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2-Amino-3-methylpyridinium hydrogen phthalate

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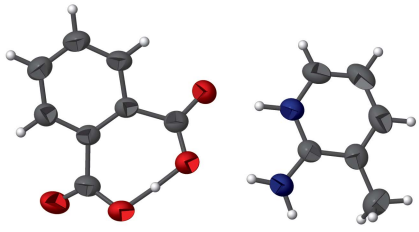
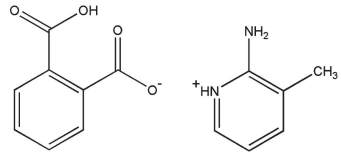
In the title molecular salt, $C_6H_9N_2^+\cdot C_8H_5O_4^-$, the cation is protonated at the pyridine N atom and the anion is deprotonated at the hydroxy O atom. The anion features an intramolecular O—H···O hydrogen bond with the H atom located almost in the middle of the two O atoms. The dihedral angle between the pyridine and benzene rings is 19.17 (12)°. The N—H···O hydrogen bonds generate $R_2^2(8)$ and $R_2^4(18)$ ring motifs. The crystal structure is stabilized by N—H···O hydrogen bonds. The structure is also influenced by weak π–π [centroid-to-centroid distance = 3.7347 (14) Å] interaction between the anions.

3D view



Chemical scheme



Structure description

Pyridine derivatives exhibit antifungal, anticancer and anti-inflammatory activities (Liu & Hu, 2002; Spanka *et al.*, 2010). We report herein the synthesis and the crystal structure of the title molecular salt (Fig. 1). The bond lengths are comparable with those in related structures (Sivakumar, Devi *et al.*, 2016; Sivakumar, Sudhahar *et al.*, 2016). The title molecular salt (Fig. 1) comprises a 2-amino-3-methylpyridinium cation and a hydrogen phthalate anion. The cation is protonated at the pyridine N atom and the anion is deprotonated at one of the hydroxy O atoms. The anion features an intramolecular O—H—O hydrogen bond with the H atom located almost in the middle of the two O atoms. The dihedral angle between the pyridine and benzene rings is 19.17 (12)°.

In the asymmetric unit, the inter-ionic N1—H1···O4 and N2—H2*A*···O3 hydrogen bonds (Table 1) link the cation and anion, generating an $R_2^2(8)$ ring motif (Fig. 2). In the crystal, the N2—H2*A*···O3 and N2—H2*B*···O1^{i} (Table 1) hydrogen bonds generate an $R_2^4(18)$ ring motif (Fig. 3). The structure is also influenced by a weak offset π–π [$Cg1\cdots Cg1(1-x, 2-y, 2-z)$ = 3.7347 (14) Å; $Cg1$ is the centroid of the (C7–C12) ring] interaction between the anions.

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H2···O2	1.18 (3)	1.25 (3)	2.417 (2)	169 (2)
N1—H1···O4	0.99 (3)	1.70 (3)	2.685 (3)	171 (3)
N2—H2A···O3	0.91 (3)	2.01 (3)	2.916 (3)	173 (2)
N2—H2B···O1^{i}	0.93 (4)	1.99 (4)	2.885 (3)	162 (3)

Symmetry code: (i) $-x+1, -y+2, -z+1$.

Synthesis and crystallization

The title compound was synthesized using 2-amino-3-methylpyridine (0.54 g) and phthalic acid (0.83 g) in an equimolar ratio. These reactants were dissolved in 15 ml acetone. The white precipitate that formed was dissolved in water and kept at room temperature. Crystals suitable for X-ray diffraction were harvested after 90 d.

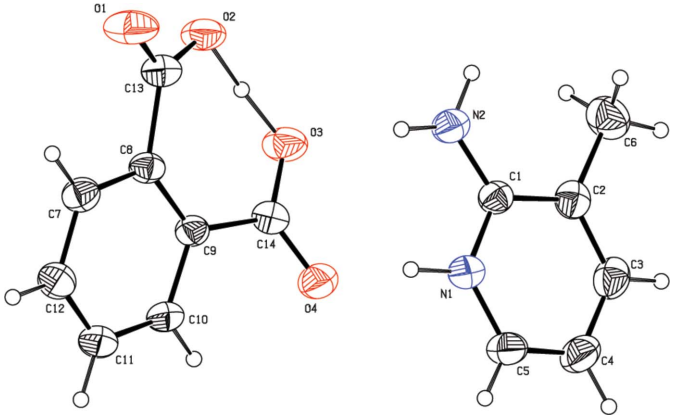


Figure 1
The molecular structure of the title molecular salt, with the atom labelling and 30% probability displacement ellipsoids.

