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# 5-Aminoisophthalic Acid Hemihydrate

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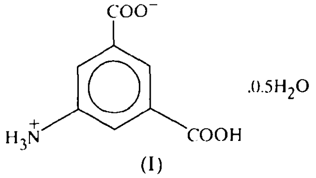
## Abstract

The title acid, $C_8H_7NO_4.0.5H_2O$, crystallized in the centrosymmetric space group *C2/c* in a zwitterionic form (5-ammonioisophthalate), with the water molecule on a twofold axis. The three ammonio H atoms and the H atom on the remaining carboxyl group, which are involved in hydrogen bonding, are ordered. Three intermolecular N—H···O hydrogen bonds have N···O distances ranging from 2.762 (2) to 2.905 (2) Å and N—H···O angles ranging from 155 (2) to 163 (2)°. Two intermolecular O—H···O hydrogen bonds have O···O distances of 2.536 (2) and 2.746 (2) Å, and O—H···O angles of 178 (2) and 176 (2)°. A three-dimensional network of hydrogen bonds is present. Through basic second-level graphs involving acid-to-acid hydrogen bonds, chains are more numerous than rings.

## Comment

This report on 5-aminoisophthalic acid hemihydrate is one of a series on hydrogen bonding in amino-substituted carboxylic acids, and follows reports on a novel tetragonal phase of $\gamma$-aminobutyric acid, on 8-aminocaprylic acid and on 3-aminoisobutyric acid monohydrate (Dobson & Gerkin, 1996, 1998*a*,*b*). The title acid crystallized in the centrosymmetric space group *C2/c* as a zwitterion, (I), one of the carboxyl protons having been transferred to the N atom. The refined molecule and the associated water molecule given in the atom list are shown in Fig. 1, together with the numbering scheme. Geometric details of five hydrogen bonds are given in Table 2. Each acid molecule is directly linked to five acid molecules and to two water molecules by a total of eight hydrogen bonds, as shown in Fig. 2. Each water molecule is directly linked to four acid molecules by four hydrogen bonds. The results of hydrogen-bond graph-set analysis (Bernstein *et al.*, 1995) involving three acid-to-acid hydrogen bonds, which are labeled *a*–*c* in the order given in Table 2, are given in Table 3 for the first-



(I)

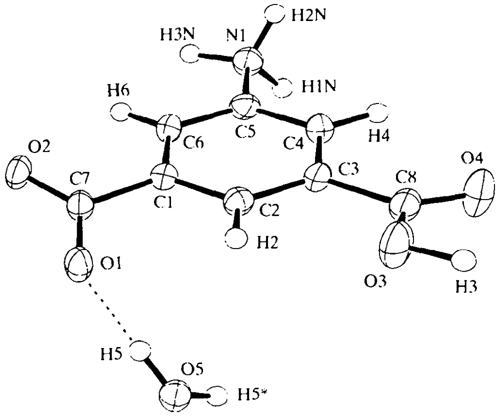


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of 5-aminoisophthalic acid hemihydrate showing the atomic numbering scheme. Displacement ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small.

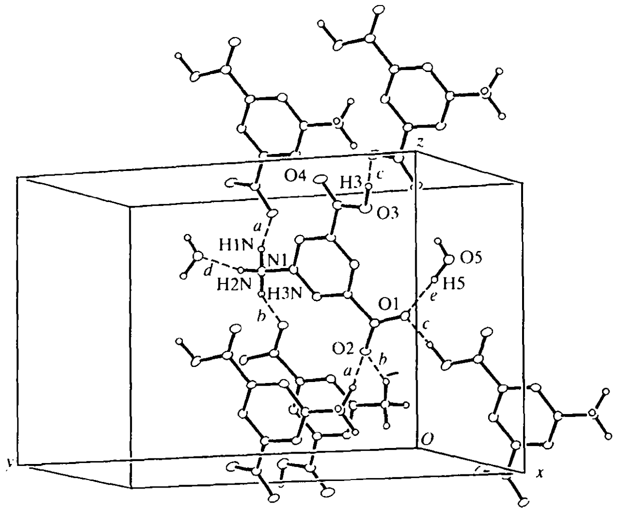


Fig. 2. *ORTEP*II (Johnson, 1976) diagram of a central 5-aminoisophthalic acid molecule and the five acid molecules and two water molecules to which it is directly hydrogen bonded. For clarity, displacement ellipsoids are drawn artificially small for all atoms, and H atoms not involved in hydrogen bonding have been omitted. Intermolecular hydrogen bonds are shown as dashed lines labeled *a*–*e* in the order given in Table 2.

and basic second-level graph sets. The tabulation shows that chains are somewhat more prominent patterns than rings in the acid-to-acid hydrogen bonding in this structure. In the order in which they are tabulated, chains propagate along **c**, $[1\bar{1}0]$, **b** and $[10\bar{1}]$. In some cases, equivalent chains propagate in other directions as well. Clearly, a three-dimensional network of acid-to-acid hydrogen bonds is present. Moreover, the hydrogen bonds involving each water molecule, labeled *d* and *e* in Fig. 2, are among the stronger hydrogen bonds in this structure.

