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2-Amino-4-methylpyridinium 4-hydroxybenzoate

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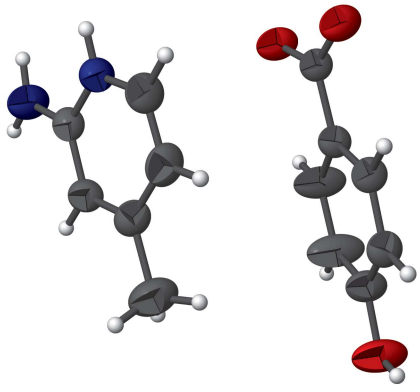
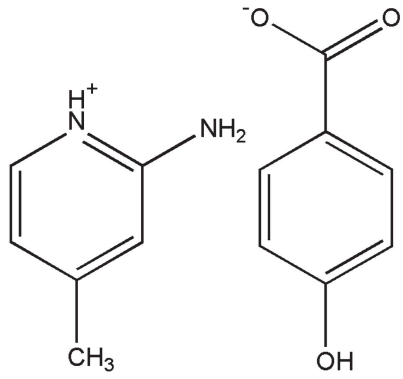
In the title molecular salt, $C_6H_9N_2^+\cdot C_7H_5O_3^-$, the cation is protonated at the pyridine N atom and the anion is deprotonated. The pyridine ring is inclined at an angle of 24.96 (11)° to the benzene ring. In the crystal, adjacent anions and cations are linked by a pair of N—H···O hydrogen bonds, generating an $R_2^2(8)$ ring motif; these motifs are further connected by another N—H···O and O—H···O hydrogen bonds into a three-dimensional network. The crystal structure also features weak C—H···O interactions.

3D view



Chemical scheme



Structure description

Pyridine derivatives are known to exhibit anti-inflammatory (Abdel-Alim *et al.*, 2005) and anxiolytic (Spanka *et al.*, 2010) activities.

We report the synthesis and the crystal structure of the title molecular salt (Fig. 1). The asymmetric unit comprises a 2-amino-4-methylpyridinium cation protonated at the pyridine N (N1) atom and a deprotonated 4-methylbenzoate anion. The benzene ring (C7–C12) makes a dihedral angle of 24.96 (11)° with the pyridine ring (N1/C1–C5). Bond lengths are comparable with those in reported structures (Sivakumar *et al.*, 2016*a*,*b*).

In the crystal, anions and cations are linked by N1—H1···O2^{i} and N2—H2*A*···O1^{i} hydrogen bonds, generating an $R_2^2(8)$ ring motif (Fig. 2) and further connected by N2—H2*B*···O2^{ii} and O—H···O^{iii} hydrogen bonds (Table 1) into an infinite three-dimensional network. The crystal structure also features weak interionic C—H···O interactions (Table 1, Fig. 3).

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2^{i}	0.87 (1)	1.81 (1)	2.666 (2)	174 (3)
N2—H2A···O1^{i}	0.86 (1)	1.95 (1)	2.806 (3)	172 (3)
N2—H2B···O2^{ii}	0.86 (1)	2.05 (1)	2.887 (3)	167 (2)
O3—H3···O1^{iii}	0.83 (1)	1.87 (1)	2.677 (2)	167 (3)
C6—H6C···O1^{iv}	0.96	2.58	3.505 (4)	161

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

Synthesis and crystallization

The title salt was synthesized using the raw materials 4-hydroxy benzoic acid (0.69 g) and 2-amino 4-methylpyridine (0.54 g) in an equimolar ratio. When these reactants were dissolved in 10 ml of methanol a white precipitate was formed. The precipitate was dissolved in 20 ml of water and kept at room temperature for slow evaporation. After 30 days, crystals suitable for X-ray diffraction were harvested.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The reflection (100) was omitted during refinement because it was obscured by the beamstop.

