

Benzylammonium hydrogen oxalate hemihydrate

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Key indicators

Single-crystal X-ray study
 $T = 120$ K
 Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.037
 wR factor = 0.095
 Data-to-parameter ratio = 15.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

α -Aminotoluene (benzylamine) reacts with ethanedioic acid (oxalic acid) to form $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3^+\cdot\text{C}_2\text{HO}_4^-\cdot 0.5\text{H}_2\text{O}$. The monohydrogenoxalate ions form hydrogen-bonded chains [2.558 (1) Å], linked into pairs by hydrogen bonds [2.758 (1) Å] to a water molecule lying on a crystallographic twofold axis. Three hydrogen bonds [2.833 (1)–2.896 (1) Å] from each benzylammonium ion connect these chains into layers.

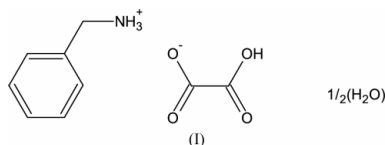
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Comment

On paper, the reaction of a simple amine with a polycarboxylic acid should yield a series of products in which the anion ranges from the fully deprotonated A^{n-} through the various possibilities of HA^{n-1} , H_2A^{n-2} etc. In practice, this happens rarely. Often only one product is isolated, regardless of the initial ratio of the components. Since crystallization from these mixtures is slow, often requiring days at room temperature, the compound obtained is likely to be the most thermodynamically stable, the deepest well in the multi-dimensional composition/energy surface. A major factor in this stability must be the ability to form an optimal extended hydrogen-bonded array. Water molecules and $-\text{COOH}$ groups play a major part in constructing these assemblies. The significance of these hydrogen-bonded networks in molecular biology has been discussed by Jeffrey & Saenger (1994). Examples from this laboratory include di- tri- and tetracarboxylates, in which the groups linking the acid functions may be rigid (Barnes *et al.*, 1991; Barnes, 1997; Barnes & Weakley, 2003) or rotationally unrestricted (Barnes & Barnes, 1996; Barnes *et al.*, 1998; Barnes & Weakley, 1998, 2000).



Oxalic acid reacts with diethylenetriamine to give crystals of the fully deprotonated $\text{C}_2\text{O}_4^{2-}$ salt as the tetrahydrate. This has been found as two polymorphs (Román *et al.*, 1997; Barnes & Weakley, 1998). More often, amine salts with oxalic acid contain the monohydrogenoxalate ion, seen, for example, in the series of $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]^{2+}$ salts (Vijayalakshmi & Srinivasan, 1983; Babu *et al.*, 1998; Barnes *et al.*, 1998). This anion also appears in the benzylammonium salt, (I), reported here. The components of (I) are shown in Fig. 1. The monohydrogenoxalate ion is not quite planar; there is a twist of 13.55 (4)° between the carboxylate groups.

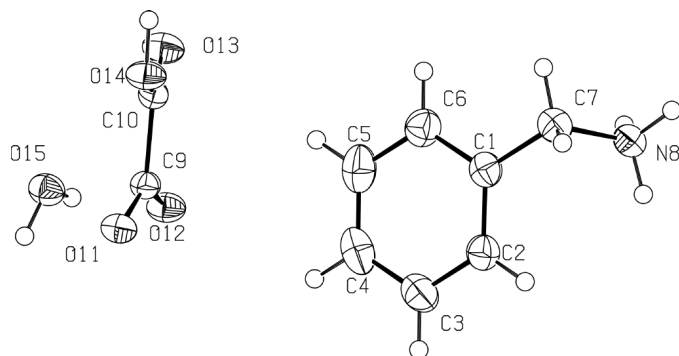


Figure 1
The components of (I), with displacement ellipsoids drawn at the 50% probability level.

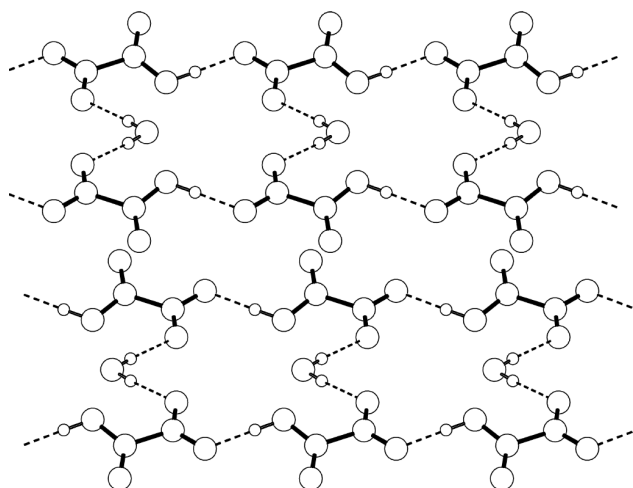


Figure 2
Mono-hydrogenoxalate chains are linked into pairs by hydrogen bonding to the water molecule. The *b* axis is horizontal.

