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2-Amino-3-methylpyridinium 3,4-dimethoxybenzoate

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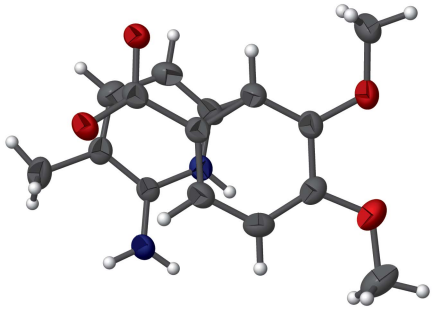
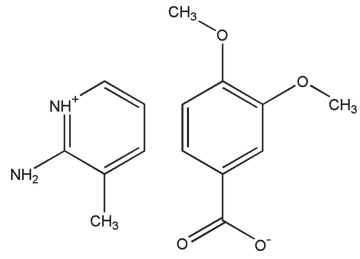
Structural data: full structural data are available from iucrdata.iucr.org

In the title molecular salt, $C_6H_9N_2^+\cdot C_9H_9O_4^-$, the cation is protonated at the pyridine N atom. In the crystal, N—H···O hydrogen bonds link the components into [010] chains, which feature $R_2^2(8)$ loops. The chains are linked by C—H···O hydrogen bonds, forming a three-dimensional network.

3D view



Chemical scheme



Structure description

We herewith report the synthesis and the crystal structure of the title molecular salt (Fig. 1). The bond lengths are comparable with related structures we have reported recently (Sivakumar *et al.*, 2016*a*,*b*). The cation is protonated at the pyridine N1 atom and the anion is deprotonated at hydroxyl O1 atom. In the anion, the dihedral angle between the carboxylate group and its attached benzene ring is 9.81 (9)° and both methoxy C atoms lie close to the plane of the ring [deviations for C13 and C14 = 0.172 (2) and 0.181 (2) Å, respectively].

In the crystal, N—H···O hydrogen bonds connect the anions and cations into infinite chains along [010] and these chains are further consolidated by C—H···O hydrogen bonds (Table 1 and Fig. 2), forming a three-dimensional network. As part of the chain motif, a pair of N—H···O (N1—H1*A*···O1^{i} and N2—H2*A*···O2^{i}) hydrogen bonds generate $R_2^2(8)$ loops.

Synthesis and crystallization

The title compound was synthesized in acetone by mixing 2-amino-3-methylpyridine (0.27 g) and 3,4-dimethoxy benzoic acid (0.45 g) in an equimolar ratio. The solution was

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1^{i}	0.88 (2)	1.73 (2)	2.6071 (19)	173 (2)
N2—H2A···O2^{i}	0.86	2.02	2.8816 (19)	177
N2—H2B···O2^{ii}	0.86	2.12	2.9051 (19)	152
C14—H14B···O4^{iii}	0.96	2.54	3.281 (3)	134

Symmetry codes: (i) $x, y+1, z$; (ii) $-x, y+\frac{1}{2}, -z+\frac{5}{2}$; (iii) $-x+1, -y-1, -z+2$.

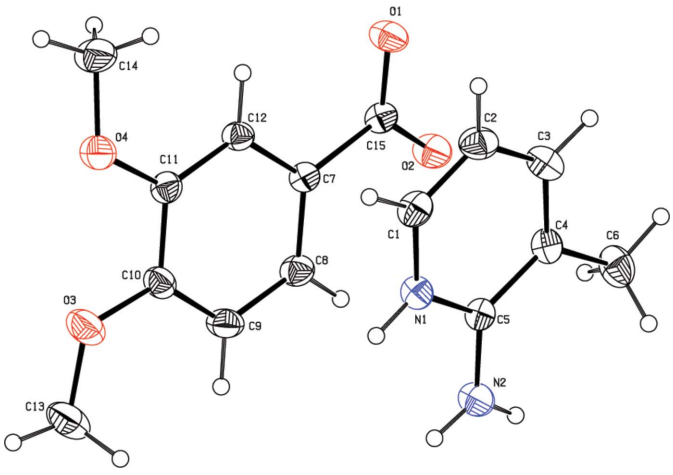


Figure 1
The molecular structure of the title molecular salt, with 30% probability displacement ellipsoids.

