

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

## 2-Aminopyridinium 4-hydroxybenzoate

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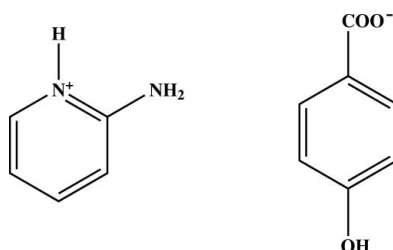
Received 24 October 2008; accepted 27 October 2008

Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.001$  Å;  $R$  factor = 0.049;  $wR$  factor = 0.140; data-to-parameter ratio = 32.1.

In the title compound,  $\text{C}_5\text{H}_7\text{N}_2^+ \cdot \text{C}_7\text{H}_5\text{O}_3^-$ , the carboxylate mean plane of the 4-hydroxybenzoate anion is twisted by  $8.78(5)^\circ$  from the attached ring. The cations and anions are linked *via*  $\text{O}-\text{H} \cdots \text{O}$ ,  $\text{N}-\text{H} \cdots \text{O}$  and  $\text{C}-\text{H} \cdots \text{O}$  hydrogen bonds, forming a three-dimensional network. In addition,  $\pi-\pi$  interactions involving the benzene and pyridinium rings, with centroid-centroid distances of 3.5500 (6) and 3.6594 (6) Å, are observed.

### Related literature

For the applications of 2-aminopyridine, see: Windholz (1976). For related structures, see: Chao *et al.* (1975); Heath *et al.* (1992); Jebas & Balasubramanian (2006); Joanna & Zaworotko (2005); Smith *et al.* (2000).



### Experimental

#### Crystal data

$\text{C}_5\text{H}_7\text{N}_2^+ \cdot \text{C}_7\text{H}_5\text{O}_3^-$   
 $M_r = 232.24$   
 Monoclinic,  $P2_1/n$   
 $a = 10.0647(2)$  Å  
 $b = 10.9369(2)$  Å  
 $c = 10.7985(2)$  Å  
 $\beta = 111.036(1)^\circ$

$V = 1109.44(4)$  Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.10$  mm<sup>-1</sup>  
 $T = 100.0(1)$  K  
 $0.34 \times 0.29 \times 0.17$  mm

#### Data collection

Bruker SMART APEXII CCD  
 area-detector diffractometer  
 Absorption correction: multi-scan  
 (SADABS; Bruker, 2005)  
 $T_{\min} = 0.966$ ,  $T_{\max} = 0.983$

22398 measured reflections  
 5078 independent reflections  
 3835 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.029$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$   
 $wR(F^2) = 0.140$   
 $S = 1.02$   
 5078 reflections  
 158 parameters  
 1 restraint

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 0.50$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.21$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{O1}-\text{H1O1} \cdots \text{O2}^{\text{i}}$	0.82	1.86	2.6257 (9)	154
$\text{N2}-\text{H1N2} \cdots \text{O2}^{\text{ii}}$	0.86	1.98	2.8224 (11)	167
$\text{N2}-\text{H2N2} \cdots \text{O3}^{\text{iii}}$	0.86	1.99	2.8396 (11)	171
$\text{N1}-\text{H1N1} \cdots \text{O3}^{\text{ii}}$	0.88 (1)	1.81 (1)	2.6861 (10)	169 (2)
$\text{C10}-\text{H10A} \cdots \text{O1}$	0.93	2.51	3.3482 (14)	149
$\text{C11}-\text{H11A} \cdots \text{O2}^{\text{i}}$	0.93	2.34	3.1899 (12)	152

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

Data collection: APEX2 (Bruker, 2005); cell refinement: APEX2 and SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 2003).

HKF and SRJ thank the Malaysian Government and Universiti Sains Malaysia for the Science Fund grant No. 305/PFIZIK/613312. SRJ thanks Universiti Sains Malaysia for a post-doctoral research fellowship. CKQ thanks Universiti Sains Malaysia for a student assistanceship.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2696).

