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4-Methylpyridinium 2-carboxy-6-nitrobenzoate

S. Reena Devi,[a] S. Kalaiyarasi,[a] R. Akilan,[b] R. Mohan Kumar[a]* and G. Chakkaravarthi[c]*

[a]Department of Physics, Presidency College, Chennai 600 005, India, [b]Department of Physics, Aksheyaa College of Engineering, Kancheepuram 603 314, India, and [c]Department of Physics, CPCL Polytechnic College, Chennai 600 068, India. *Correspondence e-mail: mohan66@hotmail.com, chakkaravarthi_2005@yahoo.com

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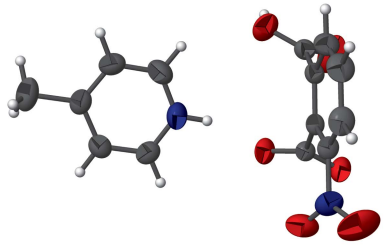
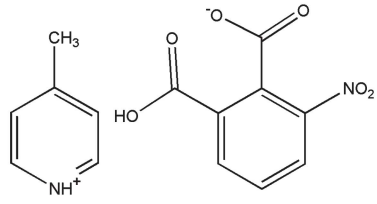
Structural data: full structural data are available from iucrdata.iucr.org

In the title molecular salt, $C_6H_8N^+\cdot C_8H_4NO_6^-$, the anion is deprotonated at the carboxylic acid group adjacent to the nitro group. In the crystal, the anions are linked into an [001] chain by O—H···O hydrogen bonds. The cations are linked to these chains by N—H···O hydrogen bonds and weak C—H···O contacts, generating a three-dimensional network.

3D view



Chemical scheme



Structure description

As part of our ongoing studies of molecular salts (Sivakumar *et al.*, 2016), we now report the synthesis and the crystal structure of the title compound (Fig. 1). Its geometric parameters are comparable with those of reported structures (Li & Chai, 2007)

The anion is deprotonated at the central carboxylic acid group (C8/O3/O4), but not the other (C7/O5/O6), hence a 1:1 stoichiometry salt arises. The dihedral angles between the C1–C6 benzene ring and the C7/O5/O6, C8/O3/O4 and N1/O1/O2 substituents are 27.09 (11), 71.59 (10) and 68.44 (11)°, respectively.

In the crystal, the N2—H2*A*···O4 hydrogen bond and C13—H13···O6 contact generate an $R_2^2(10)$ ring-set motif (Table 1, Fig. 2). The O6—H6···O3^{i} hydrogen bond (Table 1) links adjacent anions into an infinite chain along [001]. The crystal structure is consolidated by weak C—H···O contacts to form a three dimensional network (Table 1, Fig. 3).

Synthesis and crystallization

The title salt was synthesized from 4-methylpyridine (4.90 g) and 3-nitrophthalic acid (5.28 g) in a 2:1 ratio. These reactants were dissolved in water and continuously stirred

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O4	0.86 (3)	1.87 (3)	2.699 (2)	160 (2)
O6—H6···O3^{i}	0.84 (1)	1.65 (1)	2.484 (2)	170 (3)
C13—H13···O6	0.93	2.44	3.219 (3)	141
C2—H2···O4^{ii}	0.93	2.36	3.171 (3)	145
C10—H10···O3^{iii}	0.93	2.54	3.191 (3)	127

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

about 5 h and kept at 35°C using a constant temperature bath. After 20 days, crystals suitable for X-ray diffraction were harvested.

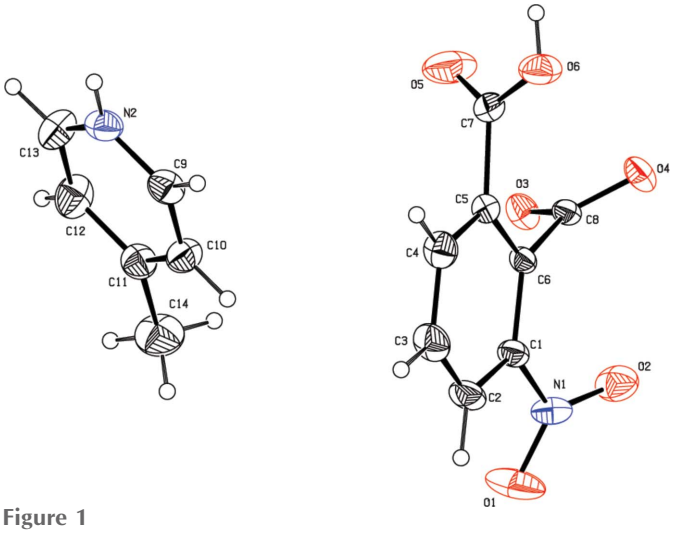


Figure 1
The molecular structure of the title molecular salt, with atom labelling and 30% probability displacement ellipsoids.

