Two-dimensional hydrogen-bonded polymers in the crystal structures of the ammonium salts of phenoxyacetic acid, (4-fluorophenoxy)acetic acid and (4-chloro-2-methylphenoxy)acetic acid

Graham Smith

*Acta Cryst.* (2014). *E70*, 528–532
Two-dimensional hydrogen-bonded polymers in the crystal structures of the ammonium salts of phenoxyacetic acid, (4-fluorophenoxy)acetic acid and (4-chloro-2-methylphenoxy)acetic acid

Graham Smith

Science and Engineering Faculty, Queensland University of Technology, GPO Box 2434, Brisbane, Queensland 4001, Australia. *Correspondence e-mail: g.smith@qut.edu.au

The structures of the ammonium salts of phenoxyacetic acid, \( \text{NH}_4^+\cdot\text{C}_8\text{H}_6\text{O}_3^- \), (I), (4-fluorophenoxy)acetic acid, \( \text{NH}_4^+\cdot\text{C}_8\text{H}_5\text{FO}_3^- \), (II), and the herbicidally active (4-chloro-2-methylphenoxy)acetic acid (MCPA), \( \text{NH}_4^+\cdot\text{C}_9\text{H}_8\text{ClO}_3^-\cdot0.5\text{H}_2\text{O} \), (III) have been determined. All have two-dimensional layered structures based on inter-species ammonium N—H—O hydrogen-bonding associations, which give core substructures consisting primarily of conjoined cyclic motifs. The crystals of (I) and (II) are isomorphous with the core comprising \( \text{R}^1_2(5) \), \( \text{R}^1_2(4) \) and centrosymmetric \( \text{R}^4_2(8) \) ring motifs, giving two-dimensional layers lying parallel to (100). In (III), the water molecule of solvation lies on a crystallographic twofold rotation axis and bridges two carboxyl O atoms in an \( \text{R}^4_3(12) \) hydrogen-bonded motif, creating two \( \text{R}^4_3(10) \) rings, which together with a conjoined centrosymmetric \( \text{R}^4_2(8) \) ring incorporating both ammonium cations, generate two-dimensional layers lying parallel to (100). No \( \pi-\pi \) ring associations are present in any of the structures.

1. Chemical context

The crystal structures of the ammonium salts of carboxylic acids are, despite their simple formulae, characterized by the presence of a complex array of hydrogen-bonding interactions. From a study of the packing motifs of the these ammonium carboxylate salts from examples in the Cambridge Structural Database (Groom & Allen, 2014), Odendal et al. (2010) found that two-dimensional hydrogen-bonded nets, ladders or cubane-type structures could be predicted on the basis of the size and conformation of the anions. These structures are often stabilized by \( \pi-\pi \) aromatic ring interactions. With the benzoic acid analogues, two-dimensional sheet structures are common with interactions involving the ammonium cations and the carboxylate anions in N—H—O hydrogen bonding, forming core layer structures, with the aromatic rings occupying the interstitial cell regions, e.g. with benzoic acid (Odendal et al., 2010), 3-nitrobenzoic acid (Eppel & Bernstein, 2009) and 2,4-dichlorobenzoic acid (Smith, 2014). Three-dimensional structures are usually only formed when interactive substituent groups are present on the benzoate rings, interlinking the layers e.g. with 3,5-dinitrobenzoic acid (Smith, 2014). The presence of water molecules of solvation may also produce a similar effect, although these are usually confined to the primary cation—anion layers.

With the phenoxyacetic acid analogues, which comprise a number of herbicidally active commercial herbicides...
(Zumdahl, 2010), this should also be the case. In the only reported structure of an ammonium salt of a phenoxyacetic acid [with the commercially important herbicide, the 2,4-dichloro-substituted analogue (2,4-D) (a hemihydrate) (Liu et al, 2009)], the expected two-dimensional layered structure is found. Herein are reported the preparation and structures of the anhydrous ammonium salts of the parent phenoxyacetic acid, \( \text{NH}_4^+\text{C}_8\text{H}_7\text{O}_3^- \) (I) and (4-fluorophenoxy)acetic acid, \( \text{NH}_4^+\text{C}_8\text{H}_5\text{FO}_3^- \) (II) and the hemihydrate salt of the herbicidally active (4-chloro-2-methylphenoxy)acetic acid (MCPA), \( \text{NH}_4^+\text{C}_9\text{H}_8\text{ClO}_3^-\cdot0.5\text{H}_2\text{O} \) (III). The structure of a hydrated chloromethylammonium salt of MCPA is known (Pernak et al., 2011).

2. Structural commentary

In the structures of the isomorphous ammonium phenoxyacetate (I) and (4-fluorophenoxy)acetate (II) (Figs. 1 and 2, respectively), the anionic species are essentially planar; the comparative defining torsion angles in the phenoxyacetate side chain (C2—C1—O11—C12, C1—O11—C12—C13 and O11—C12—C13—O14) are 178.93 (19), −177.48 (18) and −173.58 (18)°, respectively, for (I) and −179.05 (18), −178.98 (17) and −174.13 (17)°, respectively, for (II). This planarity is also found in the MCPA anion in (III) (Fig. 3) where the corresponding torsion angles are −179.13 (15), −173.34 (14) and −178.71 (15)° and is also the case with the parent acids [for (I): Kennard et al. (1982), for (II): Smith et al. (1992) and for (III): Smith & Kennard (1981; Sieron et al. (2011)]. In (III), the water molecule of solvation lies on a crystallographic twofold rotation axis.

