

Ammonium hydrogen bis[(3-chloro-2-methylphenoxy)acetate]

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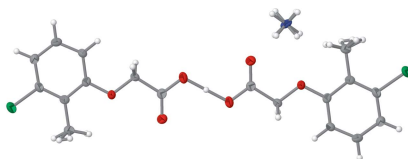
Keywords: crystal structure; phenoxyacetic acids; (3-chloro-4-methylphenoxy)acetic acid; ammonium carboxylates; hydrogen bonding.

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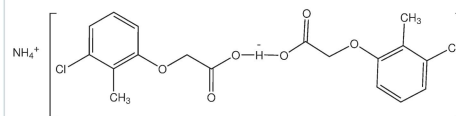
Structural data: full structural data are available from iucrdata.iucr.org

In the structure of the ammonium hydrogen salt of (3-chloro-2-methylphenoxy)acetic acid, $\text{NH}_4^+\cdot\text{C}_{18}\text{H}_{17}\text{Cl}_2\text{O}_6^-$, the dimeric anion comprises two inversion-related head-to-head components linked through a short symmetric carboxyl $\text{O}\cdots\text{H}\cdots\text{O}$ hydrogen bond in which the delocalized acid H atom lies on an inversion centre. The ammonium cation is disordered over another inversion centre. The crystal structure is based on a number of inter-species ammonium $\text{N}-\text{H}\cdots\text{O}$ hydrogen-bonding associations, giving two-dimensional layers lying parallel to (001).

3D view



Chemical scheme



Structure description

The phenoxyacetic acid analogues comprise an important group of chemicals, among which there are a number of herbicidally active commercial herbicides, including the ring-substituted members [2,4-dichloro- (2,4-D), 2,4,5-trichloro- (2,4,5-T) and 4-chloro-2-methyl- (MCPA)] (Zimdahl, 2010). The crystal structures of a large number of these acid analogs and their metal complexes are known, but the ammonium salts of only a small number have been reported, namely the hemihydrates, with 2,4-D (Liu *et al.*, 2009), with MCPA (Smith, 2014) and with (3,5-dichlorophenoxy)acetic acid (Smith, 2015), and the anhydrous salts with the parent phenoxyacetic acid and (4-fluorophenoxy)acetic acid (Smith, 2014). In these structures, the presence of characteristic two-dimensional hydrogen-bonded nets are found, predicted by Odendal *et al.* (2010) for ammonium salts of this type of monocarboxylic acid. Herein is reported the structure of the anhydrous ammonium hydrogen salt of (3-chloro-2-methylphenoxy)acetic acid, $\text{NH}_4^+\cdot\text{C}_{18}\text{H}_{17}\text{Cl}_2\text{O}_6^-$.

In the structure of the title salt, the dimeric monoanionic species is unusual in that it comprises two inversion-related components which are linked through a single delocalized carboxyl proton (H14) lying on the inversion centre at (1, 1, 0) in a short

Table 1
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>
O14—H14···O14 ⁱ	1.25	1.25	2.494 (3)	180
O14—H14···O13 ⁱ	1.25	2.55	3.326 (3)	118
N1—H10···O13 ⁱⁱⁱ	0.94 (4)	2.01 (4)	2.941 (2)	173 (6)
N1—H11···O13 ⁱⁱⁱ	0.94 (5)	1.92 (5)	2.853 (2)	171 (5)
N1—H12···O11	0.93 (3)	2.52 (4)	3.3458 (19)	147 (4)
N1—H13···O14 ^{iv}	0.93 (5)	2.29 (4)	3.194 (2)	163 (5)

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

O14···H···O14ⁱ hydrogen bond [2.493 (3) Å] (Fig. 1 and Table 1). This type of symmetric interaction (Type A) is found in the early reported potassium and rubidium hydrogen salts of 2-nitrobenzoic acid (Shrivastava & Speakman, 1961) and although no other ammonium phenoxyacetates of this type are known (Smith, 2014, 2015), the caesium–2,4-D structure has a coordinated hydrogen bis[(2,4-dichlorophenoxy)acetic acid] ligand species, with O···H···O = 2.449 (4) Å (Smith & Lynch, 2014). Other examples of ammonium and alkali metal hydrogen bis(monocarboxylates) are known, including those in which the acid H atom is disordered within the short hydrogen bond (equivalent to a 1:1:1 cation–anion–acid adduct) (Type B), *e.g.* ammonium hydrogen bis(3-bromocinnamate) (Chowdhury & Kariuki, 2006) and potassium hydrogen bis(4-nitrobenzoate) (Shrivastava & Speakman, 1961).