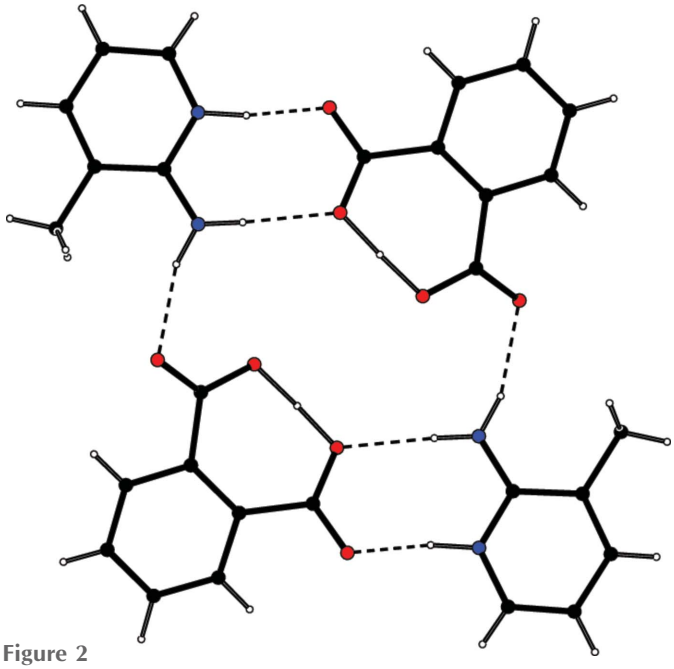


Figure 2
A partial view of the crystal packing showing the various ring motifs.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_6H_9N_2^+\cdot C_8H_5O_4^-$
M_r	274.27
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	295
a, b, c (Å)	7.1675 (4), 8.8143 (6), 10.6613 (7)
α, β, γ (°)	91.968 (4), 96.362 (3), 94.745 (3)
V (Å^3)	666.46 (7)
Z	2
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}	0.686, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17030, 3982, 2056
R_{int}	0.032
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.714
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.059, 0.189, 1.02
No. of reflections	3982
No. of parameters	198
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, −0.21

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

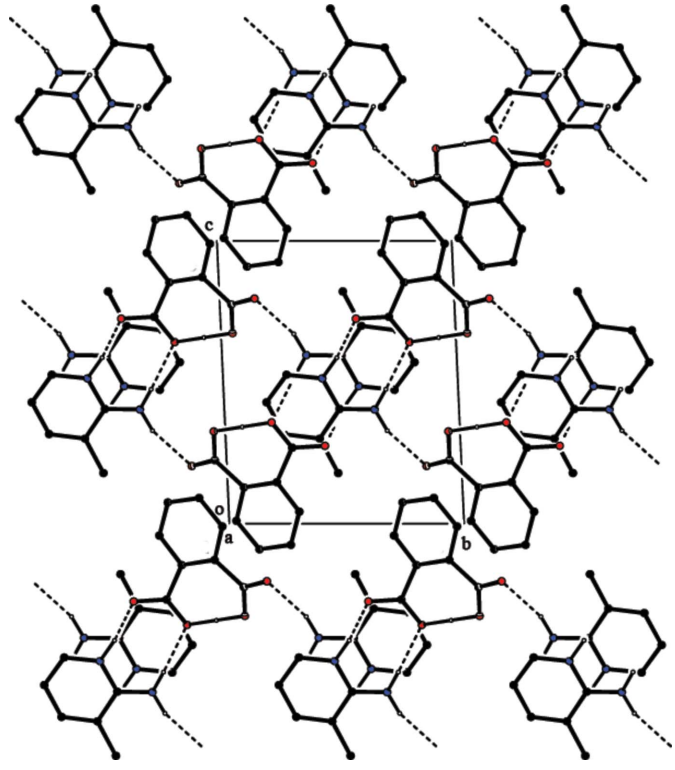


Figure 3
The crystal packing of the title molecular salt viewed along *a* axis. The hydrogen bonds are shown as dashed lines. H atoms not involving in hydrogen bonds have been omitted for clarity.

