

2-Hydroxybenzenaminium acetate

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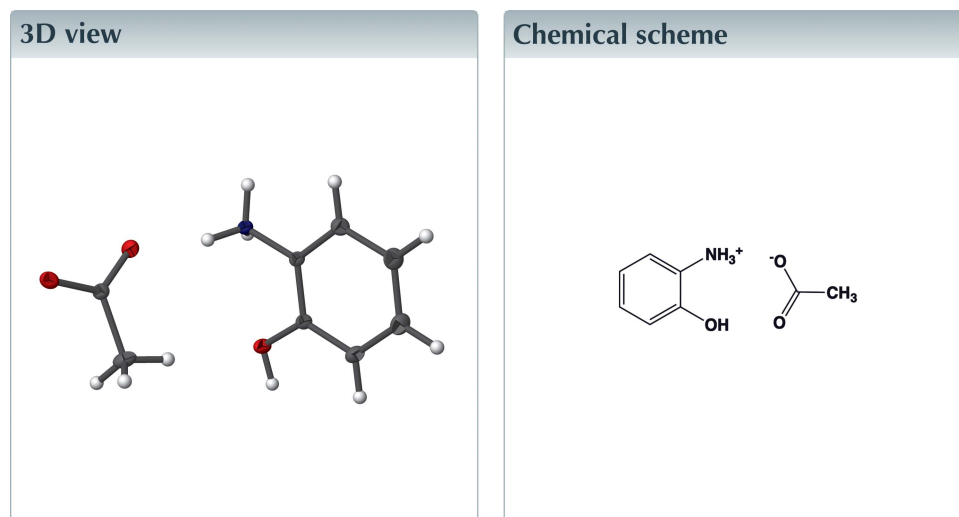
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Structural data: full structural data are available from iucrdata.iucr.org

In the title molecular salt, $C_6H_8NO^+ \cdot C_2H_3O_2^-$, the cations and anions are linked by $O-H \cdots O$ and $N-H \cdots O$ hydrogen bonds, generating a three-dimensional network.



Structure description

In recent years, substituted anilines and their derivatives have been studied extensively for applications as antibacterials and in non-linear optical systems (Vivek & Murugakoothan, 2014). Aminophenols containing equal stoichiometries of $-OH$, and $-NH_2$ groups have been widely studied to understand the supramolecular synthons existing in their assemblies (Allen *et al.*, 1997; Dey *et al.*, 2004).

In spite of this interest, there has been very little structural characterization of *ortho*-hydroxyanilinium salts. The structures reported include 2-hydroxyanilinium squarate (Yeşilel, 2007), 2-hydroxyanilinium hydrogen phthalate (Jagan & Sivakumar, 2009), 2-hydroxyanilinium 3,5-dinitrosalicylate (Smith *et al.*, 2011), 2-hydroxyanilinium 3,5-dinitrobenzoate (Zhao, 2012), and 2-hydroxyanilinium 2-hydroxy-5-nitrobenzoate and 2-hydroxyanilinium 3,5-dinitrobenzoate (Jin & Wang, 2013).

Here, we report the structure of 2-hydroxybenzenaminium acetate, $C_6H_8NO^+ \cdot C_2H_3O_2^-$, **1**, obtained from the reaction of 2-hydroxyaniline and acetic acid. The molecular structure of the title compound is shown in Fig. 1. The asymmetric unit contains one 2-hydroxybenzenaminium cation and one acetate anion. The cation is protonated at the amine N atom (N1) and linked to the anion by an $N-H \cdots O$ hydrogen bond (Fig. 1 and Table 1).