The H atoms of the ammonium anion are disordered over an inversion centre at N1 (0, $\frac{1}{2}$, 0) and are related by symmetry code ($-x, -y + 1, -z$). These atoms are involved in hydrogen-bonding interactions with phenoxy and carboxyl O-atom acceptors (Table 1), giving an overall two-dimensional layered structure which lies parallel to (001) (Fig. 2). This is also similar to the predicted two-dimensional layered structures in the other ammonium phenoxyacetates (Smith, 2014; 2015), as predicted by Odendal *et al.* (2010).

The phenoxyacetate species are essentially planar with the comparative defining torsion angles in the oxoacetate side chain, *viz.* C2—C1—O11—C12, C1—O11—C12—C13 and O11—C12—C13—O14 of -174.3 (2), 171.5 (2) and

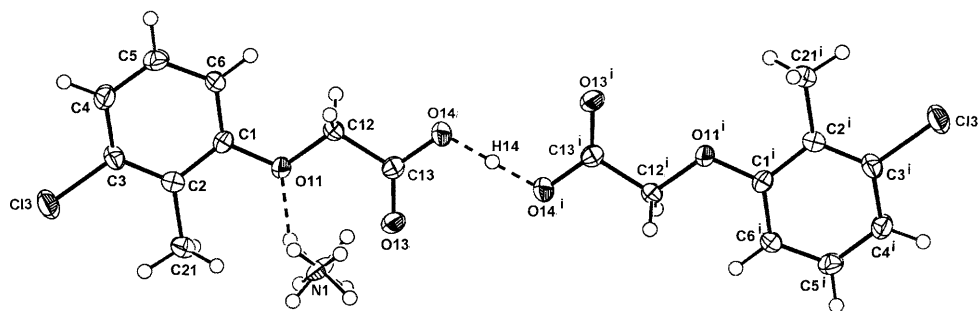


Figure 1
The molecular conformation and atom-numbering scheme for the title salt, with displacement ellipsoids drawn at the 50% probability level. The inter-species H atom (H14) and the ammonium cation are disordered over inversion centres, with the two phenoxy species related by the symmetry code (i) $-x + 2, -y + 2, -z$. H atoms of one disorder component of the rotationally disordered methyl group are not shown.

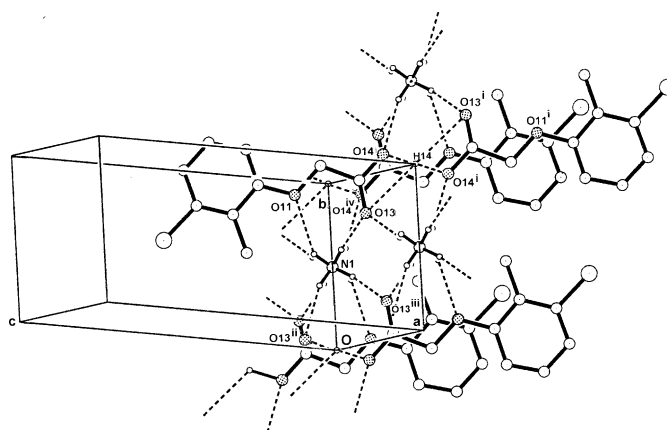


Figure 2
A perspective view of a portion of the two-dimensional hydrogen-bonded network structure of the title salt, with hydrogen bonds shown as dashed lines. Non-associative hydrogen bonds are not shown. For symmetry codes, see Table 1.

-179.3 (2)°, respectively. This planarity is also found in the parent acid (Smith, 2013) and in the majority of the phenoxyacetic acids, an exception being the 2,4-D structure (Smith *et al.*, 1976), in which the oxoacetic acid side chain adopts a *synclinal* conformation.