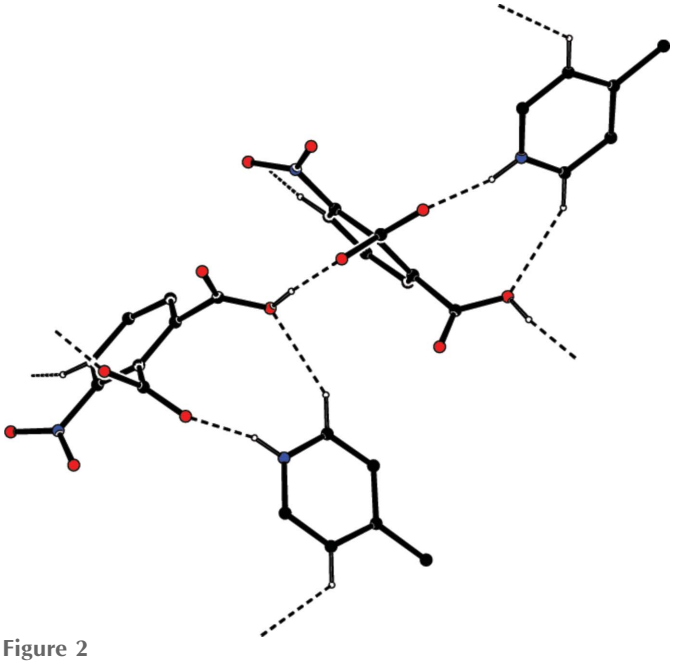


Figure 2
A partial view of the crystal packing showing ring-set motif.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_8H_4NO_6{\cdot}C_6H_8N$
M_r	304.26
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	295
a, b, c (Å)	7.683 (5), 17.309 (6), 11.172 (5)
β (°)	109.260 (5)
V (Å^3)	1402.6 (12)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.12
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}	0.504, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18131, 4295, 2572
R_{int}	0.054
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.719
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.054, 0.153, 1.04
No. of reflections	4295
No. of parameters	208
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})	0.58, −0.35

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.

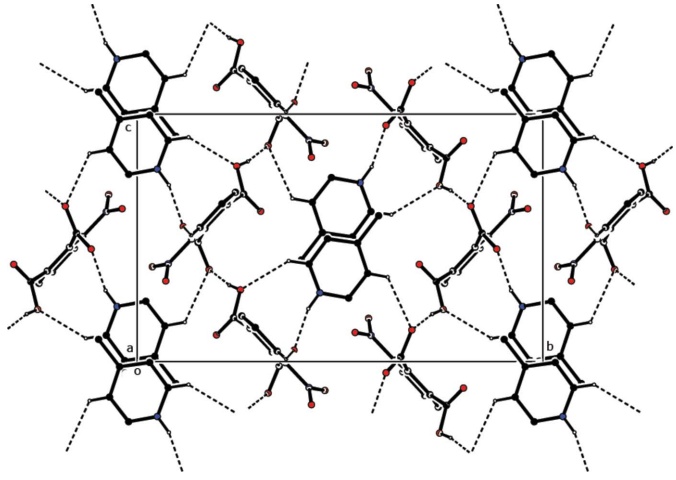


Figure 3
The crystal packing of the title molecular salt viewed along the *a* axis. Hydrogen bonds are shown as dashed lines and H atoms not involved in hydrogen bonds have been omitted for clarity.

