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2-Amino-4-methylpyridinium 4-methoxybenzoate dihydrate

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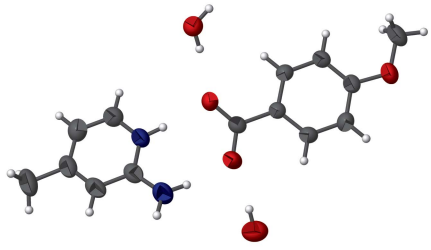
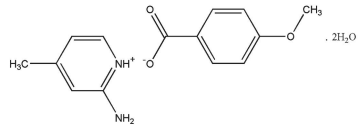
In the title hydrated molecular salt, $C_6H_9N_2^+\cdot C_8H_7O_3^-\cdot 2H_2O$, the cation is protonated at the pyridine N atom. The cation and anion are linked by a pair of N—H···O hydrogen bonds, which generates an $R_2^2(8)$ loop, and the dihedral angle between their ring planes is 16.07 (14)°. The ion pairs are linked by O—H···O hydrogen bonds involving the water molecules, generating a three-dimensional network. Weak C—H···O and aromatic π–π stacking [centroid-to-centroid distance = 3.5874 (17) Å] interactions are also observed.

3D view



Chemical scheme



Structure description

We herewith report the synthesis and the crystal structure of the title hydrated molecular salt (Fig. 1). The bond lengths are comparable with reported similar structures (Sivakumar *et al.*, 2016*a*,*b*). The cation is protonated at the pyridine N atom and the dihedral angle between the pyridine (N1/C9–C13) and benzene (C2–C7) rings is 16.07 (14)°.

In the asymmetric unit, N1—H1···O1 and N2—H2*B*···O2 hydrogen bonds link the anion and cation and generate an $R_2^2(8)$ loop. The ion-pairs are further connected with the water molecules of crystallization through O4—H4*A*···O2 and O5—H5*A*···O1 hydrogen bonds (Fig. 1 and Table 1). Further O—H···O hydrogen bonds link the components into a three-dimensional network (Fig. 2). Weak C—H···O and π–π [*Cg*2···*Cg*2($-x$, y, 1 $-$ z) = 3.5874 (17) Å; *Cg*2 is the centroid of the N1/C9–C13 ring] interactions are also observed.

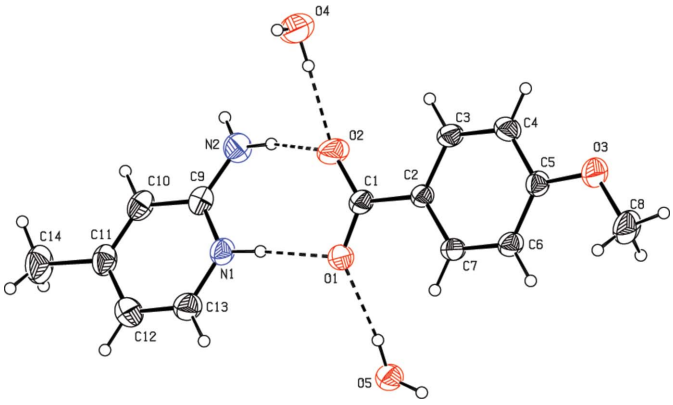


Figure 1
The molecular structure of the title molecular salt, with 30% probability displacement ellipsoids. Hydrogen bonds are shown as dashed lines.

Synthesis and crystallization

The title compound was prepared by mixing 4-methoxy benzoic acid (0.76 g) and 2-amino-4-methylpyridine (0.54 g) in an equimolar ratio in 20 ml acetone: the mixture was magnetically stirred for 3 h in a round-bottomed flask and then kept at room temperature for slow evaporation. After 30 days, colourless blocks were harvested.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The water H atoms were located in difference maps but *DFIX* and DANG commands were required to stabilize their refinement and prevent unreasonable close contacts and the location of these atoms should be regarded as less certain.