3. Supramolecular features

In the crystals of (I) and (II), two H atoms of the ammonium group give cyclic asymmetric three-centre (bifurcated) N—H···(O, O) hydrogen-bonding interactions with the anion (Tables 1 and 2, respectively). One of these is with two O-atom acceptors of the carboxyl group (O13, O14) [graph set \( R_2^2(4) \)], the other is with the carboxyl and phenoxy O-atom acceptors (O13ii, O11ii) of an inversion-related anion [graph set \( R_2^2(5) \)]. These, together with a third N1—H13···O13ii hydrogen bond, give a cyclic \( R_2^2(8) \) ring motif, forming a series of conjoined rings which extend the structures along c. The other H atom gives structure extension through an N—H···O hydrogen bond to a carboxyl O atom (O14iii), forming a two-dimensional sheet-like structure which lies parallel to (100). Present in the crystal are short inversion-related intermolecular F4···F4iv contacts of 2.793 (2) Å [symmetry code: (iv) \(-x + 2, y, -z + 1\)].

Figure 1
Molecular conformation and atom labelling for (I), with inter-species hydrogen bonds shown as a dashed lines (see Table 1 for details). Non-H atoms are shown as 40% probability displacement ellipsoids.

Figure 2
Molecular conformation and atom labelling for (II), with inter-species hydrogen bonds shown as dashed lines (see Table 2 for details). Non-H atoms are shown as 40% probability displacement ellipsoids.

Figure 3
Molecular conformation and atom labelling for (III), with inter-species hydrogen bonds shown as dashed lines (see Table 3 for details). Non-H atoms are shown as 40% probability displacement ellipsoids.
The two-dimensional hydrogen-bonded network structure of (I), which is identical to that in isostructural (II), as shown in Fig. 4.

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

| D–H···A       | D–H   | H···A   | D··A   | D–H···A   |
|---------------|--------|---------|--------|-----------|
| N1–H11···O13  | 0.96   | 1.92    | 2.849  (3) | 163       |
| N1–H11···O14  | 0.96   | 2.55    | 3.330  (3) | 138       |
| N1–H12···O13  | 0.85   | 2.03    | 2.867  (3) | 172       |
| N1–H13···O11  | 0.90   | 2.39    | 3.202  (3) | 150       |
| N1–H13···O13  | 0.90   | 2.15    | 2.869  (3) | 136       |
| N1–H14···O14  | 0.84   | 1.95    | 2.788  (3) | 178       |

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

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

| D–H···A       | D–H   | H···A   | D··A   | D–H···A   |
|---------------|--------|---------|--------|-----------|
| N1–H11···O13  | 0.90   | 1.95    | 2.847  (2) | 177       |
| N1–H11···O14  | 0.90   | 2.55    | 3.347  (2) | 135       |
| N1–H12···O13  | 0.97   | 1.88    | 2.847  (3) | 173       |
| N1–H13···O11  | 0.96   | 2.36    | 3.172  (2) | 142       |
| N1–H13···O13  | 0.96   | 2.13    | 2.892  (2) | 135       |
| N1–H14···O14  | 0.89   | 1.91    | 2.792  (2) | 173       |

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

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

| D–H···A       | D–H   | H···A   | D··A   | D–H···A   |
|---------------|--------|---------|--------|-----------|
| N1–H11···O13  | 0.82   | 2.21    | 2.998  (4) | 161       |
| N1–H12···O14  | 0.82   | 2.09    | 2.886  (4) | 166       |
| N1–H13···O13  | 0.84   | 2.04    | 2.877  (4) | 173       |
| N1–H13···O13  | 0.84   | 2.00    | 2.798  (4) | 163       |
| O1W–H11W···O14| 0.88   | 1.95    | 2.809  (4) | 165       |

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

The crystal packing and hydrogen-bonding in (I) is identical to that in isostructural (II), as shown in Fig. 4.

Figure 5
A partial extension of the basic cation–anion hydrogen-bonding associations in the structure of (III), showing conjoined cyclic R1(12), R2(10) and R2(8) ring motifs. [Symmetry code: (iv) –x + 1, y, –z + 1/2. For other codes, see Table 3].

In the crystal of (III), centrosymmetric inter-ion R2(8) rings are formed between two ammonium cations and two O13 carboxyl O-atom acceptors and are bridged by a third ammonium H donor through O13iii, extending the structure down b (Table 3 and Fig. 5). The fourth H atom gives extension along a through N1–H12···O14ii forming an enlarged conjoined R2(12) ring, which is bridged by the water molecule of solvation lying on the twofold rotation axis, through O1W–H11W···O14 hydrogen bonds. This link effectively generates two separate R2(10) ring motifs, extending the structure along a and giving the overall two-dimensional layers lying parallel to (100) (Fig. 6). In (III), no three-centre R2(4) or R2(5) motifs to carboxyl (O,O') or carboxyl-phenoxy (O,O') acceptors such as are present in (I) and (II) are found. The structure of (III) is essentially isostructural with that of ammonium (2,4-dichlorophenoxy)acetate hemihydrate (Liu et al., 2009), with isomorphous crystals [a = 37.338 (8), b = 4.388 (9), c = 12.900 (3) Å, β = 103.82 (3)°, V = 2074.7 (8) Å³, Z = 8, space group C2/c]. No π–π interactions are found in any of the structures reported here [minimum ring centroid separation = 4.8849 (16) (I), 4.8919 (15) (II) and 4.456 (5) Å (III) (the b unit-cell parameter)].