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**supplementary materials**

*Acta Cryst.* (2008). E64, o2230 [ doi:10.1107/S1600536808034934 ]

## 2-Aminopyridinium 4-hydroxybenzoate

C. K. Quah, S. R. Jebas and H.-K. Fun

### Comment

2-Aminopyridine is used in the manufacture of pharmaceuticals, especially antihistaminic drugs (Windholz, 1976). As an extension of our systematic study of hydrogen bonding patterns of 2-aminopyridine with aromatic carboxylic acids, the title compound was synthesized and its crystal structure determined.

The asymmetric unit contains one 2-aminopyridinium cation and 4-hydroxybenzoate anion. The proton transfer from the carboxyl group to atom N1 of 2-aminopyridine resulted in the widening of C8—N1—C12 angle of the pyridinium ring to 122.35°, compared to the corresponding angle of 117.7 (1)° in neutral 2-aminopyridine (Chao *et al.*, 1975). Similar feature is observed in various 2-aminopyridine acid complexes (Joanna & Zaworotko, 2005; Smith *et al.*, 2000). The bond distances and angles in the title compound are comparable to those in various 2-aminopyridine acid complexes and 4-hydroxybenzoic acid (Joanna & Zaworotko, 2005; Heath *et al.*, 1992).

The 2-aminopyridinium cation is essentially planar, with a maximum deviation of 0.016 (1) Å for atom N1. In the 4-hydroxybenzoate anion, the carboxylate group is twisted slightly from the attached ring; the dihedral angle between C1-C6 and O2/O3/C6/C7 planes is 8.78 (5)°.

The crystal packing is consolidated by intermolecular O—H...O, N—H...O and C—H...O hydrogen bonds (Table 1). These hydrogen bonds link the molecules into a three-dimensional network. The packing is further strengthened by  $\pi$ - $\pi$  interactions involving the benzene (centroid Cg1) and pyridinium (centroid Cg2) rings, with  $\text{Cg1}\cdots\text{Cg2}^{\text{iv}} = 3.6594$  (6) Å and  $\text{Cg2}\cdots\text{Cg2}^{\text{v}} = 3.5500$  (6) Å [symmetry code: (iv) 1-x, 1-y, 1-z; (v) -x, 1-y, 1-z].

### Experimental

2-Aminopyridine and 4-hydroxybenzoic acid were mixed in methanol in a 1:1 molar ratio. The clear colourless solution obtained was allowed to evaporate slowly. Colourless crystals were obtained after a week.

### Refinement

H atoms were placed in calculated positions, with C-H = 0.93 Å, N-H = 0.86 Å and O-H = 0.82 Å and refined using a riding model with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$  and  $1.5U_{\text{eq}}(\text{O})$ . Atom H1N1 was located in a difference map and was refined with an N-H distance restraint of 0.86 Å.

### Figures

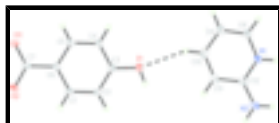


Fig. 1. The molecular structure of the title compound, showing 50% probability displacement ellipsoids and the atom numbering scheme. The dashed line indicates a hydrogen bond.

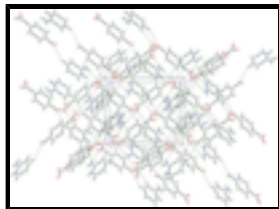


Fig. 2. The crystal packing of the title compound, viewed along the *c* axis. Hydrogen bonds are shown as dashed lines.