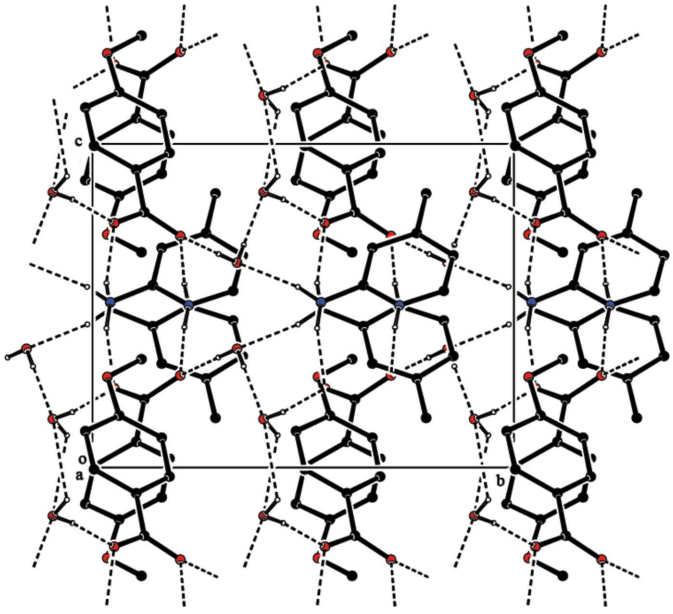


Figure 2
The crystal packing of the title molecular salt viewed along *a* axis. Hydrogen bonds are shown as dashed lines. H atoms not involving in hydrogen bonds have been omitted for clarity.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.87 (1)	1.87 (1)	2.737 (3)	175 (4)
N2—H2B···O2	0.87 (1)	1.91 (2)	2.758 (3)	165 (4)
N2—H2A···O5^{i}	0.86 (1)	2.10 (2)	2.951 (3)	169 (3)
O4—H4A···O2	0.82 (1)	1.92 (2)	2.743 (3)	173 (5)
O4—H4B···O4^{ii}	0.81 (1)	2.45 (2)	2.788 (6)	107 (1)
O5—H5A···O1	0.83 (1)	1.94 (2)	2.764 (3)	173 (4)
O5—H5B···O4^{iii}	0.82 (1)	2.01 (2)	2.814 (3)	168 (4)
C6—H6···O4^{iv}	0.93	2.57	3.455 (4)	160

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_6H_9N_2^+\cdot C_8H_7O_3^-\cdot 2H_2O$
M_r	296.32
Crystal system, space group	Monoclinic, $C2$
Temperature (K)	295
a, b, c (Å)	13.6968 (12), 12.1053 (10), 9.6353 (7)
β (°)	105.170 (3)
V (Å^3)	1541.9 (2)
Z	4
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}	0.694, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15843, 4821, 2891
R_{int}	0.048
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.725
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.133, 1.02
No. of reflections	4821
No. of parameters	217
No. of restraints	10
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, −0.16

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

Acknowledgements

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References

Bruker (2004). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* A**71**, 3–8.
Sivakumar, P., Sudhahar, S., Gunasekaran, B., Israel, S. & Chakkaravarthi, G. (2016*b*). *IUCrData*, **1**, x160817.
Sivakumar, P., Sudhahar, S., Israel, S. & Chakkaravarthi, G. (2016*a*). *IUCrData*, **1**, x160747.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

full crystallographic data

IUCrData (2017). **2**, x170649 [https://doi.org/10.1107/S2414314617006496]

2-Amino-4-methylpyridinium 4-methoxybenzoate dihydrate

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2-Amino-4-methylpyridinium 4-methoxybenzoate dihydrate

Crystal data

$C_6H_9N_2^+·C_8H_7O_3^-·2H_2O$
M_r = 296.32
Monoclinic, *C*2
a = 13.6968 (12) Å
b = 12.1053 (10) Å
c = 9.6353 (7) Å
β = 105.170 (3)°
V = 1541.9 (2) Å^3
Z = 4
F(000) = 632
D_x = 1.276 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 4368 reflections
θ = 2.6–25.0°
μ = 0.10 mm^{-1}
T = 295 K
Block, colourless
0.28 × 0.24 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
ω and *φ* scan
Absorption correction: multi-scan (SADABS; Bruker, 2004)
T_{min} = 0.694, T_{max} = 0.746
15843 measured reflections
4821 independent reflections
2891 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
θ_{max} = 31.0°, θ_{min} = 2.2°
h = −19→19
k = −17→17
l = −11→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.133
S = 1.02
4821 reflections
217 parameters
10 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.060P)^2 + 0.0879P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}
Extinction correction: SHELXL2016 (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0095 (18)