Synthesis and crystallization

The title compound was prepared by the addition of excess 5 M aqueous ammonia solution to 1 mmol of (3-chloro-2-methylphenoxy)acetic acid (200 mg) in 10 ml of 10% ethanol–water. Room-temperature evaporation of the solvent gave small colourless single-crystal plates suitable for the X-ray analysis.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The H atoms of the 50% disordered ammonium cation centred at (0, $\frac{1}{2}$, 0) were located by difference methods and were included in the refinements with

Table 2

Experimental details.

Crystal data	
Chemical formula	NH ₄ ⁺ ·C ₁₈ H ₁₇ Cl ₂ O ₆ ⁻
<i>M_r</i>	418.26
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	200
<i>a</i> , <i>b</i> , <i>c</i> (Å)	4.7434 (5), 6.8568 (8), 15.0374 (15)
α , β , γ (°)	100.880 (9), 92.184 (8), 103.053 (9)
<i>V</i> (Å ³)	466.21 (9)
<i>Z</i>	1
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.38
Crystal size (mm)	0.22 × 0.10 × 0.08
Data collection	
Diffractometer	Oxford Diffraction Gemini-S CCD-detector
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.92, 0.98
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	2774, 1834, 1444
<i>R_{int}</i>	0.026
(sin θ/λ) _{max} (Å ⁻¹)	0.617
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.052, 0.113, 1.05
No. of reflections	1834
No. of parameters	137
No. of restraints	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.25, -0.28

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008) within *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

N—H bond-length restraints and with their isotropic displa-

ment parameters riding and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N1})$. Carboxyl atom H14 was located at (1,1,0) and constrained in the refinement, with the displacement parameter allowed to ride, and $U_{\text{eq}}(\text{H}) = 1.5U_{\text{eq}}(\text{O14})$. The methyl group was found to be rotationally disordered, with H atoms split over six equivalent half-sites and was treated accordingly.

Acknowledgements

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full crystallographic data

IUCrData (2017). **2**, x171223 [https://doi.org/10.1107/S2414314617012238]

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Crystal data

$\text{NH}_4^+\cdot\text{C}_{18}\text{H}_{17}\text{Cl}_2\text{O}_6^-$
 $M_r = 418.26$
 Triclinic, $P\bar{1}$
 Hall symbol: -P 1
 $a = 4.7434$ (5) Å
 $b = 6.8568$ (8) Å
 $c = 15.0374$ (15) Å
 $\alpha = 100.880$ (9)°
 $\beta = 92.184$ (8)°
 $\gamma = 103.053$ (9)°
 $V = 466.21$ (9) Å³

$Z = 1$
 $F(000) = 218$
 $D_x = 1.490$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 818 reflections
 $\theta = 3.7\text{--}26.9^\circ$
 $\mu = 0.38$ mm⁻¹
 $T = 200$ K
 Prism, colourless
 $0.22 \times 0.10 \times 0.08$ 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; Rigaku OD, 2015)
 $T_{\min} = 0.92$, $T_{\max} = 0.98$

2774 measured reflections
 1834 independent reflections
 1444 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $\theta_{\max} = 26.0^\circ$, $\theta_{\min} = 3.1^\circ$
 $h = -5 \rightarrow 5$
 $k = -4 \rightarrow 8$
 $l = -18 \rightarrow 17$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.113$
 $S = 1.05$
 1834 reflections
 137 parameters
 4 restraints
 0 constraints
 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
 $w = 1/[\sigma^2(F_o^2) + (0.0364P)^2 + 0.3125P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.25$ e Å⁻³
 $\Delta\rho_{\min} = -0.28$ e Å⁻³

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cl3	-0.46252 (18)	0.64679 (12)	0.40172 (5)	0.0414 (3)	

