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2-Amino-6-methylpyridinium 2-hydroxybenzoate

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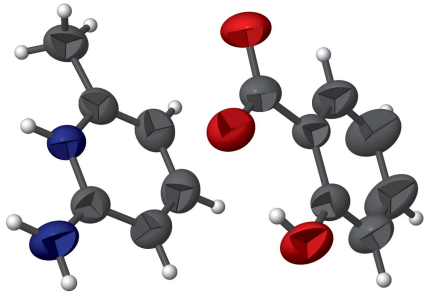
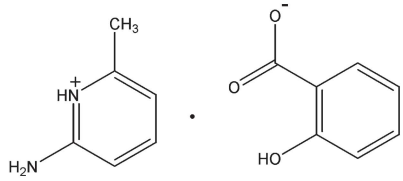
Structural data: full structural data are available from iucrdata.iucr.org

In the title molecular salt, $C_6H_9N_2^+\cdot C_7H_5O_3^-$, the cation is protonated at its pyridine N atom and and makes a dihedral angle of 16.26 (9)° with the plane of the six-membered ring of the anion. The six-membered ring makes a dihedral angle of 6.09 (3)° with the attached carboxylate group. In the anion, an intramolecular O—H···O hydrogen bond generates an $S(6)$ ring motif and a pair of N—H···O hydrogen bonds generates an $R_2^2(8)$ ring motif. In the crystal, the anions and cations are linked *via* N—H···O hydrogen bonds to form a tetramer.

3D view



Chemical scheme



Structure description

Pyridine and its derivatives play an important role in heterocyclic chemistry (Pozharski *et al.*, 1997; Katritzky *et al.*, 1996) and they are also known to exhibit non-linear optical (NLO) properties (Tomaru *et al.*, 1991). Herein, we report on the synthesis and the crystal structure of the title molecular salt. The title compound, Fig. 1, contains a 2-amino-6-methylpyridinium cation, which is protonated at atom N1, and 2-hydroxybenzoate which is deprotonated at its O2 atom. The geometric parameters are comparable with those reported for similar structures (Jin *et al.*, 2000, 2001; Quah *et al.*, 2010).

The benzene ring (C1–C6) of the anion makes a dihedral angle of 6.09 (3)° with the attached carboxylate (C7/O2/O3) group. The benzene and pyridine rings are inclined at an angle of 16.26 (9)°. In the anion, an intramolecular O—H···O hydrogen bond generates an $S(6)$ ring motif (Fig. 1). In the crystal, the anions and cations are connected by N—H···O hydrogen bonds generating an $R_2^2(8)$ ring motif (Fig. 2). Four pairs of anions and cations are linked by N—H···O hydrogen bonds (Table 1) to form a tetramer with an $R_4^4(16)$ ring motif (Fig. 3).

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···O2	0.84 (1)	1.77 (2)	2.544 (3)	152 (3)
N1—H1B···O2^{i}	0.86	1.89	2.745 (3)	177
N2—H2A···O3^{i}	0.86	1.93	2.781 (3)	169
N2—H2B···O3^{ii}	0.86	2.00	2.836 (3)	163

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $y-\frac{1}{4}, -x+\frac{3}{4}, z-\frac{1}{4}$.

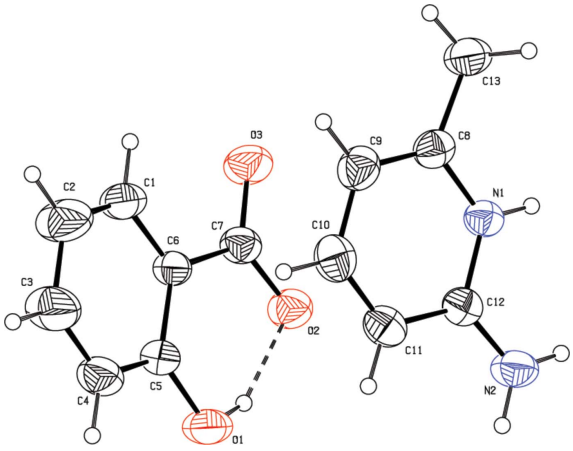


Figure 1
The molecular structure of the title molecular salt, showing the atom labelling and 30% probability displacement ellipsoids.