Figure 6
The two-dimensional hydrogen-bonded network structure of (III) in the unit cell, viewed along b.
4. Synthesis and crystallization

The title compounds were prepared by the addition of excess 5 M aqueous ammonia solution to 1 mmol of either phenoxycetic acid [150 mg for (I)], (4-fluorophenoxy)acetic acid [170 mg for (II)] or (4-chloro-2-methylphenoxy)acetic acid [200 mg for (III)] in 10 mL of 10% ethanol–water. Room-temperature evaporation of the solvent gave colourless plate-like crystals of (I), (II) and (III) from which specimens were cleaved for the X-ray analyses.

5. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 4. Hydrogen atoms potentially involved in hydrogen-bonding interactions were located in difference Fourier maps but were subsequently included in the refinements with positional parameters fixed and with $U_{iso}(H) = 1.2U_{eq}(N)$ or $1.5U_{eq}(O)$. Other H atoms were included at calculated positions $[C—H(aromatic) = 0.95, C—H(methylene) = 0.98, C—H(methyl) = 0.97 \text{ Å}]$ and also treated as riding, with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms and $1.2U_{eq}(C)$ for other H atoms. In (III), the methyl group was found to be rotationally disordered, with the H atoms distributed over six equivalent half-sites, and was treated accordingly.

Acknowledgements

The author acknowledges financial support from the Science and Engineering Faculty, Queensland University of Technology.

References

Agilent (2013). *CrysAlis PRO*. Agilent Technologies Ltd, Yarnton, England.

Altomare, A., Cascaron, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* 26, 343–350.

Eppel, S. & Bernstein, J. (2009). *J. Appl. Cryst.* 42, 658–662.

Farrugia, L. J. (2012). *Acta Cryst.* C68, 528–532.

Graham Smith · NH₄⁺·C₈H₆O₃⁻ · NH₄⁺·C₉H₈ClNO₃⁻ and NH₄⁺·C₈H₈ClNO₃⁻·0.5H₂O

---

**Table 4**

| Crystal data | Chemical formula | NH₄⁺·C₈H₆O₃⁻ | NH₄⁺·C₉H₈ClNO₃⁻ | NH₄⁺·C₈H₈ClNO₃⁻·0.5H₂O |
|--------------|-----------------|---------------|-----------------|-------------------------|
| $M_r$        |                 | 187.17        | 200             | 226.65                  |
| Crystal system, space group | Monoclinic, $P2_1/c$ | 200 | 200 | 200 |
| Temperature (K) | 17.824 (2), 7.1453 (6), 6.7243 (7) | 18.386 (2), 7.1223 (6), 6.7609 (6) | 93.399 (8) | 83.79 (14) |
| No. of measured, independent and | 856.38 (15) | 883.79 (14) | 104.575 (5) |
| Radiation type | Mo Ka | Mo Ka | Mo Ka |
| $\mu$ (mm⁻¹) | 0.10 | 0.12 | 0.35 |
| Crystal size (mm) | 0.35 × 0.25 × 0.10 | 0.26 × 0.20 × 0.05 | 0.35 × 0.35 × 0.10 |

**Computer programs**: *CrysAlis PRO* (Agilent, 2013), *SIR92* (Altomare et al., 1993), *SHELXS97* and *SHELXL97* (Sheldrick, 2008) within *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).
Smith, G. & Kennard, C. H. L. (1981). *Cryst. Struct. Commun.* **10**, 295–299.

Smith, G., Lynch, D. E., Sagatys, D. S., Kennard, C. H. L. & Katekar, G. F. (1992). *Aust. J. Chem.* **45**, 1101–1108.

Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.

Zumdahl, R. L. (2010). In *A History of Weed Science in the United States*. New York: Elsevier.
Two-dimensional hydrogen-bonded polymers in the crystal structures of the ammonium salts of phenoxyacetic acid, (4-fluorophenoxy)acetic acid and (4-chloro-2-methylphenoxy)acetic acid

Graham Smith

Computing details
For all compounds, data collection: CrysAlis PRO (Agilent, 2013); cell refinement: CrysAlis PRO (Agilent, 2013); data reduction: CrysAlis PRO (Agilent, 2013). Program(s) used to solve structure: SIR92 (Altomare et al., 1993) for (I); SHELXS97 (Sheldrick, 2008) for (II), (III). 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) Ammonium phenoxyacetate

Crystal data
\[ \text{NH}_4^+ \cdot \text{C}_8\text{H}_7\text{O}_3^- \]
Mr = 169.17
Monoclinic, \( P2_1/c \)
Hall symbol: -P 2ybc
\( a = 17.824 (2) \) Å
\( b = 7.1453 (6) \) Å
\( c = 6.7243 (7) \) Å
\( \beta = 90.321 (9)^\circ \)
\( V = 856.38 (15) \) Å³
\( Z = 4 \)

\[ F(000) = 360 \]
\[ D_x = 1.312 \text{ Mg m}^{-3} \]
Mo Ka radiation, \( \lambda = 0.71073 \) Å
Cell parameters from 1041 reflections
\( \theta = 3.4-25.5^\circ \)
\( \mu = 0.10 \text{ mm}^{-1} \)
\( T = 200 \) K
Plate, colourless
0.35 \times 0.25 \times 0.10 \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 mm\(^{-1}\)
\( \omega \) scans
Absorption correction: multi-scan
\( \text{(CrysAlis PRO; Agilent, 2013)} \)
\( T_{\text{min}} = 0.920, T_{\text{max}} = 0.980 \)
5450 measured reflections
1686 independent reflections
1218 reflections with \( I > 2\sigma(I) \)
\( R_{\text{int}} = 0.052 \)
\( \theta_{\text{max}} = 26.0^\circ, \theta_{\text{min}} = 3.4^\circ \)
\( h = -21\rightarrow21 \)
\( k = -8\rightarrow8 \)
\( l = -8\rightarrow8 \)