O11	0.2641 (4)	0.8709 (3)	0.18193 (12)	0.0249 (6)	
O13	0.5974 (4)	0.7439 (3)	0.05330 (13)	0.0294 (7)	
O14	0.8485 (4)	1.0668 (3)	0.05893 (13)	0.0290 (6)	
C1	0.1228 (5)	0.9334 (4)	0.25666 (17)	0.0219 (8)	
C2	-0.0737 (6)	0.7757 (4)	0.28509 (17)	0.0227 (8)	
C3	-0.2187 (6)	0.8335 (4)	0.35999 (18)	0.0264 (9)	
C4	-0.1806 (6)	1.0340 (4)	0.40595 (18)	0.0291 (9)	
C5	0.0156 (6)	1.1828 (4)	0.37604 (19)	0.0288 (9)	
C6	0.1685 (6)	1.1348 (4)	0.30177 (18)	0.0243 (8)	
C12	0.4836 (6)	1.0238 (4)	0.15668 (18)	0.0225 (8)	
C13	0.6498 (6)	0.9288 (4)	0.08328 (18)	0.0231 (8)	
C21	-0.1208 (6)	0.5589 (4)	0.23503 (19)	0.0307 (9)	
N1	0.00000	0.50000	0.00000	0.0293 (11)	
H4	-0.28680	1.06740	0.45660	0.0350*	
H5	0.04680	1.32120	0.40690	0.0350*	
H6	0.30380	1.23920	0.28190	0.0290*	
H14	1.00000	1.00000	0.00000	0.0440*	
H121	0.61900	1.09700	0.21050	0.0270*	
H122	0.39400	1.12430	0.13420	0.0270*	
H211	-0.22140	0.46680	0.27240	0.0460*	0.500
H212	0.06720	0.52810	0.22220	0.0460*	0.500
H213	-0.23900	0.53980	0.17780	0.0460*	0.500
H214	0.03810	0.54390	0.19660	0.0460*	0.500
H215	-0.11590	0.46310	0.27650	0.0460*	0.500
H216	-0.31780	0.51360	0.20050	0.0460*	0.500
H10	-0.187 (7)	0.422 (8)	-0.022 (4)	0.0270*	0.500
H11	0.140 (11)	0.429 (8)	-0.022 (4)	0.0270*	0.500
H12	0.017 (14)	0.565 (8)	0.0609 (17)	0.0270*	0.500
H13	0.052 (13)	0.610 (6)	-0.029 (4)	0.0270*	0.500

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C13	0.0468 (5)	0.0320 (4)	0.0378 (4)	-0.0076 (3)	0.0184 (3)	0.0056 (3)
O11	0.0233 (10)	0.0210 (10)	0.0293 (10)	0.0033 (8)	0.0108 (8)	0.0028 (8)
O13	0.0264 (11)	0.0231 (11)	0.0389 (12)	0.0086 (8)	0.0082 (8)	0.0025 (9)
O14	0.0236 (10)	0.0289 (11)	0.0373 (12)	0.0067 (8)	0.0120 (9)	0.0110 (9)
C1	0.0194 (13)	0.0247 (14)	0.0225 (14)	0.0079 (11)	0.0031 (11)	0.0038 (11)
C2	0.0239 (14)	0.0198 (14)	0.0240 (14)	0.0045 (11)	0.0003 (11)	0.0047 (11)
C3	0.0233 (15)	0.0262 (15)	0.0278 (15)	-0.0002 (12)	0.0049 (11)	0.0079 (12)
C4	0.0298 (16)	0.0288 (16)	0.0261 (15)	0.0049 (12)	0.0087 (12)	0.0005 (12)
C5	0.0311 (16)	0.0209 (15)	0.0311 (15)	0.0050 (12)	0.0033 (12)	-0.0013 (12)
C6	0.0229 (14)	0.0187 (14)	0.0290 (15)	0.0008 (11)	0.0061 (11)	0.0031 (11)
C12	0.0203 (13)	0.0182 (14)	0.0271 (14)	0.0014 (10)	0.0040 (11)	0.0032 (11)
C13	0.0197 (14)	0.0254 (15)	0.0264 (15)	0.0090 (11)	0.0015 (11)	0.0065 (12)
C21	0.0373 (17)	0.0204 (15)	0.0327 (16)	0.0028 (12)	0.0080 (13)	0.0050 (12)
N1	0.0224 (19)	0.028 (2)	0.034 (2)	0.0121 (16)	-0.0011 (15)	-0.0093 (16)

Geometric parameters (Å, °)