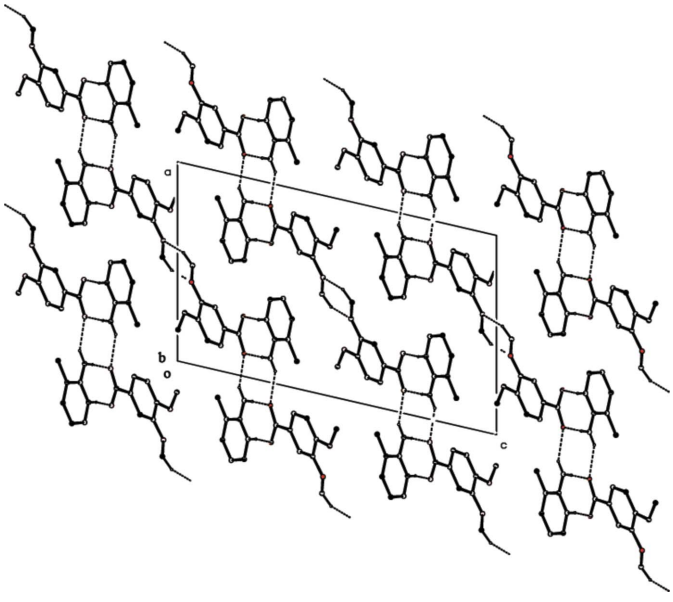


Figure 2
The crystal packing of the title molecular salt viewed along the b axis. Hydrogen bonds are shown as dashed lines. H atoms not involving in hydrogen bonding have been omitted for clarity.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_6H_9N_2^+\cdot C_9H_9O_4^-$
M_r	290.31
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	295
a, b, c (Å)	11.6972 (8), 6.6637 (5), 19.2325 (17)
β (°)	103.000 (2)
V (Å^3)	1460.7 (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}	0.973, 0.981
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17370, 3587, 2388
R_{int}	0.030
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.665
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.048, 0.128, 1.03
No. of reflections	3587
No. of parameters	197
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})	0.23, −0.23

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

allowed to evaporate slowly at room temperature. After a period of 25 days, colourless blocks were grown, which were suitable for X-ray diffraction.

Refinement

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

Acknowledgements

The authors acknowledge the SAIF, IIT, Madras for the data collection.

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Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
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Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

full crystallographic data

IUCrData (2016). **1**, x161332 [doi:10.1107/S2414314616013328]

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Crystal data

$C_6H_9N_2^+·C_9H_9O_4^-$
M_r = 290.31
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 11.6972 (8) Å
b = 6.6637 (5) Å
c = 19.2325 (17) Å
β = 103.000 (2)°
V = 1460.7 (2) Å^3
Z = 4
$F(000)$ = 616
D_x = 1.320 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4375 reflections
θ = 2.5–26.4°
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
Graphite monochromator
ω and φ scan
Absorption correction: multi-scan (SADABS; Bruker, 2004)
T_{min} = 0.973, T_{max} = 0.981
17370 measured reflections
3587 independent reflections
2388 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 28.2°, θ_{min} = 2.2°
h = −15→15
k = −8→8
l = −25→24

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.128
S = 1.03
3587 reflections
197 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
$w = 1/[\sigma^2(F_o^2) + (0.0509P)^2 + 0.5181P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 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.