Refinement
Refinement on \( F^2 \)
Least-squares matrix: full
\( R[F^2 > 2\sigma(F^2)] = 0.063 \)
\( wR(F^2) = 0.163 \)
\( S = 1.10 \)
1686 reflections
109 parameters
0 restraints
Primary atom site location: structure-invariant
direct methods
### Supporting Information

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

\[
w = \frac{1}{[\sigma^2(F_o^2) + (0.0706P)^2 + 0.1562P]}\]

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

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

\( \Delta \rho_{\text{max}} = 0.29 \text{ e Å}^{-3} \)

\( \Delta \rho_{\text{min}} = -0.24 \text{ e Å}^{-3} \)

**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 e.s.d.'s 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 \( F^2 > \sigma(F^2) \) 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     | \( U_{	ext{iso}} \) or \( U_{	ext{eq}} \) |
|---|-------|-------|-------|----------------|
| O11 | 0.71681 (10) | 0.4894 (2) | −0.0073 (2) | 0.0357 (6) |
| O13 | 0.58441 (10) | 0.4403 (2) | 0.1635 (3) | 0.0393 (6) |
| O14 | 0.60999 (11) | 0.6471 (2) | 0.4025 (3) | 0.0444 (7) |
| C1  | 0.78672 (14) | 0.4998 (3) | −0.0880 (4) | 0.0317 (8) |
| C2  | 0.79737 (16) | 0.4028 (3) | −0.2662 (4) | 0.0373 (9) |
| C3  | 0.86706 (17) | 0.3999 (4) | −0.3531 (4) | 0.0436 (10) |
| C4  | 0.92709 (16) | 0.4938 (4) | −0.2672 (4) | 0.0429 (9) |
| C5  | 0.91570 (16) | 0.5934 (3) | −0.0933 (4) | 0.0404 (9) |
| C6  | 0.84634 (14) | 0.5982 (3) | −0.0039 (4) | 0.0358 (9) |
| C12 | 0.70534 (14) | 0.5849 (3) | 0.1764 (3) | 0.0329 (8) |
| C13 | 0.62684 (15) | 0.5544 (3) | 0.2524 (3) | 0.0331 (8) |
| N1  | 0.43517 (12) | 0.5486 (3) | 0.2601 (3) | 0.0355 (7) |
| H2  | 0.75650 | 0.33900 | −0.32710 | 0.0450* |
| H3  | 0.87410 | 0.33280 | −0.47350 | 0.0530* |
| H4  | 0.97530 | 0.48990 | −0.32670 | 0.0520* |
| H5  | 0.95640 | 0.65960 | −0.03470 | 0.0480* |
| H6  | 0.83930 | 0.66830 | 0.11460 | 0.0430* |
| H121 | 0.71410 | 0.72050 | 0.15720 | 0.0390* |
| H122 | 0.74200 | 0.53900 | 0.27630 | 0.0390* |
| H11 | 0.48820 | 0.53280 | 0.24260 | 0.0430* |
| H12 | 0.43220 | 0.66300 | 0.29220 | 0.0430* |
| H13 | 0.40580 | 0.52630 | 0.15370 | 0.0430* |
| H14 | 0.42230 | 0.48720 | 0.36110 | 0.0430* |

### Atomic displacement parameters (Å²)

|   | \( U_{11} \) | \( U_{22} \) | \( U_{33} \) | \( U_{12} \) | \( U_{13} \) | \( U_{23} \) |
|---|-------------|-------------|-------------|-------------|-------------|-------------|
| O11 | 0.0366 (11) | 0.0331 (10) | 0.0373 (10) | −0.0020 (7) | 0.0004 (8) | −0.0089 (7) |
| O13 | 0.0446 (12) | 0.0323 (9)  | 0.0409 (10) | −0.0068 (8) | 0.0011 (8) | −0.0014 (8) |
| O14 | 0.0571 (13) | 0.0391 (11) | 0.0370 (10) | −0.0059 (9) | 0.0093 (9) | −0.0052 (8) |
| C1  | 0.0372 (15) | 0.0228 (12) | 0.0350 (13) | 0.0037 (10) | −0.0040 (11) | 0.0015 (10) |

