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## 3-[(2-Aminoethyl)iminomethyl]-4-hydroxybenzoic Acid 0.28-Hydrate†

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### Abstract

The title compound crystallizes as a hydrated zwitterion with the site for the water molecule only partially occupied [site-occupancy factor 0.28 (1)] and a formula of $C_{10}H_{12}N_2O_3.0.28H_2O$. The hydroxyl H atom forms an intramolecular hydrogen bond to the imine N atom. The $NH_3^+$ and $COO^-$ groups of the zwitterion form a two-dimensional hydrogen-bond network that runs parallel to the *ac* plane. The water molecule forms hydrogen bonds to a hydroxyl O atom and a carboxylate O atom of adjacent molecules.

### Comment

In our work to develop ligands to form hydrogen-bonded coordination compounds, we attempted to purify compound (1) (Matsushita & Shono, 1986) by recrystallization from a mixture of dimethyl sulfoxide (DMSO) and water. Under these conditions, one of the imine groups of (1) hydrolyzes and crystals of 3-[(2-aminoethyl)iminomethyl]-4-hydroxybenzoic acid, (2), can be isolated with 0.28 molecules of water per formula unit. Compound (2) has also been prepared by Matsushita & Shono (1986) by reaction of equimolar amounts of 3-formyl-4-hydroxybenzoic acid and 1,2-ethylenediamine in ethanol. These workers correctly formulated

this compound as a zwitterion. The molecular structure and hydrogen-bond patterns of (2) are described here.
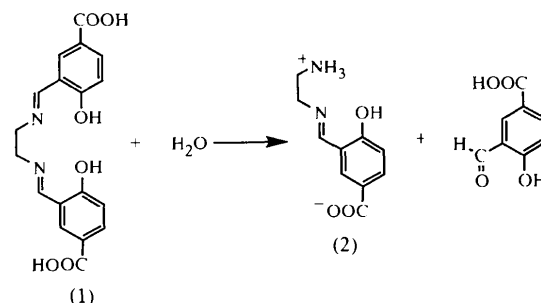


A displacement ellipsoid plot and the atom-numbering scheme for (2) are shown in Fig. 1. The crystal structure consists of the zwitterionic form of (2) and hydrate water molecules. Schiff bases like (2) can exist in either the enolimine or ketamine tautomeric forms. The C11—O11 and C18—N18 bond distances of 1.347 (4) and 1.272 (4) Å are indicative of a single and double bond, respectively, which clearly shows that the enolimine form is favored in this compound (Corden *et al.*, 1997, and references therein). Most of the non-H atoms of (2) lie nearly in a plane. The exceptions are the carboxylate O17 and O18 atoms, and the two terminal atoms of the side chain, C22 and N23. The largest deviations from the mean plane formed by all the atoms except the four just mentioned are: C21 0.110 (3), C16 −0.089 (3), C15 −0.083 (3) and C17 0.082 (2) Å. The plane formed by the three atoms at the end of the side chain (C21, C22 and N22) is approximately perpendicular to the rest of the molecule, with a dihedral angle between these three atoms and the C18, N18, C21 plane of 87.7 (4)°. The carboxylate group is tilted by 15.1 (5)° from the best plane through the six atoms of the aromatic ring. The overall shape of the molecule resembles the letter 'L' with the shorter side terminating in the ammonium group and the longer side terminating in the
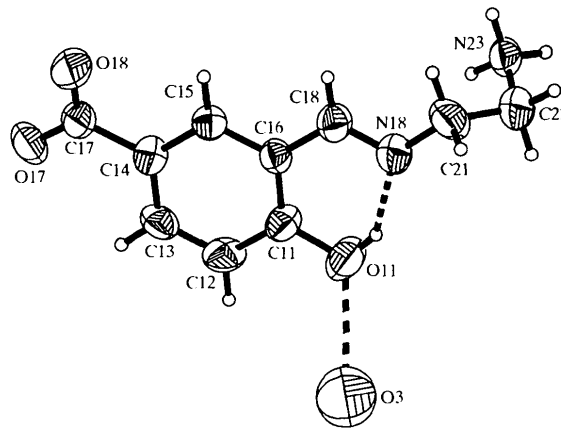


Fig. 1. The structure of (2) showing 50% probability displacement ellipsoids. H atoms have been drawn as spheres of artificially small radii.

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† Zwitterionic name: 3-[(2-ammonioethyl)iminomethyl]-4-hydroxybenzoate 0.28-hydrate.

carboxylate group. All the torsion angles in the molecule are within 5° of either 180 or 0°, except for those about the C14—C17, N18—C21, and C21—C22 bonds (Table 1). The set of torsion angles about the first bond are a consequence of the cant of the carboxylate group. The torsion angles about the latter two bonds are a result of *gauche* conformations in the side chain.