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	0.41591 (14)	−0.5512 (3)	1.29093 (10)	0.0411 (4)
H1	0.4753	−0.4995	1.2711	0.049*
C2	0.43583 (16)	−0.7179 (3)	1.33117 (11)	0.0469 (5)
H2	0.5086	−0.7810	1.3404	0.056*
C3	0.34363 (16)	−0.7937 (3)	1.35878 (11)	0.0463 (5)
H3	0.3562	−0.9089	1.3868	0.056*
C4	0.23615 (15)	−0.7048 (3)	1.34609 (9)	0.0372 (4)
C5	0.22031 (13)	−0.5260 (2)	1.30491 (9)	0.0320 (4)
C6	0.13643 (17)	−0.7891 (3)	1.37408 (11)	0.0519 (5)
H6A	0.0757	−0.8340	1.3349	0.078*
H6B	0.1058	−0.6871	1.4001	0.078*
H6C	0.1639	−0.9002	1.4051	0.078*
C7	0.21553 (13)	−0.8319 (2)	1.14744 (9)	0.0308 (4)
C8	0.12877 (14)	−0.6888 (3)	1.13558 (10)	0.0384 (4)
H8	0.0636	−0.7047	1.1552	0.046*
C9	0.13749 (15)	−0.5203 (3)	1.09443 (10)	0.0437 (4)
H9	0.0783	−0.4242	1.0870	0.052*
C10	0.23282 (15)	−0.4946 (2)	1.06465 (9)	0.0382 (4)
C11	0.32175 (14)	−0.6394 (2)	1.07619 (9)	0.0357 (4)
C12	0.31268 (14)	−0.8051 (2)	1.11728 (9)	0.0335 (4)
H12	0.3721	−0.9008	1.1251	0.040*
C13	0.1576 (2)	−0.1972 (3)	1.00187 (13)	0.0630 (6)
H13A	0.0883	−0.2660	0.9770	0.094*
H13B	0.1795	−0.0982	0.9710	0.094*
H13C	0.1421	−0.1326	1.0434	0.094*
C14	0.49645 (19)	−0.7559 (3)	1.04719 (14)	0.0650 (7)
H14A	0.5383	−0.7744	1.0957	0.098*
H14B	0.5505	−0.7192	1.0185	0.098*
H14C	0.4577	−0.8787	1.0295	0.098*
C15	0.20866 (13)	−1.0170 (2)	1.19126 (9)	0.0334 (4)
N1	0.31064 (12)	−0.4576 (2)	1.27889 (8)	0.0357 (3)
N2	0.12124 (12)	−0.4201 (2)	1.29070 (8)	0.0437 (4)
H2A	0.1166	−0.3122	1.2657	0.052*
H2B	0.0619	−0.4597	1.3065	0.052*
O1	0.29953 (10)	−1.12424 (18)	1.20672 (7)	0.0466 (3)
O2	0.11498 (10)	−1.05519 (19)	1.20953 (7)	0.0475 (4)
O3	0.24997 (13)	−0.3368 (2)	1.02274 (8)	0.0570 (4)
O4	0.41272 (11)	−0.60306 (19)	1.04403 (8)	0.0512 (4)
H1A	0.3010 (17)	−0.345 (2)	1.2541 (10)	0.057 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0280 (8)	0.0509 (11)	0.0454 (11)	−0.0045 (8)	0.0102 (7)	−0.0035 (9)
C2	0.0340 (9)	0.0511 (11)	0.0534 (12)	0.0080 (8)	0.0050 (8)	−0.0004 (9)
C3	0.0473 (11)	0.0395 (10)	0.0488 (12)	0.0028 (8)	0.0035 (9)	0.0073 (9)
C4	0.0365 (9)	0.0390 (9)	0.0353 (10)	−0.0058 (8)	0.0065 (7)	0.0013 (8)
C5	0.0276 (8)	0.0360 (9)	0.0322 (9)	−0.0042 (7)	0.0064 (6)	−0.0019 (7)
C6	0.0494 (11)	0.0530 (12)	0.0548 (13)	−0.0096 (9)	0.0147 (9)	0.0137 (10)
C7	0.0287 (8)	0.0297 (8)	0.0343 (9)	−0.0034 (6)	0.0079 (7)	−0.0018 (7)
C8	0.0317 (8)	0.0390 (9)	0.0467 (11)	0.0011 (7)	0.0133 (7)	0.0009 (8)
C9	0.0388 (10)	0.0395 (10)	0.0530 (12)	0.0106 (8)	0.0106 (8)	0.0041 (8)
C10	0.0448 (10)	0.0300 (8)	0.0393 (10)	−0.0002 (7)	0.0084 (8)	0.0043 (7)
C11	0.0362 (9)	0.0336 (9)	0.0400 (10)	−0.0027 (7)	0.0144 (7)	0.0007 (7)
C12	0.0301 (8)	0.0314 (8)	0.0397 (10)	0.0013 (7)	0.0096 (7)	0.0010 (7)
C13	0.0771 (15)	0.0417 (11)	0.0633 (15)	0.0094 (11)	0.0014 (12)	0.0126 (10)
C14	0.0635 (13)	0.0511 (12)	0.0974 (19)	0.0143 (10)	0.0537 (13)	0.0221 (12)
C15	0.0288 (8)	0.0325 (9)	0.0401 (10)	−0.0036 (7)	0.0101 (7)	−0.0029 (7)
N1	0.0296 (7)	0.0374 (8)	0.0405 (9)	−0.0047 (6)	0.0084 (6)	0.0028 (7)
N2	0.0319 (8)	0.0446 (9)	0.0580 (10)	0.0007 (6)	0.0171 (7)	0.0125 (7)
O1	0.0320 (6)	0.0419 (7)	0.0707 (10)	0.0059 (5)	0.0220 (6)	0.0186 (6)
O2	0.0307 (6)	0.0470 (7)	0.0699 (9)	0.0008 (5)	0.0222 (6)	0.0142 (7)
O3	0.0632 (9)	0.0441 (8)	0.0661 (10)	0.0082 (7)	0.0199 (7)	0.0215 (7)
O4	0.0521 (8)	0.0425 (7)	0.0687 (10)	0.0046 (6)	0.0342 (7)	0.0172 (7)