*Acta Cryst. (2014). E70, 528-532*
Geometric parameters (Å, °)

| Bond                        | Distance (Å) | Angle (°)     |
|-----------------------------|--------------|---------------|
| O11—C1                      | 1.364 (3)     | C3—C4         |
| O11—C12                     | 1.427 (2)     | C4—C5         |
| O13—C13                     | 1.261 (3)     | C5—C6         |
| O14—C13                     | 1.245 (3)     | C12—C13       |
| N1—H12                      | 0.8500        | C2—H2         |
| N1—H13                      | 0.9000        | C3—H3         |
| N1—H14                      | 0.8400        | C4—H4         |
| N1—H11                      | 0.9600        | C5—H5         |
| C1—C6                       | 1.392 (3)     | C6—H6         |
| C1—C2                       | 1.398 (4)     | C12—H121      |
| C2—C3                       | 1.376 (4)     | C12—H122      |
| C1—O11—C12                  | 117.00 (18)   | O13—C13—O14   |
| H12—N1—H14                  | 106.00        | O13—C13—C12   |
| H13—N1—H14                  | 113.00        | C3—C2—H2     |
| H11—N1—H12                  | 102.00        | C1—C2—H2     |
| H11—N1—H13                  | 117.00        | C2—C3—H3     |
| H11—N1—H14                  | 108.00        | C4—C3—H3     |
| H12—N1—H13                  | 110.00        | C5—C4—H4     |
| O11—C1—C6                   | 124.3 (2)     | C3—C4—H4     |
| C2—C1—C6                    | 119.5 (2)     | C6—C5—H5     |
| O11—C1—C2                   | 116.3 (2)     | C4—C5—H5     |
| C1—C2—C3                    | 119.9 (2)     | C1—C6—H6     |
| C2—C3—C4                    | 120.8 (3)     | C5—C6—H6     |
| C3—C4—C5                    | 119.0 (3)     | H121—C12—H122|
| C4—C5—C6                    | 121.2 (2)     | O11—C12—H121 |
| C1—C6—C5                    | 119.7 (2)     | O11—C12—H122 |
| O11—C12—C13                 | 111.22 (18)   | C13—C12—H121 |
| O14—C13—C12                 | 115.2 (2)     | C13—C12—H122 |
| C12—O11—C1—C2               | 178.93 (19)   | C1—C2—C3—C4  |
| C12—O11—C1—C6               | −0.7 (3)      | C2—C3—C4—C5  |
| C1—O11—C12—C13              | −177.48 (18)  | C3—C4—C5—C6  |
| O11—C1—C2—C3                | −177.4 (2)    | C4—C5—C6—C1  |
| C6—C1—C2—C3                 | 2.3 (4)       | O11—C12—C13—O13|
| O11—C1—C6—C5                | 177.3 (2)     | O11—C12—C13—O14|
| C2—C1—C6—C5                 | −2.3 (3)      |
Hydrogen-bond geometry (Å, °)

|        | D—H  | H···A | D···A  | D—H···A  |
|--------|------|------|-------|----------|
| N1—H11···O13 | 0.96 | 1.92 | 2.849 (3) | 163       |
| N1—H11···O14 | 0.96 | 2.55 | 3.330 (3) | 138       |
| N1—H12···O13 | 0.85 | 2.03 | 2.867 (3) | 172       |
| N1—H13···O11 | 0.90 | 2.39 | 3.202 (3) | 150       |
| N1—H13···O13 | 0.90 | 2.15 | 2.869 (3) | 136       |
| N1—H14···O14 | 0.84 | 1.95 | 2.788 (3) | 178       |

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

(II) Ammonium (4-fluorophenoxy)acetate

Crystal data

NH₄⁺·C₈H₆FO₃⁻

Mr = 187.17

Monoclinic, P2₁/c

Hall symbol: -P 2ybc

a = 18.386 (2) Å

b = 7.1223 (6) Å

c = 6.7609 (6) Å

β = 93.399 (8)°

V = 883.79 (14) Å³

Z = 4

F(000) = 392

D_x = 1.407 Mg m⁻³

Mo Kα radiation, λ = 0.71073 Å

Cell parameters from 1311 reflections

θ = 3.3–28.0°

µ = 0.12 mm⁻¹

T = 200 K

Plate, colourless

0.26 × 0.20 × 0.05 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⁻¹

ω scans

Absorption correction: multi-scan

(CrysAlis PRO; Agilent, 2013)

T_min = 0.960, T_max = 0.980

Refinement

Refinement on F²

Least-squares matrix: full

R[F² > 2σ(F²)] = 0.053

wR(F²) = 0.116

S = 1.10

1738 reflections

118 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/[σ(Fo)² + (0.0377P)² + 0.2467P]

where P = (Fo² + 2Fc²)/3

(Δ/σ)max < 0.001

Δρ_max = 0.16 e Å⁻³

Δρ_min = −0.22 e Å⁻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 e.s.d.'s 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 $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors($gt$) etc. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$-factors based on ALL data will be even larger.

