0.0011 (9)	-0.0009 (9)
C12A	0.0284 (11)	0.0287 (12)	0.0360 (12)	-0.0096 (9)	-0.0049 (9)	0.0064 (9)
C13A	0.0237 (11)	0.0456 (15)	0.0264 (11)	-0.0012 (10)	0.0042 (9)	0.0080 (10)
O4B	0.0674 (12)	0.0357 (10)	0.0378 (10)	0.0045 (8)	0.0049 (8)	0.0120 (8)
N1B	0.0414 (12)	0.0407 (12)	0.0338 (11)	0.0095 (9)	-0.0037 (9)	0.0096 (9)
C2B	0.0514 (14)	0.0278 (13)	0.0381 (13)	-0.0071 (11)	0.0001 (11)	-0.0015 (10)
C3B	0.0354 (13)	0.0572 (17)	0.0337 (13)	-0.0095 (11)	-0.0082 (10)	-0.0012 (11)
C5B	0.0343 (13)	0.0581 (17)	0.0367 (13)	-0.0181 (11)	0.0004 (10)	-0.0138 (12)
C6B	0.0626 (16)	0.0292 (13)	0.0433 (14)	-0.0040 (12)	0.0095 (12)	-0.0008 (11)

*Geometric parameters (Å, °)*

C13A—C3A	1.746 (2)	C5A—C6A	1.377 (3)
C15A—C5A	1.744 (2)	C12A—C13A	1.522 (3)
O11A—C1A	1.364 (3)	C2A—H2A	0.9500
O11A—C12A	1.421 (3)	C4A—H4A	0.9500

O13A—C13A	1.228 (3)	C6A—H6A	0.9500
O14A—C13A	1.257 (3)	C12A—H12A	0.9900
O4B—C6B	1.416 (3)	C12A—H13A	0.9900
O4B—C3B	1.407 (3)	C2B—C3B	1.490 (3)
N1B—C2B	1.485 (3)	C5B—C6B	1.489 (3)
N1B—C5B	1.477 (3)	C2B—H21B	0.9900
N1B—H12B	0.88 (2)	C2B—H22B	0.9900
N1B—H11B	0.88 (2)	C3B—H31B	0.9900
C1A—C2A	1.384 (3)	C3B—H32B	0.9900
C1A—C6A	1.388 (3)	C5B—H51B	0.9900
C2A—C3A	1.383 (3)	C5B—H52B	0.9900
C3A—C4A	1.370 (3)	C6B—H61B	0.9900
C4A—C5A	1.379 (3)	C6B—H62B	0.9900
C1A—O11A—C12A	120.24 (17)	C13A—C12A—H12A	109.00
C3B—O4B—C6B	109.96 (17)	O11A—C12A—H12A	109.00
C2B—N1B—C5B	111.72 (18)	C13A—C12A—H13A	109.00
C5B—N1B—H11B	114.7 (15)	O11A—C12A—H13A	109.00
C2B—N1B—H12B	112.3 (15)	H12A—C12A—H13A	108.00
H11B—N1B—H12B	105 (2)	N1B—C2B—C3B	110.27 (19)
C2B—N1B—H11B	106.6 (15)	O4B—C3B—C2B	111.23 (18)
C5B—N1B—H12B	106.7 (15)	N1B—C5B—C6B	109.70 (19)
O11A—C1A—C6A	114.67 (18)	O4B—C6B—C5B	111.47 (19)
C2A—C1A—C6A	120.75 (19)	N1B—C2B—H21B	110.00
O11A—C1A—C2A	124.57 (19)	N1B—C2B—H22B	110.00
C1A—C2A—C3A	117.77 (19)	C3B—C2B—H21B	110.00
C13A—C3A—C4A	118.09 (16)	C3B—C2B—H22B	110.00
C2A—C3A—C4A	123.29 (19)	H21B—C2B—H22B	108.00
C13A—C3A—C2A	118.62 (16)	O4B—C3B—H31B	109.00
C3A—C4A—C5A	117.18 (19)	O4B—C3B—H32B	109.00
C15A—C5A—C6A	119.03 (16)	C2B—C3B—H31B	109.00
C15A—C5A—C4A	118.85 (16)	C2B—C3B—H32B	109.00
C4A—C5A—C6A	122.1 (2)	H31B—C3B—H32B	108.00
C1A—C6A—C5A	118.84 (19)	N1B—C5B—H51B	110.00
O11A—C12A—C13A	113.95 (18)	N1B—C5B—H52B	110.00
O14A—C13A—C12A	115.08 (19)	C6B—C5B—H51B	110.00
O13A—C13A—O14A	125.4 (2)	C6B—C5B—H52B	110.00
O13A—C13A—C12A	119.5 (2)	H51B—C5B—H52B	108.00
C3A—C2A—H2A	121.00	O4B—C6B—H61B	109.00
C1A—C2A—H2A	121.00	O4B—C6B—H62B	109.00
C3A—C4A—H4A	121.00	C5B—C6B—H61B	109.00
C5A—C4A—H4A	121.00	C5B—C6B—H62B	109.00
C5A—C6A—H6A	121.00	H61B—C6B—H62B	108.00
C1A—C6A—H6A	121.00		
C12A—O11A—C1A—C2A	-8.1 (3)	C1A—C2A—C3A—C13A	178.48 (16)
C12A—O11A—C1A—C6A	172.70 (18)	C13A—C3A—C4A—C5A	-178.43 (16)
C1A—O11A—C12A—C13A	-76.5 (2)	C2A—C3A—C4A—C5A	1.5 (3)



