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# 2-Amino-4-methylpyridinium 4-methylbenzoate

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**Keywords:** molecular salt; crystal structure; hydrogen bonding..

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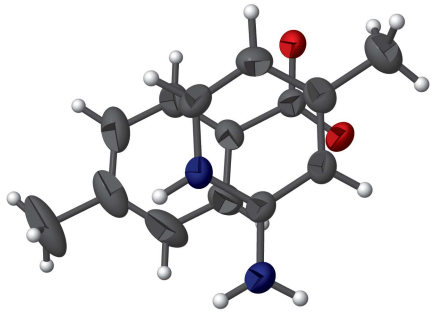
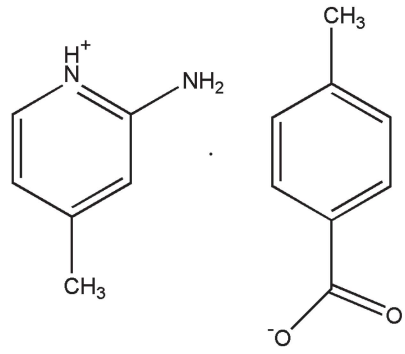
**Structural data**: full structural data are available from iucrdata.iucr.org

In the title molecular salt, $C_6H_9N_2^+\cdot C_8H_7O_2^-$, the cation is protonated at its pyridine N atom and the dihedral angle between the carboxylate group and its attached benzene ring in the anion is 8.54 (17)°. In the crystal, N—H···O hydrogen bonds link the components into [001] chains. Weak C—H···O and aromatic $\pi$–$\pi$ stacking [centroid–centroid separation = 3.8503 (18) Å] link the chains into a three-dimensional network.

**3D view**



**Chemical scheme**




## Structure description

As part of our ongoing studies of hydrogen-bonding patterns in pyridyl molecular salts (Sivakumar *et al.*, 2016*a*,*b*), we report herein the synthesis and crystal structure of the title molecular salt (Fig. 1).

Weak $\pi$–$\pi$ [*Cg*1···*Cg*2 = 3.850 (1) Å; *Cg*1 and *Cg*2 are the centroids of the rings C7–C12 and N1/C1–C5, respectively] interactions are observed between the benzene and pyridine rings. In the crystal, adjacent anions and cations are connected by N—H···O (N1—H1*A*···O1$^{i}$ and N2—H2*B*···O2$^{i}$) hydrogen bonds, thereby generating an $R_2^2(8)$ ring-motif; these units are further linked by an N2—H2*A*···O2$^{ii}$ hydrogen bond and a C1—H1···O1$^{iii}$ contact (Table 1) into chains propagating along [001] (Fig. 2).

## Synthesis and crystallization

The title salt was synthesized by mixing 2-amino-4-methylpyridine(1.081 g) and *p*-toluic acid (1.361 g) in an equimolar ratio in an acetone and methanol (1:1) solvent mixture. After a period of 30 days, colourless blocks of the title compound were obtained.

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1$A$···O1$^{i}$ | 0.86 (2) | 1.80 (2) | 2.661 (3) | 175 (3) |
| N2—H2$B$···O2$^{i}$ | 0.86 (1) | 1.93 (1) | 2.792 (4) | 176 (3) |
| N2—H2$A$···O2$^{ii}$ | 0.85 (2) | 1.99 (2) | 2.835 (3) | 169 (3) |
| C1—H1···O1$^{iii}$ | 0.93 | 2.58 | 3.223 (3) | 126 |