## 2-Aminopyridinium 4-hydroxybenzoate

### Crystal data

$C_5H_7N_2^+ \cdot C_7H_5O_3^-$

$M_r = 232.24$

Monoclinic,  $P2_1/n$

Hall symbol: -P 2yn

$a = 10.0647$  (2) Å

$b = 10.9369$  (2) Å

$c = 10.7985$  (2) Å

$\beta = 111.036$  (1)°

$V = 1109.44$  (4) Å<sup>3</sup>

$Z = 4$

$F_{000} = 488$

$D_x = 1.390$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 6837 reflections

$\theta = 2.8$ – $35.6$ °

$\mu = 0.10$  mm<sup>-1</sup>

$T = 100.0$  (1) K

Block, colourless

$0.34 \times 0.29 \times 0.17$  mm

### Data collection

Bruker SMART APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 100.0$ (1) K

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan (SADABS; Bruker, 2005)

$T_{\min} = 0.966$ ,  $T_{\max} = 0.983$

22398 measured reflections

5078 independent reflections

3835 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$

$\theta_{\max} = 35.6$ °

$\theta_{\min} = 2.4$ °

$h = -16 \rightarrow 11$

$k = -17 \rightarrow 17$

$l = -16 \rightarrow 17$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.140$

$S = 1.02$

5078 reflections

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0746P)^2 + 0.2186P]$$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.50$  e Å<sup>-3</sup>

158 parameters

$$\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$$

1 restraint

Extinction correction: none

Primary atom site location: structure-invariant direct methods

### Special details

**Experimental.** The data was collected with the Oxford Cyrosystem Cobra low-temperature attachment.

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

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) etc. and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.52173 (8)	0.67777 (7)	0.56764 (7)	0.02345 (16)
H1O1	0.5435	0.6430	0.6395	0.035*
O2	0.97943 (7)	1.10528 (6)	0.70095 (6)	0.01770 (14)
O3	0.88217 (8)	1.12535 (7)	0.48165 (6)	0.02051 (14)
N1	0.06716 (8)	0.30978 (7)	0.51061 (7)	0.01683 (15)
N2	0.18939 (9)	0.28645 (8)	0.73537 (8)	0.02239 (17)
H1N2	0.1354	0.2254	0.7348	0.027*
H2N2	0.2550	0.3085	0.8082	0.027*
C1	0.81342 (9)	0.89872 (8)	0.69825 (8)	0.01647 (16)
H1A	0.8873	0.9180	0.7769	0.020*
C2	0.72397 (10)	0.80096 (9)	0.69536 (8)	0.01740 (16)
H2A	0.7387	0.7548	0.7714	0.021*
C3	0.61195 (10)	0.77231 (9)	0.57782 (9)	0.01771 (16)
C4	0.59084 (11)	0.84236 (10)	0.46429 (9)	0.02258 (19)
H4A	0.5157	0.8243	0.3862	0.027*
C5	0.68141 (10)	0.93876 (9)	0.46745 (9)	0.02087 (18)
H5A	0.6673	0.9842	0.3910	0.025*
C6	0.79383 (9)	0.96844 (8)	0.58454 (8)	0.01518 (15)
C7	0.89111 (9)	1.07305 (8)	0.58888 (8)	0.01503 (15)
C8	0.03894 (10)	0.36798 (9)	0.39292 (9)	0.01886 (17)
H8A	-0.0348	0.3399	0.3183	0.023*
C9	0.11667 (11)	0.46682 (9)	0.38189 (10)	0.02141 (18)
H9A	0.0968	0.5068	0.3012	0.026*
C10	0.22817 (11)	0.50629 (9)	0.49691 (10)	0.02254 (19)
H10A	0.2836	0.5728	0.4919	0.027*
C11	0.25595 (10)	0.44821 (9)	0.61585 (10)	0.02098 (18)
H11A	0.3297	0.4750	0.6911	0.025*

## supplementary materials

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C12	0.17140 (10)	0.34698 (9)	0.62328 (9)	0.01766 (16)
H1N1	0.0145 (17)	0.2453 (12)	0.5101 (19)	0.051 (5)*