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x161803 [https://doi.org/10.1107/S2414314616018034]

4-Methylpyridinium 2-carboxy-6-nitrobenzoate

S. Reena Devi, S. Kalaiyarasi, R. Akilan, R. Mohan Kumar and G. Chakkaravarthi

4-Methylpyridinium 2-carboxy-6-nitrobenzoate

Crystal data

$C_6H_8N^+\cdot C_8H_4NO_6^-$
M_r = 304.26
Monoclinic, $P2_1/c$
a = 7.683 (5) Å
b = 17.309 (6) Å
c = 11.172 (5) Å
β = 109.260 (5)°
V = 1402.6 (12) Å^3
Z = 4
$F(000)$ = 632
D_x = 1.441 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5621 reflections
θ = 2.3–31.0°
μ = 0.12 mm^{-1}
T = 295 K
Block, colourless
0.28 × 0.26 × 0.22 mm

Data collection

Bruker axs kappa apex2 CCD diffractometer
ω and φ scan
Absorption correction: multi-scan (SADABS; Bruker, 2004)
T_{min} = 0.504, T_{max} = 0.746
18131 measured reflections
4295 independent reflections
2572 reflections with $I > 2\sigma(I)$
R_{int} = 0.054
θ_{max} = 30.8°, θ_{min} = 2.3°
h = −10→9
k = −24→24
l = −14→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.153
S = 1.04
4295 reflections
208 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0595P)^2 + 0.4448P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.58 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}
Extinction correction: SHELXL-2016/4 (Sheldrick 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.015 (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	0.5227 (2)	0.13436 (10)	0.49500 (16)	0.0344 (4)
C2	0.7063 (2)	0.15506 (12)	0.54221 (19)	0.0455 (5)
H2	0.792007	0.132931	0.510103	0.055*
C3	0.7598 (3)	0.20898 (13)	0.6376 (2)	0.0515 (5)
H3	0.883187	0.223208	0.670951	0.062*
C4	0.6323 (3)	0.24217 (12)	0.68415 (19)	0.0455 (5)
H4	0.670037	0.278336	0.749197	0.055*
C5	0.4471 (2)	0.22170 (10)	0.63407 (16)	0.0333 (4)
C6	0.3892 (2)	0.16713 (9)	0.53821 (15)	0.0292 (3)
C7	0.3055 (2)	0.26237 (10)	0.67731 (17)	0.0380 (4)
C8	0.1850 (2)	0.14998 (9)	0.48115 (15)	0.0307 (3)
C9	0.1140 (3)	−0.02111 (13)	0.75650 (18)	0.0462 (5)
H9	0.057618	−0.038361	0.673896	0.055*
C10	0.1235 (3)	−0.06817 (12)	0.8561 (2)	0.0490 (5)
H10	0.072761	−0.117460	0.841181	0.059*
C11	0.2077 (3)	−0.04341 (12)	0.97884 (19)	0.0474 (5)
C12	0.2786 (4)	0.03076 (14)	0.9961 (2)	0.0599 (6)
H12	0.335995	0.049530	1.077639	0.072*
C13	0.2645 (3)	0.07629 (13)	0.8942 (2)	0.0594 (6)
H13	0.310476	0.126439	0.906422	0.071*
C14	0.2237 (4)	−0.09521 (17)	1.0893 (2)	0.0760 (8)
H14A	0.110131	−0.122777	1.074606	0.114*
H14B	0.249051	−0.064691	1.164917	0.114*
H14C	0.322252	−0.131367	1.099301	0.114*
N1	0.4690 (2)	0.07633 (10)	0.39439 (15)	0.0455 (4)
N2	0.1856 (2)	0.04959 (11)	0.77753 (17)	0.0471 (4)
O1	0.5633 (2)	0.07038 (13)	0.32559 (17)	0.0863 (6)
O2	0.3329 (2)	0.03729 (9)	0.38272 (15)	0.0610 (4)
O3	0.10343 (16)	0.17716 (8)	0.37237 (12)	0.0429 (3)
O4	0.10975 (16)	0.11345 (8)	0.54551 (12)	0.0433 (3)
O5	0.1921 (3)	0.30446 (12)	0.60735 (17)	0.0875 (7)
O6	0.3113 (2)	0.24557 (9)	0.78951 (14)	0.0574 (4)
H2A	0.180 (3)	0.0781 (15)	0.713 (2)	0.064 (7)*
H6	0.233 (3)	0.2727 (16)	0.808 (3)	0.096*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0292 (8)	0.0394 (9)	0.0369 (9)	0.0043 (7)	0.0142 (7)	0.0024 (7)
C2	0.0279 (8)	0.0576 (12)	0.0550 (11)	0.0066 (8)	0.0191 (8)	0.0051 (10)
C3	0.0278 (8)	0.0607 (13)	0.0629 (13)	−0.0068 (8)	0.0110 (9)	0.0018 (11)
C4	0.0393 (10)	0.0460 (11)	0.0470 (11)	−0.0085 (8)	0.0084 (8)	−0.0049 (9)
C5	0.0337 (8)	0.0316 (8)	0.0367 (9)	−0.0002 (6)	0.0146 (7)	0.0014 (7)
C6	0.0245 (7)	0.0322 (8)	0.0333 (8)	0.0008 (6)	0.0126 (6)	0.0036 (7)
C7	0.0430 (10)	0.0330 (9)	0.0408 (10)	0.0019 (7)	0.0176 (8)	−0.0023 (8)