There are six unique hydrogen bonds in the structure (Table 2). Three of these interactions are discrete with one being intramolecular and two being intermolecular. The hydroxyl proton forms an intramolecular hydrogen bond to the imine N atom (fourth entry in Table 2). The solvent water molecule forms two hydrogen bonds (fifth and sixth entries in Table 2). Each proton on the ammonium group forms a hydrogen bond to a carboxylate O atom (first three entries in Table 2). These ionic hydrogen bonds form a two-dimensional hydrogen-bonded layer that runs parallel to the *ac* plane (Fig. 2). The layers can be roughly described as columns of molecules running parallel to **c**, generated by combinations of the $2_1$ symmetry operation and translations along **c**. These columns are linked to one another by hydrogen bonds generated by translations along **a**. Portions of two such columns are shown in Fig. 2. A similar layer is generated from that shown in Fig. 2 by combinations of the *n*- and *a*-glide operations, and translations along **a** and **c**. The layers are linked together through hydrogen
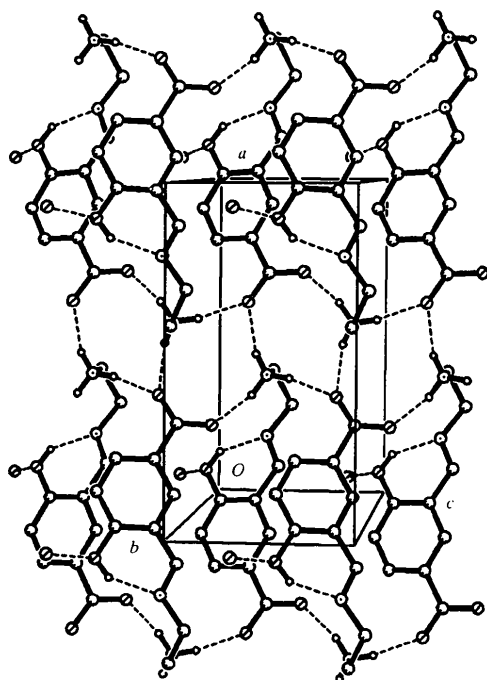


Fig. 2. View of the hydrogen bonding in (2), approximately down the *b* axis. Only H atoms involved in hydrogen bonding are shown, except for those on the partially occupied water molecule. Hydrogen bonds involving H23*A* are approximately vertical. The N23—H23*B* bond vector points towards the right of the figure. Hydrogen bonds are formed by the H23*C* atom to the singly-hydrogen-bonded carboxylate O atom.

bonds from the water molecule to a carboxylate O atom and a hydroxyl O atom in adjacent layers.

Graph-set analysis, first formulated by Etter (1990) and developed by Bernstein *et al.* (1995), clarifies the nature of the hydrogen-bonding patterns in the crystal. The first-level graph set, listed in the same order as the entries in Table 2, is $C(11)$, $C(11)$, $C(11)$, $S(6)$, $D$ and $D$. The last three descriptors identify the discrete intramolecular ($S$) and intermolecular ($D$) hydrogen bonds, respectively. The first three patterns represent the shortest path between an ammonium H atom and a carboxylate O atom in a single molecule. These graphs must pass through the entire molecule as a consequence of the criterion that the first-level motifs must contain crystallographically distinct hydrogen bonds. The motif involving the first entry is a head-to-tail linking of molecules related by translations along the *a* axis. Likewise, the patterns from the second and third entries are head-to-tail arrangements of the molecules, but these chains are generated by the $2_1$ symmetry operation along **c**.

Among the most easily seen second-level graphs is $R_2^2(22)$, which is a ring formed through hydrogen bonds between molecules related by the screw axis parallel to **c**. This ring is formed by a combination of the second and third entries from Table 2. The basic second-level graph sets (*i.e.* of lowest degree) which are generated by pairwise combination of the first three entries in Table 2 are $C(4)$ (entries 1 and 2), $C(6)$ (entries 1 and 3), and $C(6)$ (entries 2 and 3). Each of these patterns propagates in a direction parallel to **c** and can be clearly traced out in the ladder-like pattern prominent in the center of Fig. 2. The most conspicuous feature of the packing, namely the interlocking ten-membered rings, $R_3^4(10)$, shows up only in the third-level graph set because it involves all three crystallographically independent hydrogen bonds involving the ammonium group.