Geometric parameters (Å, º)

C1—C2	1.344 (3)	C9—H9	0.9300
C1—N1	1.353 (2)	C10—O3	1.367 (2)
C1—H1	0.9300	C10—C11	1.399 (2)
C2—C3	1.399 (3)	C11—O4	1.367 (2)
C2—H2	0.9300	C11—C12	1.376 (2)
C3—C4	1.361 (2)	C12—H12	0.9300
C3—H3	0.9300	C13—O3	1.414 (2)
C4—C5	1.420 (2)	C13—H13A	0.9600
C4—C6	1.499 (2)	C13—H13B	0.9600
C5—N2	1.331 (2)	C13—H13C	0.9600
C5—N1	1.346 (2)	C14—O4	1.405 (2)
C6—H6A	0.9600	C14—H14A	0.9600
C6—H6B	0.9600	C14—H14B	0.9600
C6—H6C	0.9600	C14—H14C	0.9600
C7—C8	1.374 (2)	C15—O2	1.2499 (18)
C7—C12	1.399 (2)	C15—O1	1.2597 (19)
C7—C15	1.506 (2)	N1—H1A	0.881 (9)
C8—C9	1.390 (3)	N2—H2A	0.8600
C8—H8	0.9300	N2—H2B	0.8600
C9—C10	1.374 (2)		