Refinement

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

Acknowledgements

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full crystallographic data

IUCrData (2017). **2**, x170422 [https://doi.org/10.1107/S2414314617004229]

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P. Sivakumar, C. Anzline, S. Sudhahar, S. Israel and G. Chakkaravarthi

2-Amino-3-methylpyridinium 2-carboxybenzoate

Crystal data

$C_6H_9N_2^+·C_8H_5O_4^-$
M_r = 274.27
Triclinic, $P\overline{1}$
a = 7.1675 (4) Å
b = 8.8143 (6) Å
c = 10.6613 (7) Å
α = 91.968 (4)°
β = 96.362 (3)°
γ = 94.745 (3)°
V = 666.46 (7) Å^3
Z = 2
$F(000)$ = 288
D_x = 1.367 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5483 reflections
θ = 0.7–0.8°
μ = 0.10 mm^{-1}
T = 295 K
Block, colourless
0.28 × 0.24 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
ω and φ scan
Absorption correction: multi-scan (SADABS; Bruker, 2004)
T_{min} = 0.686, T_{max} = 0.746
17030 measured reflections
3982 independent reflections
2056 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 30.5°, θ_{min} = 1.9°
h = −10→10
k = −12→12
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.189
S = 1.02
3982 reflections
198 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0632P)^2 + 0.3832P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 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	0.1981 (3)	0.4914 (2)	0.4055 (2)	0.0475 (5)
C2	0.1063 (3)	0.4009 (3)	0.3006 (2)	0.0541 (6)
C3	0.0722 (4)	0.2491 (3)	0.3165 (3)	0.0643 (7)
H3	0.008907	0.188210	0.249572	0.077*
C4	0.1284 (4)	0.1811 (3)	0.4291 (3)	0.0713 (8)
H4	0.105614	0.076634	0.437016	0.086*
C5	0.2171 (4)	0.2715 (3)	0.5265 (3)	0.0652 (7)
H5	0.256743	0.229168	0.602565	0.078*
C6	0.0549 (4)	0.4731 (4)	0.1789 (3)	0.0785 (8)
H6A	−0.003326	0.396615	0.117308	0.118*
H6B	0.166452	0.520748	0.149629	0.118*
H6C	−0.031501	0.548357	0.191184	0.118*
C7	0.7494 (3)	0.9694 (3)	0.9900 (2)	0.0530 (5)
H7	0.825134	1.060789	1.001807	0.064*
C8	0.6526 (3)	0.9306 (2)	0.8717 (2)	0.0454 (5)
C9	0.5434 (3)	0.7897 (2)	0.85357 (19)	0.0449 (5)
C10	0.5318 (4)	0.6995 (3)	0.9578 (2)	0.0551 (6)
H10	0.458464	0.606925	0.947484	0.066*
C11	0.6243 (4)	0.7420 (3)	1.0749 (2)	0.0624 (6)
H11	0.610918	0.680227	1.142917	0.075*
C12	0.7365 (4)	0.8762 (3)	1.0907 (2)	0.0606 (6)
H12	0.803702	0.904462	1.168821	0.073*
C13	0.6793 (3)	1.0500 (3)	0.7754 (2)	0.0550 (6)
C14	0.4398 (3)	0.7183 (3)	0.7314 (2)	0.0513 (5)
N1	0.2482 (3)	0.4225 (2)	0.5137 (2)	0.0549 (5)
H1	0.305 (4)	0.489 (3)	0.587 (3)	0.081 (9)*
N2	0.2385 (3)	0.6404 (2)	0.4039 (2)	0.0616 (6)
H2A	0.295 (4)	0.692 (3)	0.475 (3)	0.069 (8)*
H2B	0.214 (5)	0.690 (4)	0.329 (4)	0.102 (11)*
O1	0.8082 (3)	1.1491 (2)	0.7962 (2)	0.0837 (6)
O2	0.5619 (3)	1.0490 (2)	0.67375 (17)	0.0682 (5)
H2	0.458 (4)	0.927 (3)	0.658 (3)	0.073 (8)*
O3	0.3884 (3)	0.8012 (2)	0.64200 (17)	0.0697 (5)
O4	0.4074 (3)	0.57795 (19)	0.72482 (17)	0.0698 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0440 (11)	0.0456 (11)	0.0546 (12)	0.0028 (9)	0.0125 (9)	0.0049 (9)
C2	0.0457 (12)	0.0579 (13)	0.0590 (13)	0.0013 (10)	0.0116 (10)	−0.0018 (11)
C3	0.0598 (15)	0.0574 (14)	0.0748 (17)	−0.0079 (11)	0.0181 (13)	−0.0106 (13)
C4	0.0817 (19)	0.0452 (13)	0.090 (2)	−0.0019 (12)	0.0298 (16)	0.0021 (13)
C5	0.0791 (17)	0.0515 (14)	0.0687 (16)	0.0057 (12)	0.0204 (14)	0.0156 (12)
C6	0.0835 (19)	0.089 (2)	0.0596 (16)	0.0048 (16)	−0.0041 (14)	0.0064 (14)
C7	0.0506 (12)	0.0498 (12)	0.0576 (13)	0.0043 (10)	−0.0002 (10)	0.0059 (10)