C3B—O4B—C6B—C5B	62.3 (2)	C3A—C4A—C5A—C15A	-179.46 (16)
C6B—O4B—C3B—C2B	-61.6 (2)	C3A—C4A—C5A—C6A	0.2 (3)
C2B—N1B—C5B—C6B	51.4 (3)	C4A—C5A—C6A—C1A	-1.8 (3)
C5B—N1B—C2B—C3B	-51.2 (3)	C15A—C5A—C6A—C1A	177.83 (16)
C2A—C1A—C6A—C5A	1.8 (3)	O11A—C12A—C13A—O13A	15.0 (3)
O11A—C1A—C2A—C3A	-179.44 (19)	O11A—C12A—C13A—O14A	-167.02 (18)
C6A—C1A—C2A—C3A	-0.3 (3)	N1B—C2B—C3B—O4B	56.1 (2)
O11A—C1A—C6A—C5A	-178.92 (19)	N1B—C5B—C6B—O4B	-56.9 (2)
C1A—C2A—C3A—C4A	-1.5 (3)		

## Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1B—H11B...O13A	0.88 (2)	2.07 (2)	2.892 (3)	156 (2)
N1B—H11B...O14A	0.88 (2)	2.26 (2)	2.988 (3)	141 (2)
N1B—H12B...O14A <sup>i</sup>	0.88 (2)	1.87 (2)	2.737 (3)	170 (2)
C12A—H12A...O13A <sup>ii</sup>	0.99	2.41	3.398 (3)	173

Symmetry codes: (i)  $x-1, y, z$ ; (ii)  $x+1, y, z$ .(IV) Tetrahydro-2*H*-1,4-oxazin-4-ium (2,4-dichlorophenoxy)acetate

## Crystal data

 $C_4H_{10}NO^+ \cdot C_8H_5Cl_2O_3^-$  $M_r = 308.15$ Monoclinic,  $P2_1/c$ 

Hall symbol: -P 2ybc

 $a = 9.3657$  (5) Å $b = 7.1702$  (3) Å $c = 21.1340$  (11) Å $\beta = 97.981$  (5)° $V = 1405.48$  (12) Å<sup>3</sup> $Z = 4$  $F(000) = 640$  $D_x = 1.456$  Mg m<sup>-3</sup>Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 2359 reflections

 $\theta = 3.6$ – $28.4$ ° $\mu = 0.47$  mm<sup>-1</sup> $T = 200$  K

Plate, colourless

 $0.35 \times 0.35 \times 0.12$  mm

## Data collection

Oxford Diffraction Gemini-S CCD-detector  
diffractometer

Radiation source: Enhance (Mo) X-ray source

Graphite monochromator

Detector resolution: 16.077 pixels mm<sup>-1</sup> $\omega$  scansAbsorption correction: multi-scan  
(CrysAlis PRO; Agilent, 2014) $T_{\min} = 0.933$ ,  $T_{\max} = 0.980$ 

