

Sodium hydrogen bis(phenoxyacetate)

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In the title compound, $\text{Na}^+\cdot\text{H}^+\cdot 2\text{C}_8\text{H}_7\text{O}_3^-$, the anion contains a short Speakman-type hydrogen bond $[\text{O}\cdots\text{O} = 2.413(2) \text{ \AA}]$. The anions and the Na atoms lie across twofold axes.

Comment

The structure of the title compound, (I), was determined during an investigation into the effect of impurities on the crystallization and intermolecular interactions of phenoxyacetic acid. Anhydrous sodium phenoxyacetate was crystallized from tap water to mimic the industrial manufacturing process undergoing investigation. The ratio of sodium to phenoxyacetate ions in (I) is 1:2 so an acidic H atom is required to balance the charges. H22 was located on a twofold axis between two carboxy O atoms $\text{O22}\cdots\text{O22}^i$ [symmetry code: (i) $1-x, y, \frac{z}{2}-z$] which are $2.413(2) \text{ \AA}$ apart. This hydrogen bond is very short but preceded (Freyhardt *et al.*, 2000; Speakman & Muir, 1982; Speakman *et al.*, 1981). This link is another strand which weaves around the inner ionic $\text{Na}-\text{O}-\text{Na}$ core. H22 makes another, longer bond with O21. This carboxylate O atom has close contacts with sodium ions whereas the other O atom, O22, has a closer contact with H22 [$1.215(5) \text{ \AA}$].

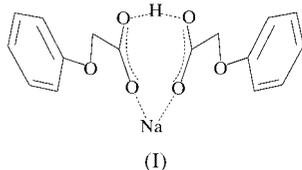


Figure 1

The asymmetric unit of (I); atoms H22 and Na1 lie on twofold rotation axes. Displacement ellipsoids are shown at the 50% probability level.

the phenoxy O atom, O1, where the $\text{Na1}-\text{O1}$ distance is $2.6102(15) \text{ \AA}$. This packing arrangement is significantly different from that in sodium phenoxyacetate hemihydrate (Prout *et al.*, 1971), where the sodium ion is surrounded by O atoms from one water and two phenoxyacetate molecules. The NaO core of (I) is surrounded on either side by the phenoxy groups which form hydrocarbon layers above and below the ionic core.

The carboxylate group is almost coplanar with the phenyl ring (angle between the planes containing COO and Ph groups, 8.2°) and several structural trends were identified in the carboxylate chain. Firstly, distortion of *exo*-O1 angles where both $\text{C15}-\text{C10}-\text{O1}$ and $\text{C11}-\text{C10}-\text{O1}$ [$123.3(18)$ and $116.34(17)^\circ$, respectively] deviate from the trigonal angle (120°). The distortion is thought to arise from the steric requirements of the carboxylate side chain, which is well documented among the phenoxyalkanoic series (Kennard *et al.*, 1982). The distances of $1.273(2)$ and $1.235(2) \text{ \AA}$ ($\text{C21}-\text{O22}$ and $\text{C21}-\text{O21}$) and the angles $111.75(16)$ and $121.59(17)^\circ$ ($\text{O22}-\text{C21}-\text{C20}$ and $\text{O21}-\text{C21}-\text{C20}$, respectively) are similar to those seen in the hemihydrate [$1.276(10)$ and $1.240(10) \text{ \AA}$; $114.2(7)$ and $117.5(7)^\circ$; Prout *et al.*, 1971].

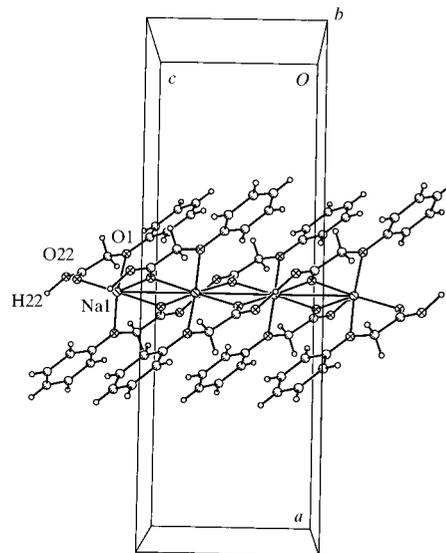


Figure 2

Packing arrangement viewed down the *b* axis. O atoms are cross-hatched and Na atoms have a diagonal stripe.

In phenoxyacetic acid, the similar C=O and C—OH distances [1.266 (3) and 1.263 (3) Å] are considered to originate from disorder of the acidic proton (Kennard *et al.*, 1982).

Experimental

A sample of powdered sodium phenoxyacetate hemihydrate (Sigma-Aldrich) was dissolved in Edinburgh tap water and single crystals of (I) were obtained by slow evaporation.

Crystal data



M_r = 326.27

Orthorhombic, *Pbcn*

a = 21.484 (3) Å

b = 9.4624 (8) Å

c = 7.3293 (7) Å

V = 1490.0 (3) Å³

Z = 4

D_x = 1.454 Mg m⁻³

Mo *K*α radiation

Cell parameters from 39

reflections

θ = 1.90–17.49°

μ = 0.135 mm⁻¹

T = 160 (2) K

Plate, colourless

0.58 × 0.34 × 0.06 mm

Data collection

Bruker *P4* diffractometer

ω scans

Absorption correction: *ψ* scan
(North *et al.*, 1968)

T_{min} = 0.966, *T_{max}* = 0.992

1814 measured reflections

1312 independent reflections

1020 reflections with *I* > 2σ(*I*)

R_{int} = 0.036

θ_{max} = 25.0°

h = −1 → 25

k = −11 → 1

l = −1 → 8

3 standard reflections

every 97 reflections

intensity decay: none

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.039

wR(*F*²) = 0.109

S = 0.959

1311 reflections

107 parameters

H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(*F_o*²) + (0.0636*P*)² + 0.2133*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.17 e Å⁻³

Δρ_{min} = −0.23 e Å⁻³

The H22 atom was located in the difference map and the coordinates were freely refined. Other H atoms were treated as riding with C—H distances in the range 0.95–0.99 Å.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Table 1

Selected geometric parameters (Å, °).

Na1—O21 ⁱ	2.3385 (15)	Na1—O1	2.6102 (15)
Na1—O21 ⁱⁱ	2.3385 (15)	Na1—Na1 ^{iv}	3.6851 (4)
Na1—O21	2.3815 (14)	Na1—Na1 ⁱⁱ	3.6851 (4)
Na1—O21 ⁱⁱⁱ	2.3815 (14)	O21—C21	1.235 (2)
Na1—O1 ⁱⁱⁱ	2.6102 (15)	O22—C21	1.273 (2)
O21—C21—C20	121.59 (17)	O22—C21—C20	111.75 (16)

Symmetry codes: (i) *x*, −*y*, *z* − ½; (ii) 1 − *x*, −*y*, 2 − *z*; (iii) 1 − *x*, *y*, ½ − *z*; (iv) 1 − *x*, −*y*, 1 − *z*.

Table 2

Hydrogen-bonding 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>
O22—H22···O22 ⁱ	1.215 (5)	1.215 (5)	2.413 (2)	166 (4)

Symmetry code: (i) 1 − *x*, *y*, ½ − *z*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1129). Services for accessing these data are described at the back of the journal.

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