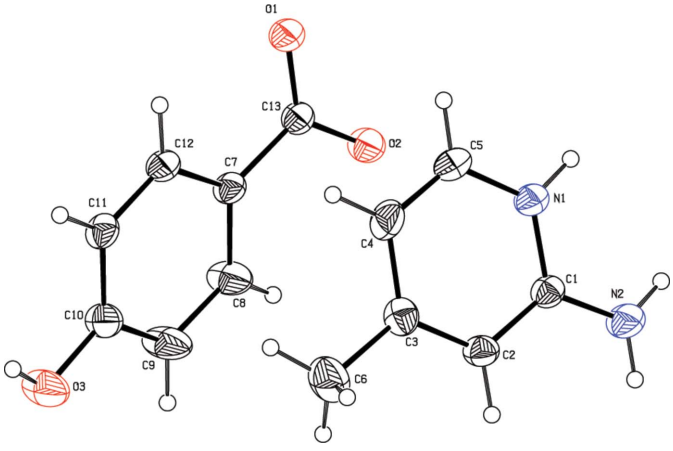


Figure 1
The molecular structure of the title molecular salt, with atom labelling and 30% probability displacement ellipsoids.

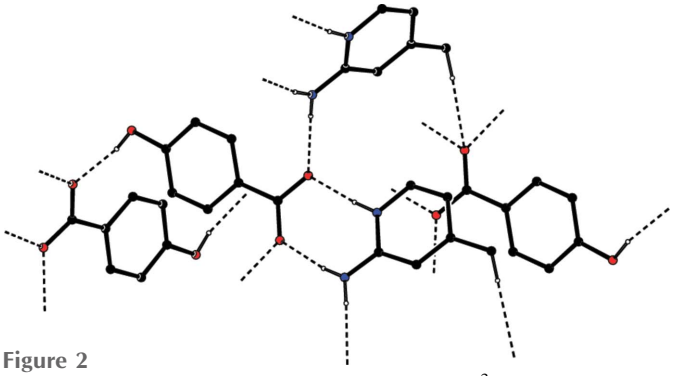


Figure 2
A partial view of the crystal packing showing the $R_2^2(8)$ ring motif.

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	Monoclinic, $P2_1/c$
Temperature (K)	295
a, b, c (Å)	13.069 (1), 9.1387 (6), 11.3367 (9)
β (°)	112.841 (3)
V (Å^3)	1247.81 (16)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.26 × 0.24 × 0.18
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2004)
T_{min}, T_{max}	0.682, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21655, 4159, 2301
R_{int}	0.034
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.769
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.069, 0.199, 1.04
No. of reflections	4159
No. of parameters	179
No. of restraints	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.23, −0.26

Computer programs: *APEX2* and *SAINT* (Bruker, 2004), *SHELXS97* (Sheldrick, 2008), *SHELXL2016* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