## Experimental

*Crystal data*

| | |
|---|---|
| $C_{10}H_{12}N_2O_3.0.28H_2O$ | Mo $K\alpha$ radiation |
| $M_r = 213.23$ | $\lambda = 0.71073$ Å |
| Orthorhombic | Cell parameters from 35 |
| $Pna2_1$ | reflections |
| $a = 11.675\,(1)$ Å | $\theta = 4.78\text{–}12.14°$ |
| $b = 14.738\,(2)$ Å | $\mu = 0.100$ mm$^{-1}$ |
| $c = 6.261\,(1)$ Å | $T = 299\,(2)$ K |
| $V = 1077.3\,(2)$ Å$^3$ | Plate |
| $Z = 4$ | $0.40 \times 0.40 \times 0.15$ mm |
| $D_x = 1.314$ Mg m$^{-3}$ | Translucent yellow |
| $D_m$ not measured | |

*Data collection*

| | |
|---|---|
| Siemens *P*4 diffractometer | $\theta_{max} = 27.49°$ |
| $\theta$–$2\theta$ scans | $h = -1 \rightarrow 15$ |
| Absorption correction: none | $k = -1 \rightarrow 19$ |
| 1532 measured reflections | $l = -1 \rightarrow 5$ |
| 1311 independent reflections | 3 standard reflections |
| 921 reflections with | every 97 reflections |
| $I > 2\sigma(I)$ | intensity decay: 2.0% |
| $R_{int} = 0.014$ | |

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.119$
$S = 1.056$
1311 reflections
141 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.055P)^2 + 0.1331P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.126$ e Å$^{-3}$
$\Delta\rho_{min} = -0.138$ e Å$^{-3}$
Extinction correction: none
Scattering factors from
*International Tables for Crystallography* (Vol. C)

Table 1. *Selected torsion angles (°)*

| | | | |
|---|---|---|---|
| C15—C14—C17—O18 | −13.4 (5) | C13—C14—C17—O17 | −15.7 (5) |
| C13—C14—C17—O18 | 162.9 (4) | C18—N18—C21—C22 | −123.6 (4) |
| C15—C14—C17—O17 | 168.0 (3) | N18—C21—C22—N23 | 65.7 (5) |

Table 2. *Hydrogen-bonding geometry (Å, °)*

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N23—H23$A$···O17$^i$ | 0.89 | 1.895 (4) | 2.748 (4) | 159.86 (16) |
| N23—H23$B$···O17$^{ii}$ | 0.89 | 1.890 (5) | 2.766 (5) | 167.78 (11) |
| N23—H23$C$···O18$^{iii}$ | 0.89 | 1.876 (5) | 2.732 (5) | 160.72 (13) |
| O11—H11···N18 | 0.82 | 1.874 (5) | 2.596 (5) | 146.25 (11) |
| O3···O11 | | | 2.675 (17) | |
| O3···O18$^{iv}$ | | | 2.921 (18) | |

Symmetry codes: (i) $x-1, y, z$; (ii) $-x, 1-y, \frac{1}{2}+z$; (iii) $-x, 1-y, z-\frac{1}{2}$; (iv) $x-\frac{1}{2}, \frac{3}{2}-y, z-1$.

All non-H atoms were refined with anisotropic displacement parameters. The H atoms were located in a difference map, positioned with idealized geometry, and refined with displacement parameters $1.2U_{eq}$ of the parent atom using a riding model. Late in the refinement, a peak in the difference map with a height of 0.58 e Å$^{-3}$ was observed. This peak was in a position at a reasonable distance for a water molecule with a hydrogen bond to O18. The peak was modeled as a water molecule with a site occupancy factor that refined to 0.28 (1). No H atoms were placed on the water molecule. The absolute structure could not be determined with the present data.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *XS* in *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *XL* in *SHELXTL*. Molecular graphics: *XP* in *SHELXTL*.

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# N—H···S and N—H···Ph Hydrogen Bonding in 1-(2-Fluorophenyl)thiourea

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## Abstract

In the title compound, $C_7H_7FN_2S$, the dominant hydrogen-bond motif is formed by ribbons of the thiourea moieties, which are linked by pairs of N—H···S=C hydrogen bonds. In addition, there is a distorted N—H···Ph hydrogen bond.

## Comment

The crystal structure of the title compound, (I), was determined in order to elucidate the hydrogen-bond interactions. The initial interest was caused by the molecular constitution of (I). The molecule contains three strong N—H hydrogen-bond donors, but only moderate and weak hydrogen-bond acceptors. S=C is known to have much weaker acceptor properties than the O=C analogue (Allen *et al.*, 1997), but it is still the strongest acceptor in (I). The next-weakest acceptor is the phenyl ring, and the weakest of all is the F atom. Organic F is known to accept hydrogen bonds only very rarely (Howard *et al.*, 1996; Dunitz & Taylor, 1997), but examples with F—$C_{sp^3}$ and F—$C_{sp^2}$ have recently been reported (Borwick *et al.*, 1997; Weiss *et al.*, 1997). In this context, it is of interest to see which kinds of hydrogen bonds would be formed in crystalline (I), where different weak acceptors compete for three strong donors.

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