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

|      | x     | y     | z     | $U_{iso}/U_{eq}$ |
|------|-------|-------|-------|------------------|
| F4   | 0.97409 (8) | 0.4959 (2) | −0.3100 (2) | 0.0761 (6) |
| O11  | 0.70924 (8) | 0.4850 (2) | 0.0189 (2) | 0.0451 (5) |
| O13  | 0.58131 (8) | 0.4391 (2) | 0.1749 (2) | 0.0439 (5) |
| O14  | 0.60820 (8) | 0.6448 (2) | 0.4167 (2) | 0.0504 (6) |
| C1   | 0.77687 (12) | 0.4984 (3) | −0.0575 (3) | 0.0409 (8) |
| C2   | 0.78437 (13) | 0.4048 (3) | −0.2361 (3) | 0.0487 (8) |
| C3   | 0.85114 (14) | 0.4052 (4) | −0.3198 (3) | 0.0548 (9) |
| C4   | 0.90870 (13) | 0.4967 (4) | −0.2263 (4) | 0.0529 (9) |
| C5   | 0.90226 (13) | 0.5918 (4) | −0.0520 (3) | 0.0520 (9) |
| C6   | 0.83562 (12) | 0.5925 (3) | 0.0333 (3) | 0.0463 (8) |
| C12  | 0.69955 (11) | 0.5819 (3) | 0.2002 (3) | 0.0411 (7) |
| C13  | 0.62335 (12) | 0.5521 (3) | 0.2684 (3) | 0.0382 (7) |
| N1   | 0.43689 (9) | 0.5487 (3) | 0.2527 (2) | 0.0417 (6) |
| H2   | 0.74400 | 0.34140 | −0.29970 | 0.0580* |
| H3   | 0.85700 | 0.34210 | −0.44160 | 0.0660* |
| H5   | 0.94280 | 0.65620 | 0.00930 | 0.0620* |
| H6   | 0.83020 | 0.65760 | 0.15420 | 0.0560* |
| H121 | 0.70810 | 0.71780 | 0.18130 | 0.0490* |
| H122 | 0.73570 | 0.53600 | 0.30340 | 0.0490* |
| H11  | 0.48210 | 0.50970 | 0.22990 | 0.0500* |
| H12  | 0.42870 | 0.67850 | 0.28670 | 0.0500* |
| H13  | 0.40960 | 0.51140 | 0.13330 | 0.0500* |
| H14  | 0.42010 | 0.48100 | 0.35030 | 0.0500* |

**Atomic displacement parameters ($\AA^2$)**

|      | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|------|----------|----------|----------|----------|----------|----------|
| F4   | 0.0554 (10) | 0.1149 (13) | 0.0604 (10) | 0.0161 (9) | 0.0230 (8) | 0.0035 (9) |
| O11  | 0.0373 (9) | 0.0661 (11) | 0.0316 (8) | 0.0035 (7) | 0.0001 (6) | −0.0140 (7) |
| O13  | 0.0428 (9) | 0.0527 (9) | 0.0362 (9) | −0.0041 (7) | 0.0034 (7) | −0.0052 (7) |
| O14  | 0.0585 (11) | 0.0630 (10) | 0.0308 (9) | −0.0037 (8) | 0.0115 (7) | −0.0097 (8) |
| C1   | 0.0382 (13) | 0.0554 (14) | 0.0291 (12) | 0.0110 (10) | 0.0012 (9) | −0.0016 (10) |
| C2   | 0.0517 (15) | 0.0630 (16) | 0.0312 (12) | 0.0072 (12) | 0.0009 (10) | −0.0062 (11) |
| C3   | 0.0636 (17) | 0.0717 (17) | 0.0298 (12) | 0.0147 (14) | 0.0085 (11) | −0.0051 (12) |
| C4   | 0.0437 (15) | 0.0744 (17) | 0.0416 (14) | 0.0159 (13) | 0.0114 (11) | 0.0054 (12) |
| C5   | 0.0397 (14) | 0.0719 (17) | 0.0441 (14) | 0.0070 (12) | 0.0002 (11) | 0.0013 (12) |
| C6   | 0.0398 (13) | 0.0651 (16) | 0.0338 (12) | 0.0072 (11) | −0.0006 (10) | −0.0073 (11) |
| C12  | 0.0409 (13) | 0.0565 (14) | 0.0253 (11) | 0.0054 (11) | −0.0033 (9) | −0.0088 (10) |
| C13  | 0.0432 (13) | 0.0445 (12) | 0.0263 (11) | 0.0034 (10) | −0.0019 (9) | 0.0032 (10) |
| N1   | 0.0438 (11) | 0.0555 (12) | 0.0257 (9) | 0.0053 (9) | 0.0024 (8) | −0.0060 (8) |
### Geometric parameters (Å, °)

| Bond                | Distance (Å) | Angle (°) |
|---------------------|--------------|-----------|
| F4—C4               | 1.359 (3)    |           |
| O11—C1              | 1.378 (3)    |           |
| O11—C12             | 1.427 (2)    |           |
| O13—C13             | 1.260 (3)    |           |
| O14—C13             | 1.246 (2)    |           |
| N1—H13              | 0.9600       |           |
| N1—H14              | 0.8900       |           |
| N1—H11              | 0.9000       |           |
| N1—H12              | 0.9700       |           |
| C1—C6               | 1.384 (3)    |           |
| C1—C2               | 1.393 (3)    |           |
| C1—O11—C12          | 116.74 (16)  |           |
| H12—N1—H14          | 106.00       |           |
| H13—N1—H14          | 107.00       |           |
| H11—N1—H12          | 120.00       |           |
| H11—N1—H13          | 102.00       |           |
| H12—N1—H14          | 113.00       |           |
| O11—C1—C6           | 124.43 (18)  |           |
| C2—C1—C6            | 120.1 (2)    |           |
| O11—C1—C2           | 115.45 (19)  |           |
| C1—C2—C3            | 119.3 (2)    |           |
| C2—C3—C4            | 119.6 (2)    |           |
| C3—C4—C5            | 122.0 (2)    |           |
| F4—C4—C3            | 119.1 (2)    |           |
| C12—O11—C1—C2      | −179.05 (18) |           |
| C12—O11—C1—C6      | 2.5 (3)      |           |
| C1—O11—C12—C13     | −178.98 (17) |           |
| O11—C1—C2—C3       | −177.7 (2)   |           |
| C6—C1—C2—C3        | 0.8 (3)      |           |
| O11—C1—C6—C5       | 177.5 (2)    |           |
| C2—C1—C6—C5        | −0.8 (3)     |           |
| C1—C2—C3—C4        | 0.2 (4)      |           |