The best planes through the 2-hydroxybenzenaminium cation and acetate anion are almost perpendicular to each other, subtending a dihedral angle of $79.23(4)^\circ$. The C—

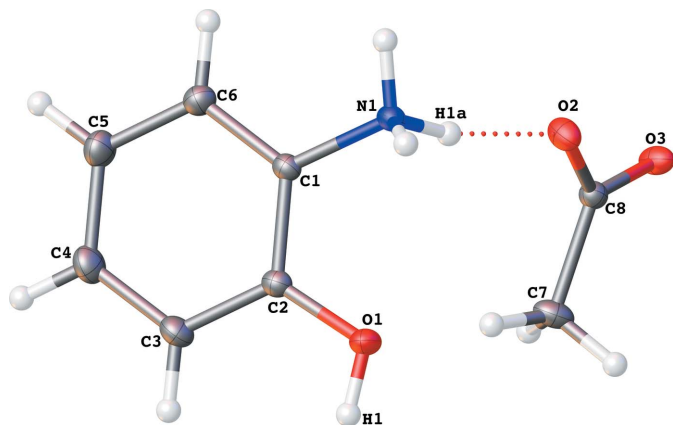


Figure 1
Diagram showing the $C_6H_8NO^+$ cation and $C_2H_3O_2^-$ anion linked by an $N-H \cdots O$ interaction (shown as a dashed line). Displacement ellipsoids are drawn at the 50% probability level.

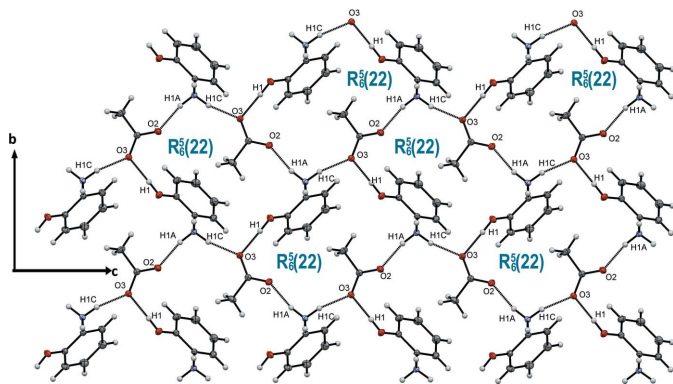


Figure 2
A portion of one corrugated layer viewed along the b -axis direction. $O-H \cdots O$ and $N-H \cdots O$ hydrogen bonds are shown as dashed lines.

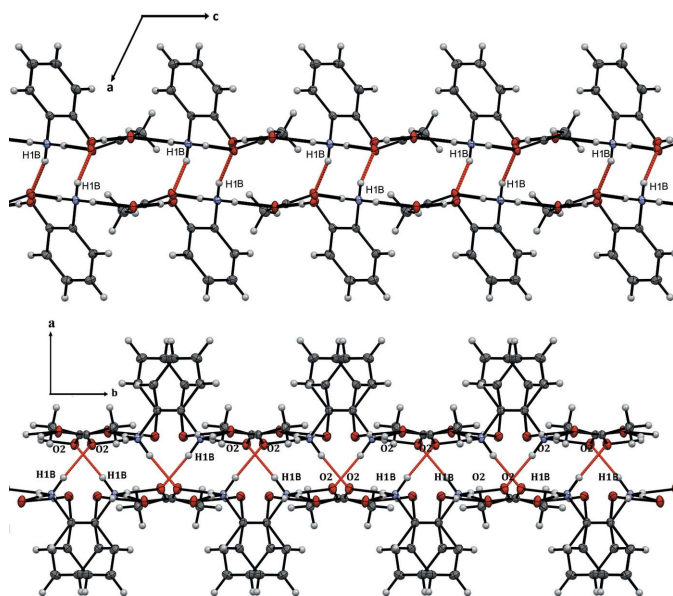


Figure 3
View of two layers viewed along the b - and c -axis directions.