Synthesis and crystallization

2-Amino-6-picoline (0.54 g) and 2-hydroxybenzoic acid (0.69 g) in an equimolar ratio were mixed in acetone and the mixture was stirred for 3 h. A single crystal of the title compound suitable for X-ray diffraction was obtained by slow evaporation.

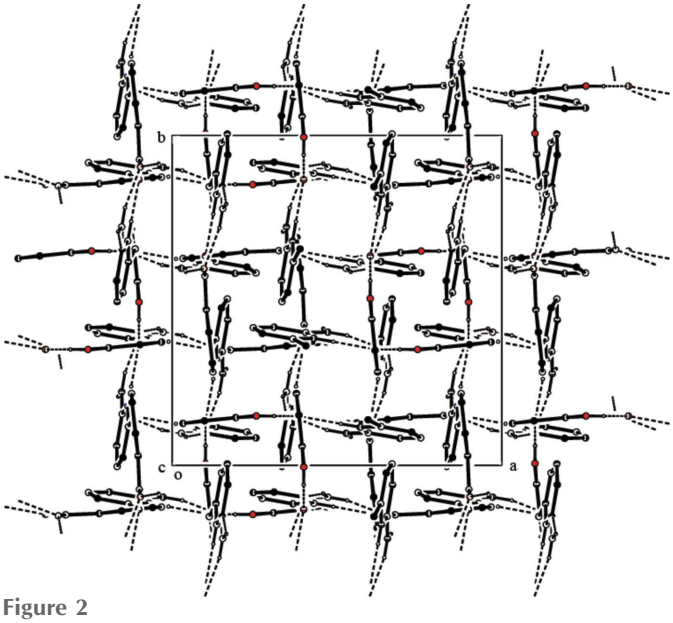


Figure 2
The crystal packing of the title compound, viewed along the c axis. The hydrogen bonds (see Table 1) are shown as dashed lines and C-bound H atoms have been omitted for clarity.

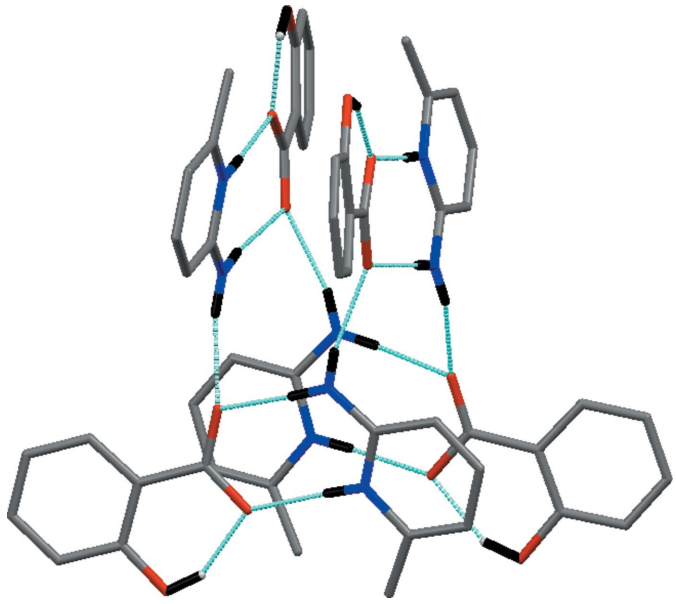


Figure 3
A partial view of the crystal packing of the title compound, showing the hydrogen-bonded tetramer.