### Hydrogen-bond geometry (Å, °)

| Bond                | D—H     | H···A    | D···A   | D—H···A  |
|---------------------|---------|---------|---------|----------|
| N1—H11···O13        | 0.90    | 1.95    | 2.847 (2)| 177      |
| N1—H11···O14        | 0.90    | 2.55    | 3.347 (2)| 135      |
| N1—H12···O13        | 0.97    | 1.88    | 2.847 (3)| 173      |
| N1—H13···O11         | 0.96    | 2.36    | 3.172 (2)| 142      |

*Acta Cryst. (2014). E70, 528-532*
Supporting information

| N1—H13···O13ii | 0.96 | 2.13 | 2.892 (2) | 135 |
| N1—H14···O14iii | 0.89 | 1.91 | 2.793 (2) | 173 |

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

(III) Ammonium (4-chloro-2-methylphenoxy)acetate hemihydrate

Crystal data

NH₄⁺·C₉H₈ClNO₃⁻·0.5H₂O
Mr = 226.65
Monoclinic, C2/c
Hall symbol: -C 2yc
a = 38.0396 (9) Å
b = 4.4560 (8) Å
c = 12.944 (5) Å
β = 104.575 (5)°
V = 2123.5 (9) Å³
Z = 8
F(000) = 952
Dₓ = 1.418 Mg m⁻³
Mo Kα radiation, λ = 0.71073 Å
Cell parameters from 1819 reflections
θ = 4.4–28.1°
µ = 0.35 mm⁻¹
T = 200 K
Plate, colourless
0.35 × 0.35 × 0.10 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⁻¹
ω scans
Absorption correction: multi-scan
(CrysAlis PRO; Agilent, 2013)
Tmin = 0.913, Tmax = 0.980
6215 measured reflections
2087 independent reflections
1771 reflections with I > 2σ(I)
Rint = 0.030
θmax = 26.0°, θmin = 3.2°
h = −46→46
k = −5→5
l = −15→15

Refinement

Refinement on F²
Least-squares matrix: full
R[F²] = 0.036
wR(F²) = 0.091
S = 1.03
2087 reflections
132 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
Δρmax = 0.32 e Å⁻³
Δρmin = −0.28 e Å⁻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 e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of R² against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F², conventional R-factors R are based on F, with F set to zero for negative F². The threshold expression of F² > σ(F²) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F² 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   | Ueq  |
|---|-----|-----|-----|------|
| Cl4 | 0.24818 (1) | 0.32330 (12) | 0.36021 (4) | 0.0372 (2) |

Acta Cryst. (2014). E70, 528-532
### Atomic displacement parameters (\(\AA^2\))

|   | \(U^{11}\)   | \(U^{22}\)   | \(U^{33}\)   | \(U^{12}\)   | \(U^{13}\)   | \(U^{23}\)   |
|---|--------------|--------------|--------------|--------------|--------------|--------------|
| Cl4 | 0.0264 (3)   | 0.0466 (3)   | 0.0378 (3)   | -0.0121 (2)  | 0.0064 (2)   | -0.0044 (2)  |
| O11 | 0.0233 (7)   | 0.0335 (7)   | 0.0230 (6)   | -0.0071 (5)  | 0.0083 (5)   | -0.0075 (5)  |
| O13 | 0.0293 (7)   | 0.0279 (6)   | 0.0355 (7)   | -0.0036 (6)  | 0.0155 (6)   | -0.0015 (6)  |
| O14 | 0.0340 (8)   | 0.0378 (7)   | 0.0268 (7)   | -0.0094 (6)  | 0.0020 (6)   | -0.0054 (6)  |
| C1  | 0.0215 (9)   | 0.0222 (8)   | 0.0224 (9)   | -0.0010 (7)  | 0.0037 (7)   | 0.0028 (7)   |
| C2  | 0.0253 (9)   | 0.0277 (9)   | 0.0198 (8)   | 0.0005 (7)   | 0.0041 (7)   | 0.0002 (7)   |
| C3  | 0.0278 (10)  | 0.0287 (9)   | 0.0223 (9)   | -0.0021 (8)  | 0.0027 (8)   | -0.0023 (8)  |
| C4  | 0.0217 (9)   | 0.0277 (9)   | 0.0277 (9)   | -0.0031 (7)  | 0.0023 (8)   | 0.0037 (8)   |
| C5  | 0.0230 (10)  | 0.0332 (10)  | 0.0282 (9)   | 0.0003 (8)   | 0.0099 (8)   | 0.0017 (8)   |
| C6  | 0.0259 (10)  | 0.0281 (9)   | 0.0234 (9)   | -0.0011 (8)  | 0.0062 (7)   | -0.0022 (8)  |
| C12 | 0.0244 (9)   | 0.0276 (9)   | 0.0208 (8)   | -0.0026 (7)  | 0.0059 (7)   | -0.0033 (7)  |
| C13 | 0.0247 (9)   | 0.0215 (8)   | 0.0232 (9)   | 0.0029 (7)   | 0.0045 (7)   | 0.0042 (7)   |
| C21 | 0.0331 (11)  | 0.0520 (12)  | 0.0278 (10)  | -0.0083 (10) | 0.0114 (9)   | -0.0126 (9)  |
| O1W | 0.0421 (13)  | 0.0259 (10)  | 0.0667 (15)  | 0.0000       | 0.0053 (11)  | 0.0000       |
### Geometric parameters (Å, °)