C2—C1—N1	120.86 (17)	O3—C10—C11	114.93 (15)
C2—C1—H1	119.6	C9—C10—C11	119.47 (16)
N1—C1—H1	119.6	O4—C11—C12	124.78 (15)
C1—C2—C3	117.92 (17)	O4—C11—C10	115.62 (15)
C1—C2—H2	121.0	C12—C11—C10	119.59 (15)
C3—C2—H2	121.0	C11—C12—C7	121.02 (15)
C4—C3—C2	122.30 (18)	C11—C12—H12	119.5
C4—C3—H3	118.8	C7—C12—H12	119.5
C2—C3—H3	118.8	O3—C13—H13A	109.5
C3—C4—C5	117.70 (16)	O3—C13—H13B	109.5
C3—C4—C6	122.29 (17)	H13A—C13—H13B	109.5
C5—C4—C6	120.01 (16)	O3—C13—H13C	109.5
N2—C5—N1	117.63 (15)	H13A—C13—H13C	109.5
N2—C5—C4	123.89 (15)	H13B—C13—H13C	109.5
N1—C5—C4	118.48 (15)	O4—C14—H14A	109.5
C4—C6—H6A	109.5	O4—C14—H14B	109.5
C4—C6—H6B	109.5	H14A—C14—H14B	109.5
H6A—C6—H6B	109.5	O4—C14—H14C	109.5
C4—C6—H6C	109.5	H14A—C14—H14C	109.5
H6A—C6—H6C	109.5	H14B—C14—H14C	109.5
H6B—C6—H6C	109.5	O2—C15—O1	124.38 (16)
C8—C7—C12	118.78 (15)	O2—C15—C7	118.98 (14)
C8—C7—C15	122.07 (14)	O1—C15—C7	116.63 (14)
C12—C7—C15	119.15 (14)	C5—N1—C1	122.70 (16)
C7—C8—C9	120.60 (16)	C5—N1—H1A	118.3 (14)
C7—C8—H8	119.7	C1—N1—H1A	119.0 (14)
C9—C8—H8	119.7	C5—N2—H2A	120.0
C10—C9—C8	120.54 (16)	C5—N2—H2B	120.0
C10—C9—H9	119.7	H2A—N2—H2B	120.0
C8—C9—H9	119.7	C10—O3—C13	117.98 (16)
O3—C10—C9	125.60 (16)	C11—O4—C14	117.25 (14)

N1—C1—C2—C3	1.4 (3)	C9—C10—C11—C12	−0.1 (3)
C1—C2—C3—C4	0.1 (3)	O4—C11—C12—C7	−179.09 (16)
C2—C3—C4—C5	−1.8 (3)	C10—C11—C12—C7	0.4 (3)
C2—C3—C4—C6	178.35 (19)	C8—C7—C12—C11	−0.2 (3)
C3—C4—C5—N2	−177.50 (17)	C15—C7—C12—C11	179.22 (15)
C6—C4—C5—N2	2.4 (3)	C8—C7—C15—O2	9.6 (3)
C3—C4—C5—N1	2.0 (2)	C12—C7—C15—O2	−169.85 (16)
C6—C4—C5—N1	−178.12 (16)	C8—C7—C15—O1	−170.75 (16)
C12—C7—C8—C9	−0.1 (3)	C12—C7—C15—O1	9.8 (2)
C15—C7—C8—C9	−179.54 (16)	N2—C5—N1—C1	178.94 (16)
C7—C8—C9—C10	0.3 (3)	C4—C5—N1—C1	−0.6 (2)
C8—C9—C10—O3	179.19 (17)	C2—C1—N1—C5	−1.1 (3)
C8—C9—C10—C11	−0.2 (3)	C9—C10—O3—C13	−6.7 (3)
O3—C10—C11—O4	−0.1 (2)	C11—C10—O3—C13	172.67 (17)
C9—C10—C11—O4	179.35 (16)	C12—C11—O4—C14	6.9 (3)
O3—C10—C11—C12	−179.59 (16)	C10—C11—O4—C14	−172.55 (18)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1^{i}	0.88 (2)	1.73 (2)	2.6071 (19)	173 (2)
N2—H2*A*···O2^{i}	0.86	2.02	2.8816 (19)	177
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Symmetry codes: (i) x, $y+1$, z; (ii) $-x$, $y+1/2$, $-z+5/2$; (iii) $-x+1$, $-y-1$, $-z+2$.