Refinement

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_6H_9N_2^+\cdot C_7H_5O_3^-$
M_r	246.26
Crystal system, space group	Tetragonal, $I4_1/a$
Temperature (K)	293
a, c (Å)	14.1096 (6), 24.6537 (11)
V (Å^3)	4908.1 (4)
Z	16
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.28 × 0.24 × 0.20
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2004)
T_{min}, T_{max}	0.974, 0.981
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	33461, 2705, 1564
R_{int}	0.041
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.641
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.055, 0.191, 1.05
No. of reflections	2705
No. of parameters	169
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.17, −0.18

Computer programs: *APEX2* and *SAINT* (Bruker, 2004), *SHELXS97* and *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

Acknowledgements

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References

Bruker (2004). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Jin, Z.-M., Pan, Y.-J., Hu, M.-L. & Liang, S. (2001). *J. Chem. Crystallogr.* **31**, 191–195.
Jin, Z.-M., Pan, Y.-J., Liu, J.-G. & Xu, D.-J. (2000). *J. Chem. Crystallogr.* **30**, 195–198.
Katritzky, A. R., Rees, C. W. & Scriven, E. F. V. (1996). In *Comprehensive Heterocyclic Chemistry II*. Oxford: Pergamon Press.
Pozharski, A. F., Soldatenkov, A. T. & Katritzky, A. R. (1997). In *Heterocycles in Life and Society*. New York: Wiley.
Quah, C. K., Hemamalini, M. & Fun, H.-K. (2010). *Acta Cryst.* E**66**, o2255–o2256.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Tomaru, S., Matsumoto, S., Kurihara, T., Suzuki, H., Ooba, N. & Kaino, T. (1991). *Appl. Phys. Lett.* **58**, 2583–2585.

full crystallographic data

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Crystal data

$C_6H_9N_2^+·C_7H_5O_3^-$
M_r = 246.26
Tetragonal, $I4_1/a$
Hall symbol: -I 4ad
a = 14.1096 (6) Å
c = 24.6537 (11) Å
V = 4908.1 (4) Å^3
Z = 16
F(000) = 2080
D_x = 1.333 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9075 reflections
θ = 2.6–27.3°
μ = 0.10 mm^{-1}
T = 293 K
Block, colourless
0.28 × 0.24 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scan
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.974, T_{max} = 0.981
33461 measured reflections
2705 independent reflections
1564 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 27.1°, θ_{min} = 2.6°
h = −17→18
k = −18→15
l = −31→31

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.191
S = 1.05
2705 reflections
169 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
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
$w = 1/[\sigma^2(F_o^2) + (0.079P)^2 + 4.2162P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0018 (4)

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. 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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.3466 (2)	0.3614 (2)	0.53227 (11)	0.0800 (9)
H1	0.3287	0.3597	0.5686	0.096*
C2	0.4403 (2)	0.3718 (3)	0.51924 (13)	0.1165 (15)
H2	0.4854	0.3779	0.5465	0.140*
C3	0.4674 (2)	0.3733 (3)	0.46571 (13)	0.1088 (13)
H3	0.5311	0.3798	0.4568	0.131*
C4	0.4020 (2)	0.3655 (2)	0.42581 (12)	0.0780 (8)
H4	0.4210	0.3666	0.3897	0.094*
C5	0.30732 (18)	0.35571 (17)	0.43851 (9)	0.0585 (6)
C6	0.27839 (17)	0.35353 (16)	0.49277 (9)	0.0544 (6)
C7	0.17649 (18)	0.34951 (17)	0.50774 (10)	0.0599 (6)
C8	0.13374 (19)	0.61715 (17)	0.54553 (10)	0.0614 (6)
C9	0.2265 (2)	0.6006 (2)	0.53459 (12)	0.0730 (7)
H9	0.2712	0.6010	0.5623	0.088*
C10	0.2540 (2)	0.5829 (2)	0.48125 (12)	0.0745 (8)
H10	0.3176	0.5717	0.4736	0.089*
C11	0.19078 (19)	0.58161 (18)	0.44066 (11)	0.0670 (7)
H11	0.2104	0.5699	0.4053	0.080*
C12	0.09491 (17)	0.59811 (17)	0.45197 (10)	0.0576 (6)
C13	0.0943 (2)	0.6378 (2)	0.59994 (11)	0.0778 (8)
H13A	0.1448	0.6403	0.6260	0.117*
H13B	0.0504	0.5888	0.6099	0.117*
H13C	0.0620	0.6977	0.5992	0.117*
N1	0.07022 (14)	0.61524 (13)	0.50402 (7)	0.0560 (5)
H1B	0.0115	0.6254	0.5113	0.067*
N2	0.02771 (16)	0.59673 (17)	0.41480 (8)	0.0744 (7)
H2A	−0.0303	0.6066	0.4239	0.089*
H2B	0.0419	0.5860	0.3814	0.089*
O1	0.24464 (16)	0.35081 (17)	0.39747 (7)	0.0842 (6)
O2	0.11578 (12)	0.35100 (14)	0.46963 (7)	0.0710 (5)
O3	0.15438 (14)	0.34665 (16)	0.55672 (7)	0.0848 (6)
H1A	0.1912 (12)	0.351 (3)	0.4121 (13)	0.103 (12)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0703 (18)	0.121 (3)	0.0491 (14)	0.0083 (16)	−0.0032 (13)	−0.0042 (15)
C2	0.068 (2)	0.210 (5)	0.071 (2)	0.003 (2)	−0.0143 (16)	−0.015 (2)
C3	0.0611 (18)	0.187 (4)	0.078 (2)	−0.001 (2)	0.0049 (16)	−0.021 (2)
C4	0.0699 (18)	0.105 (2)	0.0590 (16)	0.0030 (15)	0.0115 (13)	−0.0068 (15)