The use of the mono-functional benzylamine in (I) restricts the possibilities for hydrogen bonding by comparison with those in the di- or triamine compounds. As before (Barnes & Weakley, 1998), the mono-hydrogenoxalate ions form linear chains. In (I), these lie parallel to the *b* axis [O14—H14...O12(*x*, 1 + *y*, *z*) 2.558 (1) Å] (Fig. 2). These chains are crosslinked by the water molecule O15, which lies on the special position ($\frac{1}{2}$, *y*, $\frac{1}{2}$), [O15—H15...O11 2.758 (1) Å]. Fig. 3 shows how layers parallel to the *bc* plane are completed by hydrogen bonds from N8 to the water molecule [N8—H82...O15(*x*, *y* - 1, *z*) 2.838 (1) Å] and to two mono-hydrogenoxalate ions [N8—H81...O11 2.896 (1) and N8—H83...O12(1 - *x*, 1 - *y*, -*z*) 2.833 (1) Å]. With the position of N8 determined by the hydrogen bonding, the torsion angle C2—C1—C7—N8 [66.48 (14)°] allows for efficient packing of the phenyl rings between the layers. Although there is good overlap between adjacent rings from adjacent layers, the interplanar distance of over 4.2 Å indicates that there is no π interaction between them.

Experimental

Crystals were grown by slow evaporation of an aqueous mixture of benzylamine (0.01 mol) and oxalic acid (0.01 mol).

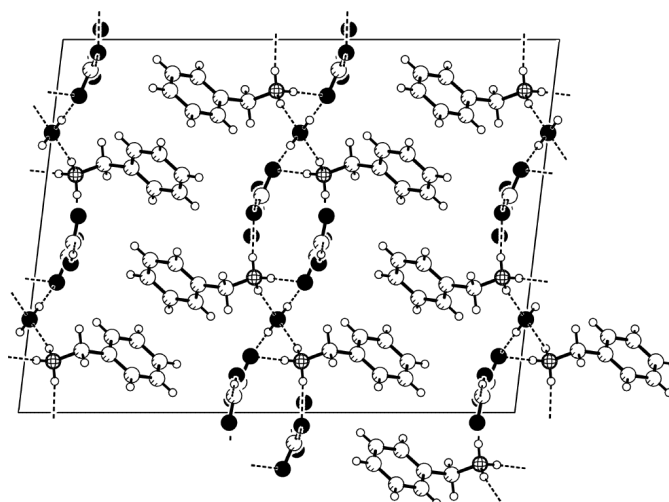


Figure 3
View down *b*, showing the inter-linking of the mono-hydrogenoxalate chains by hydrogen bonds to the benzylammonium ions. The *a* axis is horizontal.

Crystal data

$C_7H_{10}N^+ \cdot C_2HO_4^- \cdot 0.5H_2O$
 $M_r = 206.20$
Monoclinic, $C2/c$
 $a = 21.7449$ (7) Å
 $b = 5.6370$ (2) Å
 $c = 16.4499$ (5) Å
 $\beta = 96.830$ (2)°
 $V = 2002.05$ (11) Å³
 $Z = 8$

$D_x = 1.368$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 7634 reflections
 $\theta = 2.9$ – 27.5°
 $\mu = 0.11$ mm⁻¹
 $T = 120$ (2) K
Block, colourless
0.25 × 0.20 × 0.07 mm

Data collection

Enraf-Nonius KappaCCD area-detector diffractometer
 φ and ω scans
Absorption correction: none
10464 measured reflections
2284 independent reflections

1964 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.050$
 $\theta_{max} = 27.5^\circ$
 $h = -28 \rightarrow 28$
 $k = -7 \rightarrow 7$
 $l = -21 \rightarrow 20$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.095$
 $S = 1.03$
2284 reflections
152 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 0.7396P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.032$
 $\Delta\rho_{max} = 0.27$ e Å⁻³
 $\Delta\rho_{min} = -0.18$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-------------|-------------|----------------|--------------|
| C7—N8 | 1.4961 (15) | C9—C10 | 1.5487 (15) |
| C9—O11 | 1.2457 (13) | C10—O13 | 1.2046 (13) |
| C9—O12 | 1.2567 (13) | C10—O14 | 1.3109 (13) |
| O11—C9—O12 | 126.21 (10) | O13—C10—O14 | 125.88 (10) |
| O11—C9—C10 | 118.96 (9) | O13—C10—C9 | 121.26 (10) |
| O12—C9—C10 | 114.82 (9) | O14—C10—C9 | 112.84 (9) |
| C2—C1—C7—N8 | 66.48 (14) | O11—C9—C10—O13 | -165.04 (10) |

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> |
|------------------------------|-------------|---------------|-----------------------|-------------------------|
| N8—H81···O11 | 0.933 (17) | 1.964 (17) | 2.8955 (13) | 176.3 (14) |
| N8—H82···O15 ⁱ | 0.930 (16) | 1.941 (16) | 2.8397 (14) | 161.9 (13) |
| N8—H83···O12 ⁱⁱ | 0.912 (15) | 1.952 (16) | 2.8331 (13) | 161.8 (14) |
| O14—H14···O12 ⁱⁱⁱ | 0.94 (2) | 1.62 (2) | 2.5583 (11) | 178.0 (17) |
| O15—H15···O11 | 0.882 (17) | 1.881 (17) | 2.7580 (12) | 172.1 (17) |

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

H atoms attached to C atoms were placed in calculated positions and allowed to ride during the refinement, with U_{iso} constrained to be $1.3U_{\text{eq}}$ of the parent C atom. H atoms attached to O and N atoms were located in a difference synthesis. The positional and isotropic displacement parameters of these H atoms were allowed to refine.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL97*.

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Chemical Database Service (Daresbury Laboratory) (Fletcher *et al.*, 1996) and the Cambridge Structural Database (Allen, 2002).

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