C8	0.0264 (7)	0.0337 (8)	0.0351 (9)	0.0005 (6)	0.0143 (6)	−0.0013 (7)
C9	0.0410 (10)	0.0577 (13)	0.0397 (10)	−0.0020 (9)	0.0133 (8)	−0.0031 (9)
C10	0.0513 (11)	0.0430 (11)	0.0528 (12)	−0.0065 (9)	0.0173 (9)	−0.0006 (9)
C11	0.0506 (11)	0.0501 (12)	0.0432 (11)	0.0058 (9)	0.0176 (9)	0.0062 (9)
C12	0.0750 (15)	0.0550 (13)	0.0436 (12)	−0.0034 (11)	0.0113 (11)	−0.0079 (10)
C13	0.0696 (14)	0.0409 (11)	0.0643 (15)	−0.0078 (10)	0.0173 (11)	−0.0011 (10)
C14	0.0891 (19)	0.0815 (18)	0.0584 (14)	0.0061 (15)	0.0256 (13)	0.0259 (13)
N1	0.0381 (8)	0.0537 (10)	0.0452 (9)	0.0135 (7)	0.0145 (7)	−0.0059 (8)
N2	0.0437 (9)	0.0529 (10)	0.0486 (10)	0.0029 (8)	0.0204 (8)	0.0125 (9)
O1	0.0699 (11)	0.1304 (18)	0.0740 (12)	0.0046 (11)	0.0447 (9)	−0.0371 (11)
O2	0.0559 (9)	0.0570 (9)	0.0707 (10)	−0.0050 (7)	0.0215 (8)	−0.0227 (8)
O3	0.0320 (6)	0.0555 (8)	0.0393 (7)	−0.0012 (5)	0.0093 (5)	0.0098 (6)
O4	0.0311 (6)	0.0563 (8)	0.0458 (7)	−0.0048 (5)	0.0170 (5)	0.0100 (6)
O5	0.1094 (15)	0.0963 (14)	0.0725 (11)	0.0649 (12)	0.0511 (11)	0.0296 (10)
O6	0.0695 (10)	0.0642 (10)	0.0476 (8)	0.0214 (8)	0.0315 (7)	0.0034 (7)

Geometric parameters (Å, º)

C1—C2	1.380 (2)	C9—C10	1.362 (3)
C1—C6	1.391 (2)	C9—H9	0.9300
C1—N1	1.462 (2)	C10—C11	1.377 (3)
C2—C3	1.373 (3)	C10—H10	0.9300
C2—H2	0.9300	C11—C12	1.383 (3)
C3—C4	1.377 (3)	C11—C14	1.497 (3)
C3—H3	0.9300	C12—C13	1.359 (3)
C4—C5	1.392 (3)	C12—H12	0.9300
C4—H4	0.9300	C13—N2	1.327 (3)
C5—C6	1.387 (2)	C13—H13	0.9300
C5—C7	1.503 (2)	C14—H14A	0.9600
C6—C8	1.515 (2)	C14—H14B	0.9600
C7—O5	1.205 (2)	C14—H14C	0.9600
C7—O6	1.273 (2)	N1—O2	1.216 (2)
C8—O4	1.2350 (19)	N1—O1	1.222 (2)
C8—O3	1.260 (2)	N2—H2A	0.86 (3)
C9—N2	1.330 (3)	O6—H6	0.842 (10)
C2—C1—C6	122.63 (17)	C10—C9—H9	120.1
C2—C1—N1	117.77 (15)	C9—C10—C11	120.56 (19)
C6—C1—N1	119.59 (15)	C9—C10—H10	119.7
C3—C2—C1	118.66 (16)	C11—C10—H10	119.7
C3—C2—H2	120.7	C10—C11—C12	117.50 (19)
C1—C2—H2	120.7	C10—C11—C14	121.2 (2)
C2—C3—C4	120.55 (17)	C12—C11—C14	121.3 (2)
C2—C3—H3	119.7	C13—C12—C11	120.2 (2)
C4—C3—H3	119.7	C13—C12—H12	119.9
C3—C4—C5	120.14 (18)	C11—C12—H12	119.9
C3—C4—H4	119.9	N2—C13—C12	120.4 (2)
C5—C4—H4	119.9	N2—C13—H13	119.8