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

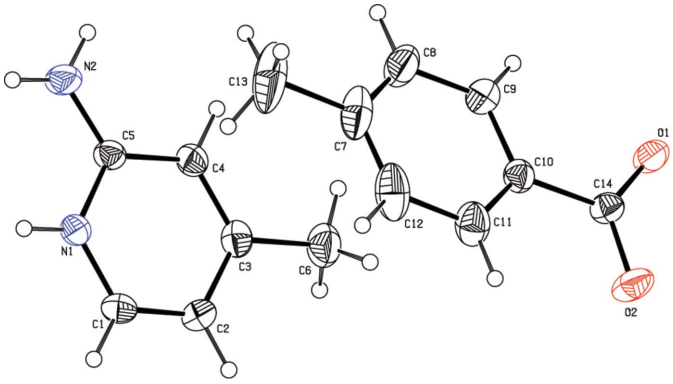



**Figure 1**
The molecular structure of the title molecular salt, with 30% probability displacement ellipsoids.

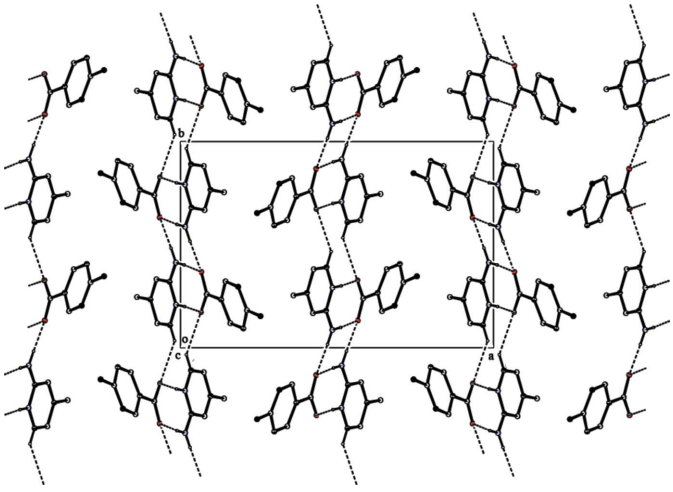



**Figure 2**
The crystal packing of the title molecular salt viewed along $c$ axis. Hydrogen bonds are shown as dashed lines. H atoms not involving in hydrogen bonding have been omitted for clarity.

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_6H_9N_2^+\cdot C_8H_7O_2^-$ |
| $M_r$ | 244.29 |
| Crystal system, space group | Orthorhombic, $Pna2_1$ |
| Temperature (K) | 295 |
| $a, b, c$ (Å) | 16.7541 (18), 11.0261 (11), 7.2064 (7) |
| $V$ (Å$^3$) | 1331.3 (2) |
| $Z$ | 4 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.08 |
| Crystal size (mm) | 0.28 × 0.26 × 0.22 |
| | |
| Data collection | |
| Diffractometer | Bruker Kappa APEXII CCD |
| Absorption correction | Multi-scan (*SADABS*; Bruker, 2004) |
| $T_{min}$, $T_{max}$ | 0.661, 0.745 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 17657, 2372, 1903 |
| $R_{int}$ | 0.037 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.626 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.039, 0.102, 1.11 |
| No. of reflections | 2372 |
| No. of parameters | 177 |
| 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$^{-3}$) | 0.12, −0.19 |

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

## 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.


## References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# full crystallographic data

*IUCrData* (2016). **1**, x161411 [doi:10.1107/S2414314616014115]

## 2-Amino-4-methylpyridinium 4-methylbenzoate

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

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*Crystal data*

$C_6H_9N_2^+·C_8H_7O_2^-$
$M_r$ = 244.29
Orthorhombic, $Pna2_1$
$a$ = 16.7541 (18) Å
$b$ = 11.0261 (11) Å
$c$ = 7.2064 (7) Å
$V$ = 1331.3 (2) Å$^3$
$Z$ = 4
$F$(000) = 520
$D_x$ = 1.219 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 6146 reflections
$\theta$ = 2.4–23.5°
$\mu$ = 0.08 mm$^{-1}$
$T$ = 295 K
Block, colourless
0.28 × 0.26 × 0.22 mm

*Data collection*

Bruker Kappa APEXII CCD diffractometer
$\omega$ and $\varphi$ scan
Absorption correction: multi-scan (SADABS; Bruker, 2004)
$T_{min}$ = 0.661, $T_{max}$ = 0.745
17657 measured reflections
2372 independent reflections
1903 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.037
$\theta_{max}$ = 26.4°, $\theta_{min}$ = 2.2°
$h$ = −20→20
$k$ = −13→13
$l$ = −9→6