6400 measured reflections

2754 independent reflections

2273 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.026$  $\theta_{\max} = 26.0$ °,  $\theta_{\min} = 3.4$ ° $h = -9 \rightarrow 11$  $k = -8 \rightarrow 8$  $l = -26 \rightarrow 20$ 

## Refinement

Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.038$  $wR(F^2) = 0.091$  $S = 1.04$ 

2754 reflections

178 parameters

2 restraints

Primary atom site location: structure-invariant  
direct methodsSecondary atom site location: difference Fourier  
mapHydrogen site location: inferred from  
neighbouring sitesH atoms treated by a mixture of independent  
and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.3419P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.28 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.26 \text{ e } \text{\AA}^{-3}$$

*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 esds are taken into account in the estimation of distances, angles and torsion angles

**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  $F^2 > 2\text{sigma}(F^2)$  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 ( $\text{\AA}^2$ )*

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl2A	0.23659 (5)	0.74483 (6)	0.41042 (2)	0.0354 (2)
Cl4A	0.15479 (6)	0.32605 (9)	0.19759 (2)	0.0500 (2)
O11A	0.13251 (13)	0.42531 (17)	0.47171 (6)	0.0276 (4)
O13A	0.34279 (13)	0.1659 (2)	0.50395 (7)	0.0390 (5)
O14A	0.19747 (12)	-0.01154 (18)	0.55307 (6)	0.0313 (4)
C1A	0.13210 (17)	0.3923 (3)	0.40846 (8)	0.0236 (5)
C2A	0.18091 (18)	0.5368 (3)	0.37274 (9)	0.0255 (5)
C3A	0.18796 (19)	0.5185 (3)	0.30830 (9)	0.0305 (6)
C4A	0.14433 (19)	0.3520 (3)	0.27899 (9)	0.0319 (6)
C5A	0.0933 (2)	0.2087 (3)	0.31247 (10)	0.0348 (6)
C6A	0.08662 (19)	0.2287 (3)	0.37705 (9)	0.0306 (6)
C12A	0.10285 (19)	0.2707 (3)	0.51091 (9)	0.0270 (6)
C13A	0.22590 (18)	0.1309 (2)	0.52275 (8)	0.0226 (5)
O4B	0.56703 (19)	0.3986 (3)	0.31170 (7)	0.0591 (6)
N1B	0.55499 (17)	0.2047 (2)	0.42729 (8)	0.0293 (5)
C2B	0.5720 (2)	0.4092 (3)	0.42590 (10)	0.0353 (7)
C3B	0.6444 (3)	0.4633 (3)	0.37002 (11)	0.0509 (8)
C5B	0.5609 (3)	0.2016 (4)	0.31253 (11)	0.0541 (9)
C6B	0.4830 (2)	0.1326 (3)	0.36568 (11)	0.0412 (7)
H3A	0.22200	0.61780	0.28470	0.0370*
H5A	0.06260	0.09580	0.29130	0.0420*
H6A	0.05060	0.12950	0.40010	0.0370*
H12A	0.01550	0.20560	0.49020	0.0320*
H13A	0.08180	0.31880	0.55260	0.0320*
H11B	0.6420 (17)	0.149 (3)	0.4381 (9)	0.0350*
H12B	0.507 (2)	0.180 (3)	0.4587 (8)	0.0350*
H21B	0.63050	0.45170	0.46590	0.0420*
H22B	0.47630	0.46970	0.42270	0.0420*
H31B	0.65250	0.60090	0.36850	0.0610*
H32B	0.74300	0.41080	0.37530	0.0610*
H51B	0.66010	0.15050	0.31820	0.0650*
H52B	0.51060	0.15630	0.27110	0.0650*
H61B	0.38150	0.17540	0.35850	0.0490*