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 for the NH and NH_2 groups were loacated from Fourier maps and refined with N—H distance restraints of 0.86 (1) Å. The C-bound H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å and U_{iso}(H) = 1.2Ueq(C) for aromatic CH and C—H = 0.96 Å and U_{iso}(H) = 1.5Ueq(C) for CH_3.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.2345 (2)	0.6229 (2)	0.2107 (3)	0.0483 (6)
C2	0.27037 (19)	0.6036 (2)	0.0794 (3)	0.0405 (5)
C3	0.2511 (2)	0.5037 (2)	0.0058 (3)	0.0510 (6)
H3	0.213561	0.449829	0.037537	0.061*
C4	0.2863 (2)	0.4830 (2)	−0.1125 (3)	0.0537 (7)
H4	0.273219	0.415525	−0.159883	0.064*
C5	0.34132 (19)	0.5633 (2)	−0.1606 (3)	0.0458 (6)
C6	0.3602 (2)	0.6642 (2)	−0.0921 (3)	0.0481 (6)
H6	0.396041	0.718693	−0.125850	0.058*
C7	0.3245 (2)	0.6827 (2)	0.0280 (3)	0.0458 (6)
H7	0.337494	0.750201	0.075218	0.055*
C8	0.4287 (3)	0.6162 (3)	−0.3348 (4)	0.0772 (10)
H8A	0.389868	0.683038	−0.354442	0.116*
H8B	0.441904	0.589405	−0.421898	0.116*
H8C	0.491630	0.630678	−0.265095	0.116*
C9	0.13362 (18)	0.6428 (3)	0.5632 (3)	0.0484 (6)
C10	0.0920 (2)	0.6643 (3)	0.6788 (3)	0.0550 (7)
H10	0.068893	0.606065	0.724535	0.066*
C11	0.0851 (2)	0.7694 (3)	0.7244 (3)	0.0584 (7)
C12	0.1220 (3)	0.8565 (3)	0.6556 (4)	0.0668 (8)
H12	0.118150	0.929002	0.685539	0.080*
C13	0.1631 (2)	0.8337 (3)	0.5456 (3)	0.0606 (8)
H13	0.188020	0.890841	0.500152	0.073*
C14	0.0384 (3)	0.7919 (4)	0.8469 (4)	0.0876 (12)
H14A	−0.006539	0.732559	0.854159	0.131*
H14B	0.001103	0.859920	0.829460	0.131*
H14C	0.090709	0.797567	0.935051	0.131*
N1	0.16822 (17)	0.7284 (2)	0.5012 (2)	0.0500 (6)
H1	0.198 (2)	0.718 (3)	0.433 (3)	0.077 (11)*
N2	0.1394 (2)	0.5422 (2)	0.5105 (3)	0.0607 (7)
H2A	0.123 (3)	0.488 (2)	0.558 (3)	0.075 (11)*
H2B	0.156 (3)	0.533 (3)	0.430 (2)	0.071 (10)*
O1	0.26234 (15)	0.70839 (18)	0.2845 (2)	0.0614 (6)
O2	0.1790 (2)	0.5517 (2)	0.2445 (3)	0.0845 (8)
O3	0.37349 (16)	0.5352 (2)	−0.2798 (2)	0.0663 (6)
O4	0.0223 (2)	0.4061 (2)	0.1497 (3)	0.0846 (8)
H4A	0.068 (2)	0.452 (3)	0.171 (5)	0.127*
H4B	−0.0250 (18)	0.439 (4)	0.0997 (15)	0.127*
O5	0.43049 (16)	0.84316 (18)	0.3669 (2)	0.0596 (5)
H5A	0.383 (2)	0.799 (3)	0.340 (4)	0.089*
H5B	0.465 (3)	0.859 (4)	0.312 (4)	0.089*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0507 (14)	0.0501 (16)	0.0493 (14)	−0.0098 (12)	0.0220 (12)	−0.0039 (13)
C2	0.0419 (12)	0.0418 (13)	0.0395 (13)	−0.0052 (10)	0.0138 (10)	−0.0023 (10)
C3	0.0596 (14)	0.0461 (16)	0.0529 (15)	−0.0147 (12)	0.0249 (12)	−0.0041 (12)
C4	0.0670 (17)	0.0479 (15)	0.0502 (15)	−0.0094 (13)	0.0224 (13)	−0.0117 (12)
C5	0.0434 (13)	0.0543 (16)	0.0413 (13)	−0.0038 (11)	0.0143 (11)	−0.0042 (12)
C6	0.0540 (15)	0.0504 (16)	0.0438 (14)	−0.0099 (12)	0.0199 (11)	−0.0006 (11)
C7	0.0513 (14)	0.0414 (14)	0.0480 (15)	−0.0094 (11)	0.0186 (11)	−0.0062 (11)
C8	0.082 (2)	0.099 (3)	0.0652 (19)	−0.016 (2)	0.0454 (18)	−0.006 (2)
C9	0.0411 (12)	0.0630 (17)	0.0408 (13)	0.0006 (12)	0.0099 (10)	0.0049 (13)
C10	0.0478 (14)	0.075 (2)	0.0431 (14)	−0.0046 (14)	0.0139 (11)	0.0086 (13)
C11	0.0492 (15)	0.083 (2)	0.0456 (15)	−0.0021 (15)	0.0165 (12)	−0.0088 (15)
C12	0.075 (2)	0.066 (2)	0.0635 (19)	−0.0022 (16)	0.0252 (16)	−0.0126 (17)
C13	0.0670 (19)	0.0617 (19)	0.0565 (17)	−0.0098 (15)	0.0226 (14)	−0.0036 (15)
C14	0.086 (2)	0.125 (3)	0.063 (2)	−0.005 (2)	0.0386 (19)	−0.021 (2)
N1	0.0518 (12)	0.0579 (14)	0.0446 (13)	−0.0047 (10)	0.0201 (10)	−0.0010 (11)
N2	0.0752 (17)	0.0586 (16)	0.0549 (15)	0.0007 (13)	0.0289 (13)	0.0080 (13)
O1	0.0736 (13)	0.0623 (12)	0.0597 (12)	−0.0203 (10)	0.0380 (10)	−0.0208 (10)
O2	0.1166 (19)	0.0796 (16)	0.0798 (16)	−0.0489 (15)	0.0659 (15)	−0.0271 (14)
O3	0.0743 (13)	0.0787 (14)	0.0568 (11)	−0.0145 (11)	0.0365 (10)	−0.0150 (11)
O4	0.0782 (16)	0.0847 (18)	0.0918 (18)	−0.0235 (14)	0.0238 (13)	−0.0047 (15)
O5	0.0634 (13)	0.0619 (13)	0.0570 (12)	−0.0125 (10)	0.0220 (10)	−0.0108 (10)