|      | 1.744 (3) | 1.387 (3) | 1.397 (16) | 2.0 (3) | 1.8 (3) |
|------|-----------|-----------|------------|---------|---------|
| Cl4—C4 |          |          |            |         |         |
| O11—C1  | 1.379 (3) | 1.375 (3) |            |         |         |
| O11—C12 | 1.425 (3) | 1.386 (3) |            |         |         |
| O13—C13 | 1.263 (3) | 1.515 (3) |            |         |         |
| O14—C13 | 1.248 (3) | 0.9300    |            |         |         |
| O1W—H11W | 0.8800 | 0.9300    |            |         |         |
| O1W—H11Wi | 0.8800 | 0.9300    |            |         |         |
| N1—H12  | 0.8200    | 0.9700    |            |         |         |
| N1—H11  | 0.8200    | 0.9700    |            |         |         |
| N1—H13  | 0.8400    | 0.9600    |            |         |         |
| N1—H14  | 0.8200    | 0.9600    |            |         |         |
| C1—C2   | 1.404 (3) | 0.9600    |            |         |         |
| C1—C6   | 1.389 (3) | 0.9600    |            |         |         |
| C2—C21  | 1.509 (3) | 0.9600    |            |         |         |
| C2—C3   | 1.388 (3) | 0.9600    |            |         |         |
| C1—O11—C12 | 115.95 (13) | 120.00  |         |         |         |
| H11W—O1W—H11Wi | 107.00 | 120.00  |         |         |         |
| H12—N1—H14 | 114.00 | 120.00  |         |         |         |
| H13—N1—H14 | 104.00 | 120.00  |         |         |         |
| H11—N1—H12 | 114.00 | 120.00  |         |         |         |
| H11—N1—H13 | 105.00 | 120.00  |         |         |         |
| H11—N1—H14 | 108.00 | 120.00  |         |         |         |
| H12—N1—H13 | 111.00 | 109.00  |         |         |         |
| O11—C1—C2 | 115.26 (16) | 109.00 |         |         |         |
| O11—C1—C6 | 124.41 (15) | 109.00 |         |         |         |
| C2—C1—C6 | 120.33 (17) | 108.00  |         |         |         |
| C1—C2—C21 | 120.32 (17) | 109.00  |         |         |         |
| C1—C2—C3  | 118.30 (17) | 109.00  |         |         |         |
| C3—C2—C21 | 121.37 (16) | 109.00  |         |         |         |
| C2—C3—C4  | 120.77 (16) | 110.00  |         |         |         |
| C3—C4—C5  | 120.76 (18) | 109.00  |         |         |         |
| Cl4—C4—C3 | 119.22 (14) | 109.00  |         |         |         |
| Cl4—C4—C5 | 120.01 (15) | 109.00  |         |         |         |
| C4—C5—C6 | 119.37 (17) | 109.00  |         |         |         |
| C1—C6—C5 | 120.46 (16) | 110.00  |         |         |         |
| O11—C12—C13 | 112.31 (15) | 109.00  |         |         |         |
| O13—C13—O14 | 125.29 (18) | 110.00  |         |         |         |
| O13—C13—C12 | 120.17 (16) | 109.00  |         |         |         |
| O14—C13—C12 | 114.55 (16) | 109.00  |         |         |         |
| C12—O11—C1—C2 | −179.13 (15) | 0.2 (3)  |         |         |         |
| C12—O11—C1—C6 | 1.0 (2)  | 179.98 (17) |         |         |         |
| C1—O11—C12—C13 | −173.34 (14) | 178.25 (14) |         |         |         |
O11—C1—C2—C3  −179.57 (15)  C2—C3—C4—C5  −0.8 (3)
O11—C1—C2—C21  0.6 (2)  C14—C4—C5—C6  −178.13 (14)
C6—C1—C2—C3  0.3 (3)  C3—C4—C5—C6  0.9 (3)
C6—C1—C2—C21  −179.46 (17)  C4—C5—C6—C1  0.4 (3)
O11—C1—C6—C5  179.67 (16)  O11—C12—C13—O13  1.7 (2)
C2—C1—C6—C5  −0.2 (3)  O11—C12—C13—O14  −178.71 (15)

Symmetry code: (i) −x+1, y, −z+3/2.

Hydrogen-bond geometry (Å, º)

| D—H···A   | D—H | H···A | D···A   | D—H···A |
|-----------|------|-------|---------|---------|
| N1—H11···O13a | 0.82 | 2.21  | 2.998 (4) | 161     |
| N1—H12···O14iv | 0.82 | 2.09  | 2.886 (4) | 166     |
| N1—H13···O13v | 0.84 | 2.04  | 2.877 (4) | 173     |
| N1—H14···O13 | 0.82 | 2.00  | 2.798 (4) | 163     |
| O1W—H11W···O14 | 0.88 | 1.95  | 2.809 (4) | 165     |

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