C6—C5—C4	120.57 (15)	C12—C13—H13	119.8
C6—C5—C7	119.04 (15)	C11—C14—H14A	109.5
C4—C5—C7	120.26 (16)	C11—C14—H14B	109.5
C5—C6—C1	117.42 (15)	H14A—C14—H14B	109.5
C5—C6—C8	118.83 (13)	C11—C14—H14C	109.5
C1—C6—C8	123.64 (15)	H14A—C14—H14C	109.5
O5—C7—O6	124.05 (17)	H14B—C14—H14C	109.5
O5—C7—C5	121.33 (17)	O2—N1—O1	123.59 (18)
O6—C7—C5	114.54 (16)	O2—N1—C1	118.63 (15)
O4—C8—O3	124.97 (15)	O1—N1—C1	117.77 (18)
O4—C8—C6	118.29 (14)	C13—N2—C9	121.48 (19)
O3—C8—C6	116.68 (13)	C13—N2—H2A	120.1 (17)
N2—C9—C10	119.90 (19)	C9—N2—H2A	118.4 (17)
N2—C9—H9	120.1	C7—O6—H6	109 (2)

C6—C1—C2—C3	1.4 (3)	C4—C5—C7—O6	−71.7 (2)
N1—C1—C2—C3	−179.43 (17)	C5—C6—C8—O4	−72.1 (2)
C1—C2—C3—C4	−0.6 (3)	C1—C6—C8—O4	111.72 (19)
C2—C3—C4—C5	−0.5 (3)	C5—C6—C8—O3	105.15 (18)
C3—C4—C5—C6	0.9 (3)	C1—C6—C8—O3	−71.0 (2)
C3—C4—C5—C7	−175.09 (18)	N2—C9—C10—C11	−0.4 (3)
C4—C5—C6—C1	−0.1 (2)	C9—C10—C11—C12	1.0 (3)
C7—C5—C6—C1	175.92 (15)	C9—C10—C11—C14	−178.3 (2)
C4—C5—C6—C8	−176.47 (16)	C10—C11—C12—C13	−0.2 (3)
C7—C5—C6—C8	−0.5 (2)	C14—C11—C12—C13	179.1 (2)
C2—C1—C6—C5	−1.1 (3)	C11—C12—C13—N2	−1.1 (4)
N1—C1—C6—C5	179.78 (15)	C2—C1—N1—O2	153.77 (18)
C2—C1—C6—C8	175.13 (16)	C6—C1—N1—O2	−27.0 (2)
N1—C1—C6—C8	−4.0 (2)	C2—C1—N1—O1	−26.9 (3)
C6—C5—C7—O5	−64.6 (3)	C6—C1—N1—O1	152.23 (19)
C4—C5—C7—O5	111.4 (2)	C12—C13—N2—C9	1.8 (3)
C6—C5—C7—O6	112.27 (19)	C10—C9—N2—C13	−1.0 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O4	0.86 (3)	1.87 (3)	2.699 (2)	160 (2)
O6—H6···O3^{i}	0.84 (1)	1.65 (1)	2.484 (2)	170 (3)
C13—H13···O6	0.93	2.44	3.219 (3)	141
C2—H2···O4^{ii}	0.93	2.36	3.171 (3)	145
C10—H10···O3^{iii}	0.93	2.54	3.191 (3)	127

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