C5	0.0649 (15)	0.0631 (14)	0.0475 (12)	0.0037 (11)	0.0001 (11)	−0.0051 (11)
C6	0.0623 (14)	0.0560 (13)	0.0449 (12)	0.0022 (10)	0.0010 (10)	−0.0011 (10)
C7	0.0691 (16)	0.0600 (14)	0.0507 (13)	−0.0006 (11)	0.0066 (12)	0.0029 (11)
C8	0.0746 (17)	0.0528 (13)	0.0567 (14)	−0.0034 (11)	−0.0060 (12)	0.0019 (11)
C9	0.0693 (17)	0.0729 (17)	0.0769 (18)	0.0000 (13)	−0.0128 (14)	−0.0029 (14)
C10	0.0637 (16)	0.0726 (18)	0.087 (2)	0.0004 (13)	0.0039 (15)	−0.0033 (15)
C11	0.0678 (16)	0.0675 (16)	0.0656 (15)	−0.0039 (12)	0.0113 (13)	−0.0032 (12)
C12	0.0634 (15)	0.0533 (13)	0.0562 (14)	−0.0036 (11)	0.0045 (11)	0.0005 (10)
C13	0.101 (2)	0.0790 (19)	0.0537 (15)	0.0022 (15)	−0.0050 (14)	0.0003 (13)
N1	0.0612 (12)	0.0571 (11)	0.0498 (11)	−0.0018 (8)	0.0038 (9)	0.0008 (9)
N2	0.0680 (14)	0.1037 (18)	0.0515 (12)	−0.0038 (12)	0.0052 (10)	−0.0041 (11)
O1	0.0745 (14)	0.1301 (18)	0.0479 (10)	0.0021 (12)	−0.0030 (10)	−0.0113 (11)
O2	0.0595 (11)	0.0935 (14)	0.0599 (11)	−0.0034 (9)	−0.0014 (8)	−0.0029 (9)
O3	0.0791 (13)	0.1217 (17)	0.0536 (11)	0.0050 (11)	0.0131 (9)	0.0169 (10)

Geometric parameters (Å, º)