C13—C3	1.749 (3)	C4—C5	1.373 (4)
O11—C1	1.379 (3)	C5—C6	1.383 (4)
O11—C12	1.419 (3)	C12—C13	1.514 (4)
O13—C13	1.227 (3)	C4—H4	0.9500
O14—C13	1.293 (3)	C5—H5	0.9500
O14—H14	1.2500	C6—H6	0.9500
N1—H12	0.93 (3)	C12—H122	0.9900
N1—H10	0.94 (4)	C12—H121	0.9900
N1—H11	0.94 (5)	C21—H212	0.9800
N1—H13	0.93 (5)	C21—H213	0.9800
C1—C2	1.404 (4)	C21—H211	0.9800
C1—C6	1.384 (4)	C21—H215	0.9900
C2—C21	1.497 (4)	C21—H216	1.0100
C2—C3	1.383 (4)	C21—H214	0.9800
C3—C4	1.386 (4)		
C1—O11—C12	116.2 (2)	C3—C4—H4	121.00
C13—O14—H14	115.00	C5—C4—H4	121.00
H10—N1—H11	110 (5)	C4—C5—H5	119.00
H10—N1—H12	115 (5)	C6—C5—H5	119.00
H10—N1—H13	111 (5)	C5—C6—H6	120.00
H12—N1—H13	102 (5)	C1—C6—H6	120.00
H11—N1—H12	120 (5)	O11—C12—H121	110.00
H11—N1—H13	98 (5)	O11—C12—H122	110.00
O11—C1—C6	123.7 (2)	C13—C12—H121	110.00
O11—C1—C2	114.9 (2)	C13—C12—H122	110.00
C2—C1—C6	121.5 (2)	H121—C12—H122	108.00
C1—C2—C21	120.6 (2)	H214—C21—H215	104.00
C1—C2—C3	116.3 (2)	H214—C21—H216	113.00
C3—C2—C21	123.2 (2)	H215—C21—H216	107.00
C13—C3—C4	116.8 (2)	C2—C21—H211	109.00
C2—C3—C4	123.7 (3)	C2—C21—H212	109.00
C13—C3—C2	119.5 (2)	C2—C21—H213	109.00
C3—C4—C5	117.9 (3)	C2—C21—H214	110.00
C4—C5—C6	121.2 (3)	C2—C21—H215	112.00
C1—C6—C5	119.5 (3)	C2—C21—H216	110.00
O11—C12—C13	110.4 (2)	H211—C21—H212	109.00
O13—C13—O14	126.3 (3)	H211—C21—H213	109.00
O14—C13—C12	111.1 (2)	H212—C21—H213	110.00
O13—C13—C12	122.6 (2)		
C12—O11—C1—C2	−174.3 (2)	C1—C2—C3—C4	0.5 (4)
C12—O11—C1—C6	5.3 (4)	C21—C2—C3—C13	1.9 (4)
C1—O11—C12—C13	171.5 (2)	C21—C2—C3—C4	−178.9 (3)
O11—C1—C2—C3	179.9 (2)	C13—C3—C4—C5	178.3 (2)
O11—C1—C2—C21	−0.7 (4)	C2—C3—C4—C5	−1.0 (4)

C6—C1—C2—C3	0.3 (4)	C3—C4—C5—C6	0.7 (4)
C6—C1—C2—C21	179.7 (3)	C4—C5—C6—C1	0.1 (4)
O11—C1—C6—C5	179.8 (2)	O11—C12—C13—O13	-1.3 (4)
C2—C1—C6—C5	-0.6 (4)	O11—C12—C13—O14	179.3 (2)
C1—C2—C3—C13	-178.7 (2)		

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>
O14—H14...O14 ⁱ	1.25	1.25	2.494 (3)	180
O14—H14...O13 ⁱ	1.25	2.55	3.326 (3)	118
N1—H10...O13 ⁱⁱ	0.94 (4)	2.01 (4)	2.941 (2)	173 (6)
N1—H11...O13 ⁱⁱⁱ	0.94 (5)	1.92 (5)	2.853 (2)	171 (5)
N1—H12...O11	0.93 (3)	2.52 (4)	3.3458 (19)	147 (4)
N1—H13...O14 ^{iv}	0.93 (5)	2.29 (4)	3.194 (2)	163 (5)
C21—H211...C13	0.98	2.55	3.075 (3)	113
C21—H214...O11	0.98	2.31	2.746 (3)	106

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