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0264 (4)	0.0269 (4)	0.0164 (3)	-0.0110 (3)	0.0069 (3)	0.0002 (3)
O2	0.0180 (3)	0.0203 (3)	0.0128 (3)	-0.0017 (2)	0.0032 (2)	-0.0020 (2)
O3	0.0219 (3)	0.0218 (3)	0.0143 (3)	-0.0048 (3)	0.0023 (2)	0.0040 (2)
N1	0.0170 (3)	0.0179 (3)	0.0144 (3)	-0.0029 (3)	0.0042 (3)	-0.0020 (3)
N2	0.0227 (4)	0.0254 (4)	0.0147 (3)	-0.0055 (3)	0.0015 (3)	-0.0015 (3)
C1	0.0167 (4)	0.0186 (4)	0.0127 (3)	-0.0001 (3)	0.0036 (3)	0.0001 (3)
C2	0.0189 (4)	0.0194 (4)	0.0136 (3)	-0.0011 (3)	0.0056 (3)	0.0016 (3)
C3	0.0192 (4)	0.0198 (4)	0.0151 (3)	-0.0037 (3)	0.0073 (3)	-0.0011 (3)
C4	0.0230 (4)	0.0288 (5)	0.0126 (3)	-0.0093 (4)	0.0024 (3)	0.0002 (3)
C5	0.0225 (4)	0.0245 (5)	0.0133 (3)	-0.0053 (3)	0.0036 (3)	0.0023 (3)
C6	0.0159 (3)	0.0164 (4)	0.0127 (3)	0.0000 (3)	0.0044 (3)	0.0002 (3)
C7	0.0154 (3)	0.0156 (4)	0.0129 (3)	0.0010 (3)	0.0037 (3)	0.0001 (3)
C8	0.0185 (4)	0.0218 (4)	0.0159 (4)	-0.0018 (3)	0.0057 (3)	-0.0008 (3)
C9	0.0226 (4)	0.0220 (4)	0.0206 (4)	-0.0025 (3)	0.0090 (3)	0.0011 (3)
C10	0.0210 (4)	0.0205 (4)	0.0276 (4)	-0.0052 (3)	0.0105 (4)	-0.0025 (3)
C11	0.0169 (4)	0.0213 (4)	0.0229 (4)	-0.0034 (3)	0.0049 (3)	-0.0046 (3)
C12	0.0162 (4)	0.0190 (4)	0.0163 (4)	-0.0005 (3)	0.0040 (3)	-0.0032 (3)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

O1—C3	1.3543 (11)	C3—C4	1.3957 (13)
O1—H1O1	0.8200	C4—C5	1.3861 (13)
O2—C7	1.2675 (10)	C4—H4A	0.93
O3—C7	1.2654 (10)	C5—C6	1.3990 (12)
N1—C12	1.3528 (11)	C5—H5A	0.93
N1—C8	1.3571 (12)	C6—C7	1.4956 (12)
N1—H1N1	0.881 (9)	C8—C9	1.3644 (13)
N2—C12	1.3338 (12)	C8—H8A	0.93
N2—H1N2	0.86	C9—C10	1.4099 (14)
N2—H2N2	0.86	C9—H9A	0.93
C1—C2	1.3908 (13)	C10—C11	1.3687 (14)
C1—C6	1.3980 (12)	C10—H10A	0.93
C1—H1A	0.93	C11—C12	1.4161 (13)
C2—C3	1.3975 (12)	C11—H11A	0.93
C2—H2A	0.93		
C3—O1—H1O1	109.5	C1—C6—C5	118.72 (8)
C12—N1—C8	122.35 (8)	C1—C6—C7	120.36 (8)
C12—N1—H1N1	121.1 (13)	C5—C6—C7	120.92 (8)
C8—N1—H1N1	116.5 (13)	O3—C7—O2	122.89 (8)
C12—N2—H1N2	120.0	O3—C7—C6	119.10 (7)
C12—N2—H2N2	120.0	O2—C7—C6	118.00 (7)
H1N2—N2—H2N2	120.0	N1—C8—C9	121.30 (9)