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O1-H1 \cdots O3^i$	0.894 (14)	1.709 (14)	2.6025 (9)	177.8 (16)
$N1-H1A \cdots O2$	0.930 (13)	1.807 (13)	2.7251 (9)	168.7 (12)
$N1-H1B \cdots O2^{ii}$	0.923 (12)	1.891 (12)	2.8019 (9)	168.8 (11)
$N1-H1C \cdots O3^{iii}$	0.935 (12)	1.834 (12)	2.7531 (8)	167.2 (12)
$C6-H6 \cdots O3^{iii}$	0.95	2.55	3.2493 (11)	131

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_6H_8NO^+ \cdot C_2H_3O_2^-$
M_r	169.18
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (\AA)	9.9150 (2), 7.2523 (2), 11.9573 (3)
β ($^\circ$)	98.558 (2)
V (\AA^3)	850.23 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.10 \times 0.10 \times 0.08
Data collection	
Diffractometer	Oxford Diffraction Xcalibur Sapphire2 CCD
Absorption correction	Integration (<i>ABSORB</i> ; DeTitta, 1985)
T_{\min}, T_{\max}	0.966, 0.991
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	52913, 3105, 2736
R_{int} ($\sin \theta/\lambda$) $_{\text{max}}$ (\AA^{-1})	0.038 0.766
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.038, 0.109, 1.05
No. of reflections	3105
No. of parameters	122
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ ($e \text{\AA}^{-3}$)	0.49, -0.27

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SHELXS* (Sheldrick, 2008), *SHELXL2018/3* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

OH bond length ($C2-O1$) of 1.3520 (9) \AA is similar to that observed for structures containing 2-hydroxybenzenium as a cation [1.350 (3) \AA ; Jin & Wang, 2013]. All bond lengths and angles in the 2-hydroxybenzenium cation are within normal ranges (Zhao, 2012).

The presence of hydroxyl groups leads to the formation of intermolecular $O1-H1 \cdots O3$ hydrogen bonds. The $O1-H1 \cdots O3$ and $N1-H1C \cdots O3$ cation-anion hydrogen bonds generate a succession of infinite chains [graph set $C_2^1(7)$] that propagate in a zigzag manner along the c -axis direction (Fig. 2 and Table 1). The $N1-H1A \cdots O2$ hydrogen bonds (Table 1) link the chains into corrugated layers parallel to the bc plane, which are formed by a succession of $R_6^5(22)$ rings (Fig. 2). $N1-H1B \cdots O2$ hydrogen bonds lead to the formation of a three-dimensional network (Fig. 3). No significant $\pi-\pi$ stacking interactions were observed, despite the presence of an aromatic ring in the cation.

Synthesis and crystallization

The title compound was prepared by heating of a mixture of 2-aminophenol (Alfa Aesar, purity 98%) and acetic acid. This mixture was obtained by dissolution and agitation under reflux for 3 h of 0.5 g of the 2-aminophenol and 0.27 g of acetic acid in a 1:1 stoichiometric ratio in a hot ethanolic solution (20 ml). After warming for a few minutes using a water bath, the solution was cooled and kept at room temperature. Within a few days, yellow needle-like crystals suitable for the X-ray analysis were obtained (yield 60%) by evaporation of the solution.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2022). 7, x220112 [<https://doi.org/10.1107/S2414314622001122>]

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Crystal data

$C_6H_8NO^+ \cdot C_2H_3O_2^-$
 $M_r = 169.18$
 Monoclinic, $P2_1/c$
 $a = 9.9150$ (2) Å
 $b = 7.2523$ (2) Å
 $c = 11.9573$ (3) Å
 $\beta = 98.558$ (2)°
 $V = 850.23$ (4) Å³
 $Z = 4$

$F(000) = 360$
 $D_x = 1.322$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 52927 reflections
 $\theta = 3.3$ – 33.0 °
 $\mu = 0.10$ mm⁻¹
 $T = 100$ K
 Prism, yellow
 0.1 × 0.1 × 0.08 mm