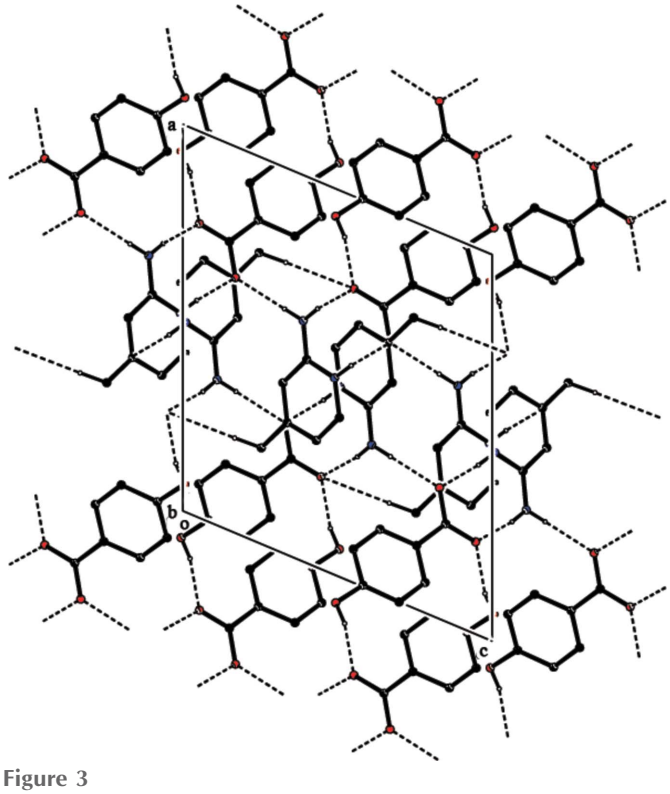


Figure 3
The crystal packing of the title molecular salt viewed along b axis. The hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonds have been omitted for clarity.

Acknowledgements

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full crystallographic data

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Crystal data

$C_6H_9N_2^+·C_7H_5O^{3-}$
M_r = 246.26
Monoclinic, $P2_1/c$
a = 13.069 (1) Å
b = 9.1387 (6) Å
c = 11.3367 (9) Å
β = 112.841 (3)°
V = 1247.81 (16) Å^3
Z = 4
$F(000)$ = 520
D_x = 1.311 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5844 reflections
θ = 2.8–32.5°
μ = 0.10 mm^{-1}
T = 295 K
Block, colourless
0.26 × 0.24 × 0.18 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
ω and φ scan
Absorption correction: multi-scan (SADABS; Bruker, 2004)
T_{min} = 0.682, T_{max} = 0.747
21655 measured reflections
4159 independent reflections
2301 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 33.1°, θ_{min} = 2.8°
h = −19→19
k = −13→13
l = −17→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.069
$wR(F^2)$ = 0.199
S = 1.04
4159 reflections
179 parameters
4 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0694P)^2 + 0.7446P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
C1	0.52644 (16)	0.3239 (2)	0.90045 (18)	0.0392 (4)