In this structure, the benzene ring is very nearly planar; the maximum deviation of the ring C atoms from the best-fit plane describing them is 0.010 (2) Å, and the average deviation 0.006 (3) Å. The dihedral angle between the two sets of non-parallel ring planes is only 2.01 (6)°. Thus, all the ring planes are virtually parallel, as is reflected in Fig. 2. The dihedral angle between the carboxylate group plane (O1, O2, C7) and the ring plane is 16.2 (2)°, while that between the carboxyl group plane (O3, O4, C8) and the ring plane is 9.4 (2)°; the dihedral angle between these two substituent planes is 24.0 (3)°.

Distances and angles of special interest in the title molecule are given in Table 1. All distances and angles fall within normal ranges. Since the benzene ring of the title molecule has three different substituents and these are in *meta* orientations with respect to each other (so there should be no through-conjugation effects on the benzene interior bond angles), it is of interest to compare the observed interior angles with those calculated by the linear superposition procedure (see Norrestam & Schepper, 1981). Since values for the angular increments $\Delta_1$, $\Delta_2$, $\Delta_3$ and $\Delta_4$ for the $COO^-$ group are not available in the compilations of either Norrestam & Schepper (1981) or Domenicano & Murray-Rust (1979), they were derived from the observed benzene angles in the deprotonated form of 2,4,6-trinitrobenzoic acid (Lynch *et al.*, 1992) using the $\Delta_1$–$\Delta_4$ values for the $NO_2$ group of Domenicano *et al.* (1989). The values found for $COO^-$ are: $\Delta_1 = -1.9\,(3)°$, $\Delta_2 = 0.5\,(3)°$, $\Delta_3 = 1.0\,(4)°$ and $\Delta_4 = -0.7\,(3)°$. [Since only a single ion was used to derive these values, their s.u.'s are approximately three times as large as those given in the compilations cited above based on large data sets.] Using these values, the COOH values (free of through-conjugation effects) of Domenicano *et al.* (1989) and the $NH_3^+$ values of Norrestam & Schepper (1981), the interior angles of the benzene ring of the title molecule were calculated. The observed values of the interior angles at vertices $C_1$–$C_6$, with the calculated values in brackets, are: 119.4 (2) [118.4 (3)], 120.6 (1) [120.2 (4)], 120.1 (1) [121.3 (4)], 118.5 (1) [117.9 (4)], 121.8 (1) [122.8 (5)], and 119.4 (1)° [119.8 (4)°]. The r.m.s. deviation between these pairs of values is 0.7°, which may be compared with values of 0.5 and 0.6° calculated in a similar way for the related molecules 3-aminobenzoic acid (Voogd *et al.*, 1980) and isophthalic acid (Derissen, 1974), respectively. Further, when the calculated and observed interior ring angles are ordered by magnitude, the orderings differ by only a single inversion.

The closest intermolecular approaches in this structure, excluding pairs of atoms in groups hydrogen bonded to each other, occur between O2 and $H6^{iii}$ [symmetry code: (iii) $2-x$, $1-y$, $1-z$] and are 0.27 Å less than the corresponding Bondi (1964) van der Waals radius sum. It may be noted, however, that these two atoms lie in molecules hydrogen bonded to each other.

## Experimental

5-Aminoisophthalic acid was obtained as a pale tan powder from the Aldrich Chemical Company. This solid was dissolved in ethanol at room temperature and the solution was treated with decolorizing carbon and filtered. Room-temperature evaporation of the filtrate produced thick plates, one of which was cut to provide the experimental sample.