C8	0.0430 (11)	0.0459 (11)	0.0488 (11)	0.0094 (9)	0.0050 (9)	0.0110 (9)
C9	0.0481 (11)	0.0427 (11)	0.0454 (11)	0.0107 (9)	0.0053 (9)	0.0077 (9)
C10	0.0710 (15)	0.0419 (11)	0.0532 (13)	0.0086 (10)	0.0055 (11)	0.0122 (10)
C11	0.0827 (17)	0.0547 (14)	0.0508 (13)	0.0121 (12)	0.0031 (12)	0.0151 (11)
C12	0.0698 (15)	0.0622 (15)	0.0488 (13)	0.0101 (12)	−0.0029 (11)	0.0067 (11)
C13	0.0545 (13)	0.0506 (13)	0.0612 (14)	0.0055 (10)	0.0072 (11)	0.0150 (10)
C14	0.0511 (12)	0.0530 (13)	0.0502 (12)	0.0038 (10)	0.0063 (10)	0.0095 (10)
N1	0.0619 (12)	0.0476 (11)	0.0554 (11)	0.0023 (9)	0.0079 (9)	0.0065 (9)
N2	0.0789 (15)	0.0460 (11)	0.0576 (13)	−0.0022 (10)	0.0026 (11)	0.0049 (10)
O1	0.0794 (13)	0.0740 (13)	0.0917 (14)	−0.0203 (10)	−0.0063 (11)	0.0352 (11)
O2	0.0857 (12)	0.0547 (10)	0.0608 (10)	0.0000 (9)	−0.0071 (9)	0.0206 (8)
O3	0.0829 (12)	0.0593 (11)	0.0597 (10)	−0.0096 (9)	−0.0156 (9)	0.0151 (8)
O4	0.0957 (14)	0.0493 (10)	0.0600 (10)	−0.0054 (9)	−0.0018 (9)	0.0042 (8)

Geometric parameters (Å, º)