C2	0.44042 (17)	0.4162 (2)	0.82341 (19)	0.0425 (5)
H2	0.451228	0.474391	0.761933	0.051*
C3	0.34175 (17)	0.4219 (2)	0.8372 (2)	0.0465 (5)
C4	0.32794 (19)	0.3336 (3)	0.9316 (2)	0.0555 (6)
H4	0.260897	0.334077	0.942314	0.067*
C5	0.41194 (19)	0.2487 (3)	1.0062 (2)	0.0531 (6)
H5	0.402979	0.192189	1.069749	0.064*
C6	0.2488 (2)	0.5176 (4)	0.7536 (3)	0.0755 (8)
H6A	0.261945	0.616509	0.784452	0.113*
H6B	0.179993	0.483581	0.755475	0.113*
H6C	0.245072	0.514134	0.667401	0.113*
C7	0.16520 (15)	0.0386 (2)	0.75602 (18)	0.0382 (4)
C8	0.1671 (2)	0.0718 (3)	0.6378 (2)	0.0663 (8)
H8	0.223915	0.034629	0.616305	0.080*
C9	0.0869 (2)	0.1585 (4)	0.5514 (3)	0.0761 (9)
H9	0.088821	0.177112	0.471584	0.091*
C10	0.00385 (18)	0.2180 (3)	0.5823 (2)	0.0504 (5)
C11	−0.00016 (16)	0.1854 (2)	0.6991 (2)	0.0429 (5)
H11	−0.055959	0.224857	0.721143	0.051*
C12	0.07840 (16)	0.0946 (2)	0.78317 (19)	0.0408 (4)
H12	0.073067	0.070264	0.860227	0.049*
C13	0.25253 (16)	−0.0537 (2)	0.84967 (18)	0.0389 (4)
N1	0.50941 (15)	0.2439 (2)	0.99064 (17)	0.0435 (4)
N2	0.62321 (17)	0.3102 (3)	0.8892 (2)	0.0581 (5)
O1	0.23876 (12)	−0.09774 (19)	0.94694 (14)	0.0525 (4)
O2	0.33935 (12)	−0.08189 (18)	0.83009 (14)	0.0511 (4)
O3	−0.07119 (16)	0.3049 (2)	0.49415 (18)	0.0724 (6)
H1	0.560 (2)	0.189 (3)	1.045 (2)	0.090 (10)*
H2A	0.6699 (18)	0.247 (2)	0.936 (2)	0.067 (8)*
H2B	0.6333 (19)	0.356 (2)	0.8288 (17)	0.051 (7)*
H3	−0.115 (2)	0.339 (3)	0.523 (3)	0.076*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0423 (10)	0.0429 (10)	0.0366 (9)	−0.0021 (8)	0.0198 (8)	−0.0028 (8)
C2	0.0474 (11)	0.0466 (11)	0.0378 (10)	0.0020 (9)	0.0211 (8)	0.0040 (8)
C3	0.0436 (11)	0.0502 (12)	0.0463 (11)	0.0040 (9)	0.0182 (9)	−0.0043 (9)
C4	0.0417 (11)	0.0720 (16)	0.0605 (13)	−0.0011 (11)	0.0285 (10)	−0.0005 (12)
C5	0.0514 (12)	0.0656 (15)	0.0517 (12)	−0.0034 (11)	0.0302 (10)	0.0096 (11)
C6	0.0573 (15)	0.088 (2)	0.0773 (19)	0.0229 (14)	0.0215 (13)	0.0161 (16)
C7	0.0378 (9)	0.0423 (10)	0.0407 (10)	0.0032 (8)	0.0220 (8)	0.0025 (8)
C8	0.0663 (15)	0.0905 (19)	0.0618 (14)	0.0410 (14)	0.0465 (13)	0.0314 (14)
C9	0.0796 (18)	0.109 (2)	0.0623 (15)	0.0500 (17)	0.0522 (14)	0.0408 (16)
C10	0.0479 (11)	0.0562 (13)	0.0535 (12)	0.0161 (10)	0.0267 (10)	0.0137 (10)
C11	0.0389 (9)	0.0489 (12)	0.0483 (11)	0.0036 (8)	0.0250 (8)	−0.0006 (9)
C12	0.0419 (10)	0.0496 (11)	0.0382 (9)	0.0018 (8)	0.0234 (8)	0.0014 (8)
C13	0.0388 (9)	0.0429 (10)	0.0385 (10)	0.0016 (8)	0.0190 (8)	0.0002 (8)

N1	0.0435 (9)	0.0499 (10)	0.0422 (9)	0.0014 (8)	0.0221 (7)	0.0053 (8)
N2	0.0508 (11)	0.0753 (15)	0.0609 (12)	0.0146 (10)	0.0354 (10)	0.0203 (11)
O1	0.0433 (8)	0.0731 (11)	0.0479 (8)	0.0088 (7)	0.0252 (7)	0.0157 (8)
O2	0.0471 (8)	0.0666 (10)	0.0483 (8)	0.0169 (7)	0.0279 (7)	0.0115 (7)
O3	0.0717 (12)	0.0929 (14)	0.0660 (11)	0.0431 (11)	0.0412 (9)	0.0318 (10)

Geometric parameters (Å, º)