Data collection

Oxford Diffraction Xcalibur Sapphire2 CCD
 diffractometer
 φ and ω scans
 Absorption correction: integration
 (ABSORB; DeTitta, 1985)
 $T_{\min} = 0.966$, $T_{\max} = 0.991$
 52913 measured reflections

3105 independent reflections
 2736 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$
 $\theta_{\max} = 33.0$ °, $\theta_{\min} = 3.3$ °
 $h = -15 \rightarrow 15$
 $k = -11 \rightarrow 11$
 $l = -17 \rightarrow 18$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.109$
 $S = 1.05$
 3105 reflections
 122 parameters
 0 restraints

Primary atom site location: structure-invariant
 direct methods
 Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0542P)^2 + 0.320P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.49$ e Å⁻³
 $\Delta\rho_{\min} = -0.27$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. The hydrogen atoms of the NH₃ and hydroxyl groups were localized in the difference-Fourier map and refined with $U_{\text{iso}}(\text{H})$ set to $1.5U_{\text{eq}}(\text{O})$ or $1.2U_{\text{eq}}(\text{N})$. All the other hydrogen atoms were placed in calculated positions with C—H = 0.95 Å for aromatic CH and C—H = 0.96 Å for CH₃ and refined using a riding model with fixed isotropic displacement parameters [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C-aromatic})$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C-methyl})$].

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.12872 (6)	0.83288 (9)	0.65994 (5)	0.01629 (13)
H1	0.1381 (14)	0.928 (2)	0.6142 (12)	0.024*
O2	0.09592 (7)	0.29888 (8)	0.65411 (5)	0.01686 (13)
O3	0.15033 (7)	0.10731 (8)	0.52349 (5)	0.01664 (13)
N1	0.12133 (7)	0.56570 (9)	0.81635 (5)	0.01242 (13)
H1A	0.1133 (12)	0.4870 (19)	0.7543 (10)	0.015*
H1B	0.0461 (12)	0.6407 (18)	0.8160 (10)	0.015*
H1C	0.1280 (12)	0.4909 (18)	0.8806 (10)	0.015*
C3	0.35594 (9)	0.93249 (12)	0.74235 (7)	0.01774 (16)
H3	0.358215	1.025256	0.686567	0.021*
C5	0.46510 (9)	0.77468 (13)	0.90970 (8)	0.01994 (17)
H5	0.540747	0.760726	0.967953	0.024*
C4	0.46648 (9)	0.91021 (13)	0.82754 (8)	0.02042 (17)
H4	0.543738	0.988327	0.829677	0.025*
C2	0.24139 (8)	0.81883 (11)	0.73847 (6)	0.01328 (14)
C6	0.35205 (8)	0.65957 (12)	0.90596 (7)	0.01606 (15)
H6	0.350402	0.566114	0.961414	0.019*
C1	0.24197 (8)	0.68208 (10)	0.82091 (6)	0.01217 (14)
C8	0.13683 (8)	0.26870 (11)	0.56096 (6)	0.01288 (14)
C7	0.16938 (9)	0.42886 (12)	0.48900 (8)	0.01940 (16)
H7A	0.096016	0.443787	0.425025	0.029*
H7B	0.255531	0.405118	0.460661	0.029*
H7C	0.177717	0.541719	0.534587	0.029*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0172 (3)	0.0157 (3)	0.0153 (3)	-0.0014 (2)	0.0001 (2)	0.0046 (2)
O2	0.0220 (3)	0.0142 (3)	0.0157 (3)	-0.0024 (2)	0.0073 (2)	-0.0030 (2)
O3	0.0255 (3)	0.0124 (3)	0.0124 (2)	0.0019 (2)	0.0041 (2)	-0.00051 (19)
N1	0.0147 (3)	0.0109 (3)	0.0120 (3)	-0.0006 (2)	0.0030 (2)	0.0005 (2)
C3	0.0180 (3)	0.0161 (3)	0.0198 (4)	-0.0030 (3)	0.0053 (3)	0.0024 (3)
C5	0.0150 (3)	0.0222 (4)	0.0217 (4)	-0.0007 (3)	-0.0003 (3)	0.0001 (3)
C4	0.0154 (3)	0.0212 (4)	0.0248 (4)	-0.0040 (3)	0.0036 (3)	0.0000 (3)
C2	0.0149 (3)	0.0121 (3)	0.0131 (3)	0.0002 (2)	0.0032 (2)	0.0005 (2)
C6	0.0162 (3)	0.0160 (3)	0.0157 (3)	0.0013 (3)	0.0015 (3)	0.0011 (3)
C1	0.0133 (3)	0.0110 (3)	0.0126 (3)	-0.0001 (2)	0.0033 (2)	0.0000 (2)
C8	0.0128 (3)	0.0123 (3)	0.0135 (3)	0.0001 (2)	0.0019 (2)	0.0007 (2)
C7	0.0213 (4)	0.0154 (3)	0.0229 (4)	0.0008 (3)	0.0078 (3)	0.0063 (3)