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.102
$S$ = 1.11
2372 reflections
177 parameters
4 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 0.3164P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.12 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.19 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 | −0.03357 (17) | 0.1098 (2) | 0.5620 (5) | 0.0458 (7) |

| | | | | |
|---|---|---|---|---|
| H1 | −0.018668 | 0.033638 | 0.605372 | 0.055* |
| C2 | −0.07416 (19) | 0.1189 (3) | 0.4012 (5) | 0.0481 (8) |
| H2 | −0.087627 | 0.049539 | 0.334745 | 0.058* |
| C3 | −0.09593 (17) | 0.2338 (3) | 0.3350 (4) | 0.0442 (7) |
| C4 | −0.07669 (17) | 0.3322 (2) | 0.4382 (4) | 0.0414 (7) |
| H4 | −0.091582 | 0.408950 | 0.397487 | 0.050* |
| C5 | −0.03497 (16) | 0.3202 (2) | 0.6043 (4) | 0.0376 (6) |
| C6 | −0.1390 (2) | 0.2460 (3) | 0.1553 (5) | 0.0639 (9) |
| H6A | −0.146260 | 0.330402 | 0.127061 | 0.096* |
| H6B | −0.190096 | 0.207161 | 0.164216 | 0.096* |
| H6C | −0.108306 | 0.208399 | 0.058567 | 0.096* |
| C7 | 0.2124 (2) | 0.1820 (5) | 0.5775 (5) | 0.0713 (11) |
| C8 | 0.2006 (2) | 0.0940 (4) | 0.4461 (6) | 0.0705 (11) |
| H8 | 0.220675 | 0.016444 | 0.465941 | 0.085* |
| C9 | 0.1591 (2) | 0.1190 (3) | 0.2836 (5) | 0.0574 (9) |
| H9 | 0.151011 | 0.057853 | 0.196778 | 0.069* |
| C10 | 0.12997 (17) | 0.2337 (3) | 0.2502 (4) | 0.0413 (7) |
| C11 | 0.1437 (2) | 0.3221 (3) | 0.3798 (5) | 0.0595 (9) |
| H11 | 0.125739 | 0.400643 | 0.358355 | 0.071* |
| C12 | 0.1841 (2) | 0.2957 (4) | 0.5422 (6) | 0.0786 (12) |
| H12 | 0.192168 | 0.356814 | 0.629174 | 0.094* |
| C13 | 0.2554 (3) | 0.1533 (5) | 0.7564 (6) | 0.1122 (19) |
| H13A | 0.217202 | 0.144162 | 0.854656 | 0.168* |
| H13B | 0.291374 | 0.218301 | 0.785960 | 0.168* |
| H13C | 0.285005 | 0.079365 | 0.742203 | 0.168* |
| C14 | 0.08400 (17) | 0.2600 (2) | 0.0769 (4) | 0.0403 (7) |
| N1 | −0.01429 (14) | 0.2087 (2) | 0.6605 (3) | 0.0397 (6) |
| N2 | −0.01482 (18) | 0.4132 (2) | 0.7108 (4) | 0.0547 (7) |
| O1 | 0.06504 (14) | 0.17304 (17) | −0.0243 (3) | 0.0545 (6) |
| O2 | 0.06616 (14) | 0.36798 (18) | 0.0423 (3) | 0.0597 (7) |
| H2B | 0.0117 (17) | 0.402 (3) | 0.812 (3) | 0.056 (10)* |
| H2A | −0.0303 (17) | 0.4832 (16) | 0.675 (4) | 0.054 (10)* |
| H1A | 0.0133 (15) | 0.200 (2) | 0.760 (3) | 0.039 (8)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0521 (16) | 0.0305 (14) | 0.0548 (19) | 0.0018 (12) | −0.0027 (16) | 0.0029 (15) |
| C2 | 0.0507 (17) | 0.0412 (16) | 0.052 (2) | −0.0013 (13) | −0.0055 (15) | −0.0108 (15) |
| C3 | 0.0377 (15) | 0.0546 (18) | 0.0403 (17) | 0.0010 (13) | −0.0007 (13) | 0.0005 (15) |
| C4 | 0.0438 (15) | 0.0376 (14) | 0.0426 (19) | 0.0020 (12) | −0.0046 (13) | 0.0059 (14) |
| C5 | 0.0422 (14) | 0.0312 (13) | 0.0394 (17) | 0.0007 (11) | −0.0005 (13) | 0.0029 (13) |