C1—N2	1.326 (3)	C7—C13	1.483 (3)
C1—N1	1.344 (3)	C8—C9	1.375 (3)
C1—C2	1.406 (3)	C8—H8	0.9300
C2—C3	1.359 (3)	C9—C10	1.376 (3)
C2—H2	0.9300	C9—H9	0.9300
C3—C4	1.407 (3)	C10—O3	1.353 (3)
C3—C6	1.498 (3)	C10—C11	1.379 (3)
C4—C5	1.342 (3)	C11—C12	1.375 (3)
C4—H4	0.9300	C11—H11	0.9300
C5—N1	1.353 (3)	C12—H12	0.9300
C5—H5	0.9300	C13—O1	1.251 (2)
C6—H6A	0.9600	C13—O2	1.264 (2)
C6—H6B	0.9600	N1—H1	0.865 (10)
C6—H6C	0.9600	N2—H2A	0.859 (10)
C7—C12	1.384 (3)	N2—H2B	0.855 (10)
C7—C8	1.384 (3)	O3—H3	0.827 (10)
N2—C1—N1	117.89 (19)	C9—C8—H8	119.3
N2—C1—C2	124.03 (19)	C7—C8—H8	119.3
N1—C1—C2	118.07 (18)	C8—C9—C10	120.4 (2)
C3—C2—C1	121.14 (19)	C8—C9—H9	119.8
C3—C2—H2	119.4	C10—C9—H9	119.8
C1—C2—H2	119.4	O3—C10—C9	117.5 (2)
C2—C3—C4	118.3 (2)	O3—C10—C11	123.33 (19)
C2—C3—C6	121.5 (2)	C9—C10—C11	119.2 (2)
C4—C3—C6	120.3 (2)	C12—C11—C10	119.96 (18)
C5—C4—C3	119.7 (2)	C12—C11—H11	120.0
C5—C4—H4	120.1	C10—C11—H11	120.0
C3—C4—H4	120.1	C11—C12—C7	121.69 (18)
C4—C5—N1	121.2 (2)	C11—C12—H12	119.2
C4—C5—H5	119.4	C7—C12—H12	119.2
N1—C5—H5	119.4	O1—C13—O2	122.34 (18)
C3—C6—H6A	109.5	O1—C13—C7	118.69 (17)
C3—C6—H6B	109.5	O2—C13—C7	118.95 (17)
H6A—C6—H6B	109.5	C1—N1—C5	121.58 (19)
C3—C6—H6C	109.5	C1—N1—H1	123 (2)
H6A—C6—H6C	109.5	C5—N1—H1	115 (2)
H6B—C6—H6C	109.5	C1—N2—H2A	118.8 (19)
C12—C7—C8	117.33 (18)	C1—N2—H2B	118.6 (16)
C12—C7—C13	121.37 (17)	H2A—N2—H2B	122 (2)

C8—C7—C13	121.29 (17)	C10—O3—H3	110 (2)
C9—C8—C7	121.4 (2)		
N2—C1—C2—C3	177.9 (2)	O3—C10—C11—C12	179.2 (2)
N1—C1—C2—C3	−1.7 (3)	C9—C10—C11—C12	0.1 (4)
C1—C2—C3—C4	0.5 (3)	C10—C11—C12—C7	2.6 (3)
C1—C2—C3—C6	−178.7 (2)	C8—C7—C12—C11	−3.0 (3)
C2—C3—C4—C5	1.0 (3)	C13—C7—C12—C11	177.11 (19)
C6—C3—C4—C5	−179.8 (2)	C12—C7—C13—O1	10.0 (3)
C3—C4—C5—N1	−1.4 (4)	C8—C7—C13—O1	−169.9 (2)
C12—C7—C8—C9	0.8 (4)	C12—C7—C13—O2	−168.28 (19)
C13—C7—C8—C9	−179.3 (3)	C8—C7—C13—O2	11.9 (3)
C7—C8—C9—C10	1.8 (5)	N2—C1—N1—C5	−178.3 (2)
C8—C9—C10—O3	178.6 (3)	C2—C1—N1—C5	1.3 (3)
C8—C9—C10—C11	−2.2 (5)	C4—C5—N1—C1	0.2 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2^{i}	0.87 (1)	1.81 (1)	2.666 (2)	174 (3)
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N2—H2*B*···O2^{ii}	0.86 (1)	2.05 (1)	2.887 (3)	167 (2)
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Symmetry codes: (i) −*x*+1, −*y*, −*z*+2; (ii) −*x*+1, *y*+1/2, −*z*+3/2; (iii) −*x*, *y*+1/2, −*z*+3/2; (iv) *x*, −*y*+1/2, *z*−1/2.