Geometric parameters (Å, º)

C1—O2	1.247 (3)	C9—C10	1.401 (4)
C1—O1	1.257 (3)	C10—C11	1.357 (5)
C1—C2	1.491 (3)	C10—H10	0.9300
C2—C7	1.380 (3)	C11—C12	1.407 (5)
C2—C3	1.391 (4)	C11—C14	1.508 (4)
C3—C4	1.372 (4)	C12—C13	1.352 (4)
C3—H3	0.9300	C12—H12	0.9300
C4—C5	1.382 (4)	C13—N1	1.352 (4)
C4—H4	0.9300	C13—H13	0.9300
C5—O3	1.376 (3)	C14—H14A	0.9600
C5—C6	1.381 (4)	C14—H14B	0.9600
C6—C7	1.387 (3)	C14—H14C	0.9600
C6—H6	0.9300	N1—H1	0.870 (13)
C7—H7	0.9300	N2—H2A	0.864 (14)
C8—O3	1.422 (4)	N2—H2B	0.868 (13)
C8—H8A	0.9600	O4—H4A	0.823 (14)
C8—H8B	0.9600	O4—H4B	0.805 (14)
C8—H8C	0.9600	O5—H5A	0.830 (14)
C9—N2	1.330 (4)	O5—H5B	0.822 (14)
C9—N1	1.342 (4)		