C1—N2	1.322 (3)	C8—C13	1.511 (3)
C1—N1	1.350 (3)	C9—C10	1.394 (3)
C1—C2	1.417 (3)	C9—C14	1.516 (3)
C2—C3	1.360 (3)	C10—C11	1.372 (3)
C2—C6	1.488 (4)	C10—H10	0.9300
C3—C4	1.395 (4)	C11—C12	1.369 (4)
C3—H3	0.9300	C11—H11	0.9300
C4—C5	1.353 (4)	C12—H12	0.9300
C4—H4	0.9300	C13—O1	1.214 (3)
C5—N1	1.345 (3)	C13—O2	1.295 (3)
C5—H5	0.9300	C14—O4	1.238 (3)
C6—H6A	0.9600	C14—O3	1.262 (3)
C6—H6B	0.9600	N1—H1	0.99 (3)
C6—H6C	0.9600	N2—H2A	0.91 (3)
C7—C12	1.380 (3)	N2—H2B	0.93 (4)
C7—C8	1.388 (3)	O2—H2	1.25 (3)
C7—H7	0.9300	O3—H2	1.18 (3)
C8—C9	1.407 (3)		
N2—C1—N1	117.6 (2)	C10—C9—C8	117.8 (2)
N2—C1—C2	123.9 (2)	C10—C9—C14	114.34 (19)
N1—C1—C2	118.6 (2)	C8—C9—C14	127.84 (19)
C3—C2—C1	117.4 (2)	C11—C10—C9	122.6 (2)
C3—C2—C6	122.9 (2)	C11—C10—H10	118.7
C1—C2—C6	119.7 (2)	C9—C10—H10	118.7
C2—C3—C4	122.6 (3)	C12—C11—C10	119.3 (2)
C2—C3—H3	118.7	C12—C11—H11	120.3
C4—C3—H3	118.7	C10—C11—H11	120.3
C5—C4—C3	118.0 (2)	C11—C12—C7	119.7 (2)
C5—C4—H4	121.0	C11—C12—H12	120.2
C3—C4—H4	121.0	C7—C12—H12	120.2
N1—C5—C4	120.2 (3)	O1—C13—O2	120.6 (2)

N1—C5—H5	119.9	O1—C13—C8	119.3 (2)
C4—C5—H5	119.9	O2—C13—C8	120.1 (2)
C2—C6—H6A	109.5	O4—C14—O3	122.6 (2)
C2—C6—H6B	109.5	O4—C14—C9	117.2 (2)
H6A—C6—H6B	109.5	O3—C14—C9	120.2 (2)
C2—C6—H6C	109.5	C5—N1—C1	123.1 (2)
H6A—C6—H6C	109.5	C5—N1—H1	119.8 (18)
H6B—C6—H6C	109.5	C1—N1—H1	117.0 (18)
C12—C7—C8	121.9 (2)	C1—N2—H2A	119.4 (17)
C12—C7—H7	119.1	C1—N2—H2B	120 (2)
C8—C7—H7	119.1	H2A—N2—H2B	121 (3)
C7—C8—C9	118.69 (19)	C13—O2—H2	111.5 (12)
C7—C8—C13	113.89 (19)	C14—O3—H2	112.0 (13)
C9—C8—C13	127.4 (2)		

N2—C1—C2—C3	−179.4 (2)	C14—C9—C10—C11	176.7 (2)
N1—C1—C2—C3	0.8 (3)	C9—C10—C11—C12	−1.6 (4)
N2—C1—C2—C6	1.7 (4)	C10—C11—C12—C7	2.4 (4)
N1—C1—C2—C6	−178.1 (2)	C8—C7—C12—C11	−0.6 (4)
C1—C2—C3—C4	−1.8 (4)	C7—C8—C13—O1	16.2 (3)
C6—C2—C3—C4	177.0 (3)	C9—C8—C13—O1	−163.9 (2)
C2—C3—C4—C5	1.3 (4)	C7—C8—C13—O2	−161.7 (2)
C3—C4—C5—N1	0.3 (4)	C9—C8—C13—O2	18.3 (4)
C12—C7—C8—C9	−2.1 (3)	C10—C9—C14—O4	−21.6 (3)
C12—C7—C8—C13	177.8 (2)	C8—C9—C14—O4	155.8 (2)
C7—C8—C9—C10	2.8 (3)	C10—C9—C14—O3	157.6 (2)
C13—C8—C9—C10	−177.1 (2)	C8—C9—C14—O3	−24.9 (3)
C7—C8—C9—C14	−174.5 (2)	C4—C5—N1—C1	−1.4 (4)
C13—C8—C9—C14	5.5 (4)	N2—C1—N1—C5	−179.0 (2)
C8—C9—C10—C11	−1.0 (3)	C2—C1—N1—C5	0.8 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H2···O2	1.18 (3)	1.25 (3)	2.417 (2)	169 (2)
N1—H1···O4	0.99 (3)	1.70 (3)	2.685 (3)	171 (3)
N2—H2*A*···O3	0.91 (3)	2.01 (3)	2.916 (3)	173 (2)
N2—H2*B*···O1^{i}	0.93 (4)	1.99 (4)	2.885 (3)	162 (3)

Symmetry code: (i) −*x*+1, −*y*+2, −*z*+1.