H62B            0.48330            -0.00540            0.36630            0.0490\*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl2A	0.0474 (3)	0.0221 (3)	0.0376 (3)	-0.0043 (2)	0.0088 (2)	0.0006 (2)
Cl4A	0.0576 (4)	0.0620 (4)	0.0312 (3)	0.0069 (3)	0.0087 (2)	-0.0094 (3)
O11A	0.0339 (7)	0.0222 (7)	0.0274 (7)	0.0037 (6)	0.0072 (5)	0.0055 (6)
O13A	0.0247 (7)	0.0429 (9)	0.0524 (9)	0.0066 (6)	0.0162 (6)	0.0154 (7)
O14A	0.0291 (7)	0.0282 (7)	0.0368 (8)	0.0031 (6)	0.0056 (6)	0.0117 (6)
C1A	0.0202 (8)	0.0236 (9)	0.0265 (10)	0.0059 (7)	0.0019 (7)	0.0052 (8)
C2A	0.0228 (9)	0.0222 (9)	0.0315 (10)	0.0032 (8)	0.0036 (7)	0.0015 (8)
C3A	0.0290 (10)	0.0325 (11)	0.0307 (11)	0.0034 (9)	0.0063 (8)	0.0071 (9)
C4A	0.0295 (10)	0.0386 (12)	0.0268 (10)	0.0064 (9)	0.0010 (8)	-0.0019 (9)
C5A	0.0328 (10)	0.0302 (11)	0.0389 (12)	-0.0021 (9)	-0.0040 (9)	-0.0053 (9)
C6A	0.0283 (10)	0.0260 (10)	0.0363 (11)	-0.0026 (8)	0.0003 (8)	0.0041 (9)
C12A	0.0259 (9)	0.0278 (10)	0.0288 (10)	0.0031 (8)	0.0090 (7)	0.0080 (8)
C13A	0.0236 (9)	0.0225 (9)	0.0214 (9)	0.0011 (8)	0.0025 (7)	-0.0005 (8)
O4B	0.0774 (12)	0.0641 (12)	0.0344 (9)	-0.0058 (10)	0.0026 (8)	0.0203 (9)
N1B	0.0245 (8)	0.0311 (9)	0.0338 (9)	0.0047 (7)	0.0089 (7)	0.0114 (8)
C2B	0.0385 (11)	0.0292 (11)	0.0367 (12)	0.0044 (9)	0.0001 (9)	0.0014 (9)
C3B	0.0611 (15)	0.0443 (14)	0.0466 (14)	-0.0155 (12)	0.0046 (11)	0.0164 (12)
C5B	0.0596 (15)	0.0678 (18)	0.0337 (13)	0.0014 (14)	0.0025 (11)	-0.0126 (13)
C6B	0.0362 (11)	0.0337 (12)	0.0524 (14)	-0.0035 (10)	0.0012 (10)	-0.0015 (10)

*Geometric parameters (Å, °)*

Cl2A—C2A	1.737 (2)	C5A—C6A	1.382 (3)
Cl4A—C4A	1.7466 (19)	C12A—C13A	1.522 (3)
O11A—C1A	1.357 (2)	C3A—H3A	0.9500
O11A—C12A	1.434 (2)	C5A—H5A	0.9500
O13A—C13A	1.241 (2)	C6A—H6A	0.9500
O14A—C13A	1.254 (2)	C12A—H12A	0.9900
O4B—C5B	1.414 (4)	C12A—H13A	0.9900
O4B—C3B	1.418 (3)	C2B—C3B	1.492 (3)
N1B—C2B	1.476 (3)	C5B—C6B	1.506 (3)
N1B—C6B	1.474 (3)	C2B—H21B	0.9900
N1B—H12B	0.870 (18)	C2B—H22B	0.9900
N1B—H11B	0.908 (18)	C3B—H31B	0.9900
C1A—C2A	1.396 (3)	C3B—H32B	0.9900
C1A—C6A	1.386 (3)	C5B—H51B	0.9900
C2A—C3A	1.379 (3)	C5B—H52B	0.9900
C3A—C4A	1.380 (3)	C6B—H61B	0.9900
C4A—C5A	1.371 (3)	C6B—H62B	0.9900
C1A—O11A—C12A	117.39 (15)	C13A—C12A—H12A	109.00
C3B—O4B—C5B	109.44 (17)	O11A—C12A—H12A	109.00
C2B—N1B—C6B	111.61 (16)	C13A—C12A—H13A	109.00