C2—C1—C6	120.90 (8)	N1—C8—H8A	119.3
C2—C1—H1A	119.5	C9—C8—H8A	119.3
C6—C1—H1A	119.5	C8—C9—C10	117.75 (9)
C1—C2—C3	119.83 (8)	C8—C9—H9A	121.1
C1—C2—H2A	120.1	C10—C9—H9A	121.1
C3—C2—H2A	120.1	C11—C10—C9	120.96 (9)
O1—C3—C4	117.49 (8)	C11—C10—H10A	119.5
O1—C3—C2	122.94 (8)	C9—C10—H10A	119.5
C4—C3—C2	119.57 (8)	C10—C11—C12	119.44 (9)
C5—C4—C3	120.30 (8)	C10—C11—H11A	120.3
C5—C4—H4A	119.9	C12—C11—H11A	120.3
C3—C4—H4A	119.9	N2—C12—N1	118.41 (8)
C4—C5—C6	120.67 (8)	N2—C12—C11	123.43 (8)
C4—C5—H5A	119.7	N1—C12—C11	118.17 (8)
C6—C5—H5A	119.7		
C6—C1—C2—C3	-0.63 (14)	C5—C6—C7—O3	-8.78 (13)
C1—C2—C3—O1	179.36 (9)	C1—C6—C7—O2	-8.40 (12)
C1—C2—C3—C4	-0.07 (14)	C5—C6—C7—O2	171.26 (9)
O1—C3—C4—C5	-178.61 (9)	C12—N1—C8—C9	1.07 (14)
C2—C3—C4—C5	0.84 (15)	N1—C8—C9—C10	0.35 (14)
C3—C4—C5—C6	-0.92 (16)	C8—C9—C10—C11	-0.87 (15)
C2—C1—C6—C5	0.55 (13)	C9—C10—C11—C12	0.02 (15)
C2—C1—C6—C7	-179.78 (8)	C8—N1—C12—N2	178.22 (9)
C4—C5—C6—C1	0.22 (14)	C8—N1—C12—C11	-1.90 (14)
C4—C5—C6—C7	-179.44 (9)	C10—C11—C12—N2	-178.79 (9)
C1—C6—C7—O3	171.56 (8)	C10—C11—C12—N1	1.33 (14)

Hydrogen-bond 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>
O1—H1O1...O2 <sup>i</sup>	0.82	1.86	2.6257 (9)	154
N2—H1N2...O2 <sup>ii</sup>	0.86	1.98	2.8224 (11)	167
N2—H2N2...O3 <sup>iii</sup>	0.86	1.99	2.8396 (11)	171
N1—H1N1...O3 <sup>ii</sup>	0.88 (1)	1.81 (1)	2.6861 (10)	169 (2)
C10—H10A...O1	0.93	2.51	3.3482 (14)	149
C11—H11A...O2 <sup>i</sup>	0.93	2.34	3.1899 (12)	152

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

Fig. 1

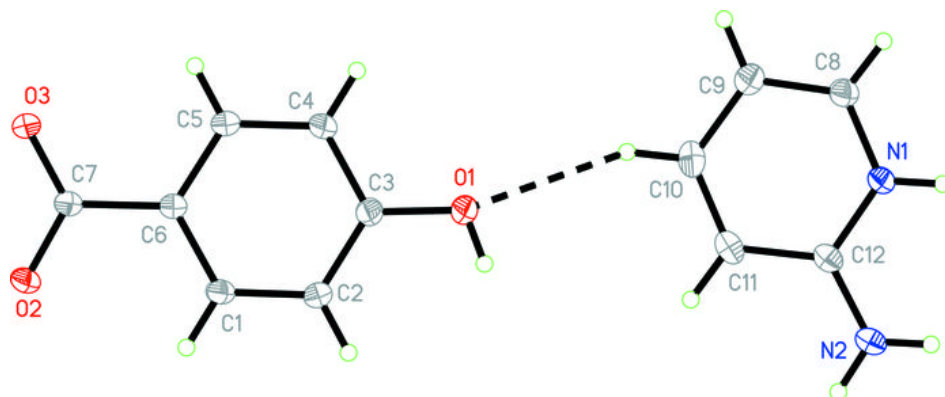




Fig. 2