*Crystal data*

$C_8H_7NO_4.0.5H_2O$
$M_r = 190.16$
Monoclinic
$C2/c$
$a = 8.207\,(2)$ Å
$b = 17.445\,(2)$ Å
$c = 11.151\,(1)$ Å
$\beta = 93.69\,(1)°$
$V = 1593.4\,(4)$ Å$^3$
$Z = 8$
$D_x = 1.585$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.6$–$17.4°$
$\mu = 0.132$ mm$^{-1}$
$T = 296$ K
Cut plate
0.50 × 0.23 × 0.16 mm
Very pale rose

*Data collection*

Rigaku AFC-5*S* diffractometer
$\omega$–$2\theta$ scans
Absorption correction: none
2040 measured reflections
1850 independent reflections
1304 reflections with $I > 2\sigma_I$
$R_{\rm int} = 0.013$

$\theta_{\rm max} = 27.56°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 22$
$l = -14 \rightarrow 14$
6 standard reflections every 150 reflections intensity variation: ±1.6% (average maximum relative intensity)

*Refinement*

Refinement on $F^2$
$R(F) = 0.043$
$wR(F^2) = 0.074$
$S = 1.80$
1850 reflections
144 parameters
H atoms: see below
$w = 1/\sigma^2(F^2)$
$(\Delta/\sigma)_{\rm max} < 0.01$

$\Delta\rho_{\rm max} = 0.38$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.30$ e Å$^{-3}$
Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: $1.4\,(2) \times 10^{-7}$
Scattering factors from Stewart *et al.* (1965) (H) and Creagh & McAuley (1992) (C, N, O)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| O1—C7 | 1.255 (2) | O3—C8 | 1.311 (2) |
| O2—C7 | 1.258 (2) | O4—C8 | 1.212 (2) |

| | | | |
|---|---|---|---|
| N1—C5—C4 | 118.7 (2) | O2—C7—C1 | 118.7 (1) |
| N1—C5—C6 | 119.4 (2) | O3—C8—O4 | 124.3 (2) |
| O1—C7—O2 | 124.3 (2) | O3—C8—C3 | 113.1 (2) |
| O1—C7—C1 | 117.1 (1) | O4—C8—C3 | 122.6 (2) |

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

| | *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|---|
| *a* | $N1—H1N\cdots O2^{i}$ | 0.99 (2) | 1.80 (2) | 2.762 (2) | 163 (2) |
| *b* | $N1—H3N\cdots O2^{ii}$ | 1.00 (2) | 1.97 (2) | 2.905 (2) | 155 (2) |
| *c* | $O3—H3\cdots O1^{iii}$ | 1.03 (2) | 1.51 (2) | 2.536 (2) | 178 (2) |
| *d* | $N1—H2N\cdots O5^{iv}$ | 0.99 (2) | 1.83 (2) | 2.796 (2) | 163 (2) |
| *e* | $O5—H5\cdots O1$ | 0.95 (2) | 1.80 (2) | 2.746 (2) | 176 (2) |

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

Table 3. *First- and basic second-level graph set descriptors involving hydrogen bonds between acid molecules which are designated a–c in the order given in Table 2*

| | *a* | *b* | *c* |
|---|---|---|---|
| *a* | $C(7)$ | $R_4^2(8)$ | $C_2^2(11)$ |
| *b* | | $R_2^2(14)$ | $C_2^2(11)$ |
| *c* | | | $C(8)$ |

Fourier difference methods were used to locate the initial H-atom positions and the H atoms were then refined isotropically; refined C—H distances ranged from 0.98 (1) to 1.01 (1) Å, with a mean value of 0.99 (1) Å. Subsequently, the ring H atoms were made canonical, with C—H = 0.98 Å and $U_{iso} = 1.2U_{eq}$ of the attached C atom. Refined N—H and O—H distances are given in Table 2.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *MITHRIL*84 (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1449). Services for accessing these data are described at the back of the journal.

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# *cis*-4,6-Dimethyl-2-phenyl-1,3-diselenane

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## Abstract

In the crystal of the title compound, $C_{12}H_{16}Se_2$, the packing involves quadrupolar interactions, and the 1,3-diselenane cycle adopts a chair conformation. This compound was synthesized using diselenocyanate and benzaldehyde.

## Comment

The 1,3-dithianes are very interesting synthetic intermediates. Seebach & Corey (1975) have shown that these compounds, when metallated in position 2, are synthetically equivalent to acyl anions. 1,3-Diselenanes are the selenium analogues of 1,3-dithianes. We have recently shown that those bearing at least one H atom at position 2 react selectively with *n*-butyllithium and lead to give products resulting from the cleavage at C-2, of the C—Se or of the C—H bond, depending upon the nature of the substituents present at the 2, 4 and 6 positions (Krief & Defrère, 1996). The title 1,3-diselenane, (3),

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