C6B—N1B—H11B	110.6 (12)	O11A—C12A—H13A	109.00
C2B—N1B—H12B	106.6 (14)	H12A—C12A—H13A	108.00
H11B—N1B—H12B	105.0 (17)	N1B—C2B—C3B	109.65 (17)
C2B—N1B—H11B	110.3 (13)	O4B—C3B—C2B	111.7 (2)
C6B—N1B—H12B	112.4 (12)	O4B—C5B—C6B	111.2 (2)
O11A—C1A—C6A	125.33 (17)	N1B—C6B—C5B	109.52 (17)
C2A—C1A—C6A	118.12 (16)	N1B—C2B—H21B	110.00
O11A—C1A—C2A	116.55 (17)	N1B—C2B—H22B	110.00
C1A—C2A—C3A	121.85 (19)	C3B—C2B—H21B	110.00
C12A—C2A—C3A	118.83 (16)	C3B—C2B—H22B	110.00
C12A—C2A—C1A	119.32 (14)	H21B—C2B—H22B	108.00
C2A—C3A—C4A	118.28 (19)	O4B—C3B—H31B	109.00
C3A—C4A—C5A	121.29 (18)	O4B—C3B—H32B	109.00
C14A—C4A—C3A	118.72 (15)	C2B—C3B—H31B	109.00
C14A—C4A—C5A	119.99 (16)	C2B—C3B—H32B	109.00
C4A—C5A—C6A	119.92 (19)	H31B—C3B—H32B	108.00
C1A—C6A—C5A	120.52 (18)	O4B—C5B—H51B	109.00
O11A—C12A—C13A	113.66 (14)	O4B—C5B—H52B	109.00
O14A—C13A—C12A	114.26 (15)	C6B—C5B—H51B	109.00
O13A—C13A—O14A	126.00 (15)	C6B—C5B—H52B	109.00
O13A—C13A—C12A	119.72 (15)	H51B—C5B—H52B	108.00
C4A—C3A—H3A	121.00	N1B—C6B—H61B	110.00
C2A—C3A—H3A	121.00	N1B—C6B—H62B	110.00
C4A—C5A—H5A	120.00	C5B—C6B—H61B	110.00
C6A—C5A—H5A	120.00	C5B—C6B—H62B	110.00
C5A—C6A—H6A	120.00	H61B—C6B—H62B	108.00
C1A—C6A—H6A	120.00		
C12A—O11A—C1A—C2A	-171.22 (15)	C6A—C1A—C2A—C3A	-1.6 (3)
C12A—O11A—C1A—C6A	9.2 (2)	C12A—C2A—C3A—C4A	179.56 (14)
C1A—O11A—C12A—C13A	72.91 (19)	C1A—C2A—C3A—C4A	0.4 (3)
C5B—O4B—C3B—C2B	-61.7 (2)	C2A—C3A—C4A—C14A	-179.24 (14)
C3B—O4B—C5B—C6B	61.5 (3)	C2A—C3A—C4A—C5A	0.9 (3)
C6B—N1B—C2B—C3B	-52.8 (2)	C14A—C4A—C5A—C6A	179.27 (15)
C2B—N1B—C6B—C5B	52.8 (2)	C3A—C4A—C5A—C6A	-0.9 (3)
O11A—C1A—C6A—C5A	-178.82 (17)	C4A—C5A—C6A—C1A	-0.5 (3)
C2A—C1A—C6A—C5A	1.6 (3)	O11A—C12A—C13A—O13A	6.5 (2)
O11A—C1A—C2A—C3A	178.80 (16)	O11A—C12A—C13A—O14A	-175.12 (14)
C6A—C1A—C2A—C12A	179.20 (14)	N1B—C2B—C3B—O4B	57.1 (2)
O11A—C1A—C2A—C12A	-0.4 (2)	O4B—C5B—C6B—N1B	-57.3 (2)

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1B—H11B...O13A <sup>i</sup>	0.91 (2)	2.56 (2)	3.115 (2)	120 (1)
N1B—H11B...O14A <sup>i</sup>	0.91 (2)	1.79 (2)	2.683 (2)	169 (2)
N1B—H12B...O13A	0.87 (2)	1.92 (2)	2.747 (2)	158 (2)
C12A—H12A...O14A <sup>ii</sup>	0.99	2.50	3.484 (2)	173

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$C2B-H21B \cdots O11A^{iii}$	0.99	2.57	3.477 (2)	151
$C5B-H52B \cdots O4B^{iv}$	0.99	2.58	3.489 (3)	153

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