| C6 | 0.059 (2) | 0.081 (2) | 0.052 (2) | 0.0050 (19) | −0.0138 (17) | −0.0044 (19) |
| C7 | 0.0448 (18) | 0.125 (3) | 0.045 (2) | 0.004 (2) | −0.0062 (17) | 0.011 (2) |
| C8 | 0.058 (2) | 0.083 (3) | 0.070 (3) | 0.0028 (19) | −0.0138 (19) | 0.029 (2) |
| C9 | 0.061 (2) | 0.0524 (19) | 0.059 (2) | −0.0040 (15) | −0.0159 (17) | 0.0100 (16) |
| C10 | 0.0395 (15) | 0.0471 (16) | 0.0373 (15) | −0.0038 (12) | −0.0023 (13) | 0.0028 (14) |
| C11 | 0.058 (2) | 0.067 (2) | 0.053 (2) | 0.0074 (17) | −0.0110 (16) | −0.0150 (18) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C12 | 0.063 (2) | 0.118 (3) | 0.055 (3) | 0.006 (2) | −0.0154 (19) | −0.029 (2) |
| C13 | 0.068 (3) | 0.217 (6) | 0.052 (3) | 0.015 (3) | −0.019 (2) | 0.019 (3) |
| C14 | 0.0480 (16) | 0.0367 (14) | 0.0362 (16) | 0.0021 (12) | 0.0008 (14) | 0.0005 (14) |
| N1 | 0.0468 (14) | 0.0346 (13) | 0.0378 (14) | 0.0034 (10) | −0.0087 (11) | 0.0045 (11) |
| N2 | 0.081 (2) | 0.0319 (14) | 0.0516 (18) | 0.0052 (13) | −0.0215 (15) | 0.0002 (13) |
| O1 | 0.0787 (15) | 0.0360 (10) | 0.0489 (14) | 0.0060 (11) | −0.0226 (11) | 0.0005 (11) |
| O2 | 0.0981 (17) | 0.0337 (10) | 0.0474 (15) | 0.0131 (11) | −0.0163 (13) | −0.0015 (10) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—N1 | 1.340 (4) | C8—C9 | 1.389 (5) |
| C1—C2 | 1.347 (4) | C8—H8 | 0.9300 |
| C1—H1 | 0.9300 | C9—C10 | 1.377 (4) |
| C2—C3 | 1.403 (4) | C9—H9 | 0.9300 |
| C2—H2 | 0.9300 | C10—C11 | 1.369 (4) |
| C3—C4 | 1.354 (4) | C10—C14 | 1.495 (4) |
| C3—C6 | 1.489 (5) | C11—C12 | 1.383 (5) |
| C4—C5 | 1.392 (4) | C11—H11 | 0.9300 |
| C4—H4 | 0.9300 | C12—H12 | 0.9300 |
| C5—N2 | 1.325 (4) | C13—H13A | 0.9600 |
| C5—N1 | 1.340 (3) | C13—H13B | 0.9600 |
| C6—H6A | 0.9600 | C13—H13C | 0.9600 |
| C6—H6B | 0.9600 | C14—O1 | 1.246 (3) |
| C6—H6C | 0.9600 | C14—O2 | 1.253 (3) |
| C7—C12 | 1.365 (6) | N1—H1A | 0.858 (13) |
| C7—C8 | 1.370 (6) | N2—H2B | 0.860 (13) |
| C7—C13 | 1.510 (5) | N2—H2A | 0.855 (13) |
| | | | |
| N1—C1—C2 | 121.1 (3) | C10—C9—C8 | 120.5 (3) |
| N1—C1—H1 | 119.5 | C10—C9—H9 | 119.8 |
| C2—C1—H1 | 119.5 | C8—C9—H9 | 119.8 |
| C1—C2—C3 | 119.4 (3) | C11—C10—C9 | 118.3 (3) |
| C1—C2—H2 | 120.3 | C11—C10—C14 | 121.2 (3) |
| C3—C2—H2 | 120.3 | C9—C10—C14 | 120.4 (3) |
| C4—C3—C2 | 118.4 (3) | C10—C11—C12 | 120.7 (3) |
| C4—C3—C6 | 121.4 (3) | C10—C11—H11 | 119.7 |
| C2—C3—C6 | 120.2 (3) | C12—C11—H11 | 119.7 |
| C3—C4—C5 | 121.0 (3) | C7—C12—C11 | 121.4 (4) |
| C3—C4—H4 | 119.5 | C7—C12—H12 | 119.3 |
| C5—C4—H4 | 119.5 | C11—C12—H12 | 119.3 |
| N2—C5—N1 | 118.0 (3) | C7—C13—H13A | 109.5 |
| N2—C5—C4 | 123.5 (2) | C7—C13—H13B | 109.5 |
| N1—C5—C4 | 118.5 (2) | H13A—C13—H13B | 109.5 |
| C3—C6—H6A | 109.5 | C7—C13—H13C | 109.5 |
| C3—C6—H6B | 109.5 | H13A—C13—H13C | 109.5 |
| H6A—C6—H6B | 109.5 | H13B—C13—H13C | 109.5 |
| C3—C6—H6C | 109.5 | O1—C14—O2 | 123.6 (3) |
| H6A—C6—H6C | 109.5 | O1—C14—C10 | 118.1 (2) |