O2—C1—O1	122.4 (2)	N1—C9—C10	118.3 (3)
O2—C1—C2	118.2 (2)	C11—C10—C9	120.6 (3)
O1—C1—C2	119.4 (2)	C11—C10—H10	119.7
C7—C2—C3	117.9 (2)	C9—C10—H10	119.7
C7—C2—C1	121.6 (2)	C10—C11—C12	119.0 (3)
C3—C2—C1	120.5 (2)	C10—C11—C14	120.2 (3)
C4—C3—C2	121.4 (2)	C12—C11—C14	120.8 (3)
C4—C3—H3	119.3	C13—C12—C11	119.4 (3)
C2—C3—H3	119.3	C13—C12—H12	120.3
C3—C4—C5	119.4 (2)	C11—C12—H12	120.3
C3—C4—H4	120.3	C12—C13—N1	120.4 (3)
C5—C4—H4	120.3	C12—C13—H13	119.8
O3—C5—C6	123.8 (2)	N1—C13—H13	119.8
O3—C5—C4	115.4 (2)	C11—C14—H14A	109.5
C6—C5—C4	120.8 (2)	C11—C14—H14B	109.5
C5—C6—C7	118.6 (2)	H14A—C14—H14B	109.5
C5—C6—H6	120.7	C11—C14—H14C	109.5
C7—C6—H6	120.7	H14A—C14—H14C	109.5
C2—C7—C6	121.8 (2)	H14B—C14—H14C	109.5
C2—C7—H7	119.1	C9—N1—C13	122.2 (2)
C6—C7—H7	119.1	C9—N1—H1	121 (3)
O3—C8—H8A	109.5	C13—N1—H1	117 (3)
O3—C8—H8B	109.5	C9—N2—H2A	117 (2)
H8A—C8—H8B	109.5	C9—N2—H2B	121 (3)
O3—C8—H8C	109.5	H2A—N2—H2B	122 (4)
H8A—C8—H8C	109.5	C5—O3—C8	117.3 (3)
H8B—C8—H8C	109.5	H4A—O4—H4B	105 (2)
N2—C9—N1	118.3 (2)	H5A—O5—H5B	119 (4)
N2—C9—C10	123.4 (3)		

O2—C1—C2—C7	174.3 (3)	C5—C6—C7—C2	−0.6 (4)
O1—C1—C2—C7	−7.1 (4)	N2—C9—C10—C11	−177.7 (3)
O2—C1—C2—C3	−6.6 (4)	N1—C9—C10—C11	1.3 (4)
O1—C1—C2—C3	172.0 (3)	C9—C10—C11—C12	−1.1 (4)
C7—C2—C3—C4	1.3 (4)	C9—C10—C11—C14	178.8 (3)
C1—C2—C3—C4	−177.9 (3)	C10—C11—C12—C13	0.2 (5)
C2—C3—C4—C5	−0.6 (5)	C14—C11—C12—C13	−179.7 (3)
C3—C4—C5—O3	180.0 (3)	C11—C12—C13—N1	0.4 (5)
C3—C4—C5—C6	−0.8 (4)	N2—C9—N1—C13	178.4 (3)
O3—C5—C6—C7	−179.5 (3)	C10—C9—N1—C13	−0.7 (4)
C4—C5—C6—C7	1.3 (4)	C12—C13—N1—C9	−0.1 (5)
C3—C2—C7—C6	−0.7 (4)	C6—C5—O3—C8	−0.4 (4)
C1—C2—C7—C6	178.5 (2)	C4—C5—O3—C8	178.8 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.87 (1)	1.87 (1)	2.737 (3)	175 (4)

N2—H2*B*···O2	0.87 (1)	1.91 (2)	2.758 (3)	165 (4)
N2—H2*A*···O5^{i}	0.86 (1)	2.10 (2)	2.951 (3)	169 (3)
O4—H4*A*···O2	0.82 (1)	1.92 (2)	2.743 (3)	173 (5)
O4—H4*B*···O4^{ii}	0.81 (1)	2.45 (2)	2.788 (6)	107 (1)
O5—H5*A*···O1	0.83 (1)	1.94 (2)	2.764 (3)	173 (4)
O5—H5*B*···O4^{iii}	0.82 (1)	2.01 (2)	2.814 (3)	168 (4)
C6—H6···O4^{iv}	0.93	2.57	3.455 (4)	160

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