Geometric parameters (\AA , $^\circ$)

O1—H1	0.892 (14)	C5—H5	0.9500
O1—C2	1.3520 (9)	C5—C4	1.3912 (13)
O2—C8	1.2600 (9)	C5—C6	1.3930 (12)

O3—C8	1.2675 (9)	C4—H4	0.9500
N1—H1A	0.930 (13)	C2—C1	1.3978 (11)
N1—H1B	0.922 (13)	C6—H6	0.9500
N1—H1C	0.935 (12)	C6—C1	1.3863 (11)
N1—C1	1.4583 (10)	C8—C7	1.5087 (11)
C3—H3	0.9500	C7—H7A	0.9800
C3—C4	1.3903 (12)	C7—H7B	0.9800
C3—C2	1.3985 (11)	C7—H7C	0.9800
C2—O1—H1	109.4 (9)	O1—C2—C1	117.36 (7)
H1A—N1—H1B	112.7 (11)	C1—C2—C3	118.48 (7)
H1A—N1—H1C	106.7 (11)	C5—C6—H6	120.2
H1B—N1—H1C	107.7 (10)	C1—C6—C5	119.66 (8)
C1—N1—H1A	110.9 (8)	C1—C6—H6	120.2
C1—N1—H1B	108.5 (8)	C2—C1—N1	117.84 (7)
C1—N1—H1C	110.3 (7)	C6—C1—N1	120.74 (7)
C4—C3—H3	119.9	C6—C1—C2	121.40 (7)
C4—C3—C2	120.24 (8)	O2—C8—O3	122.53 (7)
C2—C3—H3	119.9	O2—C8—C7	119.65 (7)
C4—C5—H5	120.2	O3—C8—C7	117.81 (7)
C4—C5—C6	119.55 (8)	C8—C7—H7A	109.5
C6—C5—H5	120.2	C8—C7—H7B	109.5
C3—C4—C5	120.66 (8)	C8—C7—H7C	109.5
C3—C4—H4	119.7	H7A—C7—H7B	109.5
C5—C4—H4	119.7	H7A—C7—H7C	109.5
O1—C2—C3	124.17 (7)	H7B—C7—H7C	109.5
O1—C2—C1—N1	-0.22 (10)	C4—C3—C2—O1	178.84 (8)
O1—C2—C1—C6	-178.85 (7)	C4—C3—C2—C1	-0.83 (12)
C3—C2—C1—N1	179.48 (7)	C4—C5—C6—C1	-0.39 (13)
C3—C2—C1—C6	0.85 (12)	C2—C3—C4—C5	0.22 (13)
C5—C6—C1—N1	-178.83 (7)	C6—C5—C4—C3	0.40 (14)
C5—C6—C1—C2	-0.24 (12)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots O3 ⁱ	0.894 (14)	1.709 (14)	2.6025 (9)	177.8 (16)
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