| | | | |
|---|---|---|---|
| H6B—C6—H6C | 109.5 | O2—C14—C10 | 118.3 (2) |
| C12—C7—C8 | 118.2 (3) | C5—N1—C1 | 121.6 (2) |
| C12—C7—C13 | 121.1 (4) | C5—N1—H1A | 119.7 (19) |
| C8—C7—C13 | 120.7 (4) | C1—N1—H1A | 118.7 (19) |
| C7—C8—C9 | 120.9 (4) | C5—N2—H2B | 120 (2) |
| C7—C8—H8 | 119.5 | C5—N2—H2A | 116 (2) |
| C9—C8—H8 | 119.5 | H2B—N2—H2A | 123 (3) |
| | | | |
| N1—C1—C2—C3 | 0.6 (5) | C9—C10—C11—C12 | −1.7 (5) |
| C1—C2—C3—C4 | −1.4 (4) | C14—C10—C11—C12 | 177.9 (3) |
| C1—C2—C3—C6 | 178.4 (3) | C8—C7—C12—C11 | 0.8 (6) |
| C2—C3—C4—C5 | 1.2 (4) | C13—C7—C12—C11 | −179.1 (4) |
| C6—C3—C4—C5 | −178.6 (3) | C10—C11—C12—C7 | 0.9 (6) |
| C3—C4—C5—N2 | −179.8 (3) | C11—C10—C14—O1 | −171.3 (3) |
| C3—C4—C5—N1 | −0.2 (4) | C9—C10—C14—O1 | 8.2 (4) |
| C12—C7—C8—C9 | −1.7 (6) | C11—C10—C14—O2 | 8.1 (4) |
| C13—C7—C8—C9 | 178.2 (4) | C9—C10—C14—O2 | −172.3 (3) |
| C7—C8—C9—C10 | 1.0 (5) | N2—C5—N1—C1 | 178.9 (3) |
| C8—C9—C10—C11 | 0.7 (5) | C4—C5—N1—C1 | −0.7 (4) |
| C8—C9—C10—C14 | −178.8 (3) | C2—C1—N1—C5 | 0.5 (4) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1*A*···O1$^{i}$ | 0.86 (2) | 1.80 (2) | 2.661 (3) | 175 (3) |
| N2—H2*B*···O2$^{i}$ | 0.86 (1) | 1.93 (1) | 2.792 (4) | 176 (3) |
| N2—H2*A*···O2$^{ii}$ | 0.85 (2) | 1.99 (2) | 2.835 (3) | 169 (3) |
| C1—H1···O1$^{iii}$ | 0.93 | 2.58 | 3.223 (3) | 126 |

Symmetry codes: (i) *x*, *y*, *z*+1; (ii) −*x*, −*y*+1, *z*+1/2; (iii) −*x*, −*y*, *z*+1/2.