C1—C2	1.368 (4)	C8—C13	1.481 (4)
C1—C6	1.374 (3)	C9—C10	1.394 (4)
C1—H1	0.9300	C9—H9	0.9300
C2—C3	1.374 (4)	C10—C11	1.341 (4)
C2—H2	0.9300	C10—H10	0.9300
C3—C4	1.353 (4)	C11—C12	1.401 (4)
C3—H3	0.9300	C11—H11	0.9300
C4—C5	1.379 (4)	C12—N2	1.319 (3)
C4—H4	0.9300	C12—N1	1.351 (3)
C5—O1	1.346 (3)	C13—H13A	0.9600
C5—C6	1.399 (3)	C13—H13B	0.9600
C6—C7	1.485 (3)	C13—H13C	0.9600
C7—O3	1.248 (3)	N1—H1B	0.8600
C7—O2	1.272 (3)	N2—H2A	0.8600
C8—C9	1.357 (4)	N2—H2B	0.8600
C8—N1	1.361 (3)	O1—H1A	0.835 (10)
C2—C1—C6	121.3 (3)	C8—C9—H9	120.4
C2—C1—H1	119.4	C10—C9—H9	120.4
C6—C1—H1	119.4	C11—C10—C9	121.4 (3)
C1—C2—C3	119.7 (3)	C11—C10—H10	119.3
C1—C2—H2	120.1	C9—C10—H10	119.3
C3—C2—H2	120.1	C10—C11—C12	119.4 (3)
C4—C3—C2	120.5 (3)	C10—C11—H11	120.3
C4—C3—H3	119.8	C12—C11—H11	120.3
C2—C3—H3	119.7	N2—C12—N1	118.5 (2)
C3—C4—C5	120.2 (3)	N2—C12—C11	123.6 (2)
C3—C4—H4	119.9	N1—C12—C11	117.9 (2)
C5—C4—H4	119.9	C8—C13—H13A	109.5
O1—C5—C4	118.1 (2)	C8—C13—H13B	109.5
O1—C5—C6	121.7 (2)	H13A—C13—H13B	109.5

C4—C5—C6	120.1 (2)	C8—C13—H13C	109.5
C1—C6—C5	118.1 (2)	H13A—C13—H13C	109.5
C1—C6—C7	120.3 (2)	H13B—C13—H13C	109.5
C5—C6—C7	121.4 (2)	C12—N1—C8	123.2 (2)
O3—C7—O2	123.2 (2)	C12—N1—H1B	118.4
O3—C7—C6	118.9 (2)	C8—N1—H1B	118.4
O2—C7—C6	117.9 (2)	C12—N2—H2A	120.0
C9—C8—N1	118.8 (2)	C12—N2—H2B	120.0
C9—C8—C13	125.2 (3)	H2A—N2—H2B	120.0
N1—C8—C13	115.9 (2)	C5—O1—H1A	106 (2)
C8—C9—C10	119.1 (3)		
C6—C1—C2—C3	−0.8 (6)	C1—C6—C7—O2	173.6 (3)
C1—C2—C3—C4	0.6 (7)	C5—C6—C7—O2	−2.1 (3)
C2—C3—C4—C5	−0.1 (6)	N1—C8—C9—C10	0.5 (4)
C3—C4—C5—O1	178.2 (3)	C13—C8—C9—C10	−179.4 (3)
C3—C4—C5—C6	−0.2 (4)	C8—C9—C10—C11	−0.2 (4)
C2—C1—C6—C5	0.4 (5)	C9—C10—C11—C12	−0.2 (4)
C2—C1—C6—C7	−175.4 (3)	C10—C11—C12—N2	−178.9 (3)
O1—C5—C6—C1	−178.3 (3)	C10—C11—C12—N1	0.3 (4)
C4—C5—C6—C1	0.1 (4)	N2—C12—N1—C8	179.2 (2)
O1—C5—C6—C7	−2.4 (4)	C11—C12—N1—C8	0.0 (3)
C4—C5—C6—C7	175.9 (2)	C9—C8—N1—C12	−0.4 (4)
C1—C6—C7—O3	−5.0 (4)	C13—C8—N1—C12	179.5 (2)
C5—C6—C7—O3	179.2 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···O2	0.84 (1)	1.77 (2)	2.544 (3)	152 (3)
N1—H1*B*···O2^{i}	0.86	1.89	2.745 (3)	177
N2—H2*A*···O3^{i}	0.86	1.93	2.781 (3)	169
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Symmetry codes: (i) −*x*, −*y*+1, −*z*+1; (ii) *y*−1/4, −*x*+3/4, *z*−1/4.