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2-Methylpyridinium 2-carboxy-6-nitrobenzoate

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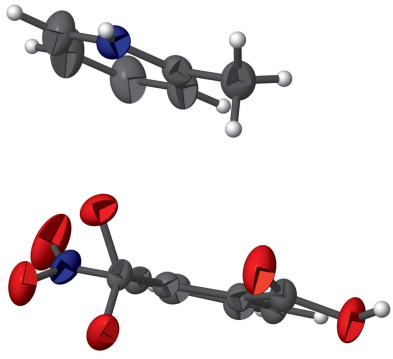
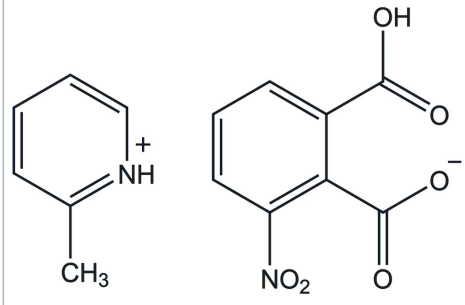
In the title molecular salt, $C_6H_8N^+\cdot C_8H_4NO_6^-$, the pyridine ring is protonated at the N atom and the anion is deprotonated at one of the hydroxy O atoms. The dihedral angle between the planes of the benzene and pyridine rings is 8.45 (9)°. In the anion, the deprotonated carboxylate group is twisted at an angle of 73.78 (11)° from the attached benzene ring, whereas the carboxy group is slightly oriented at an angle of 14.98 (10)°. N—H···O and O—H···O hydrogen bonds link the anions and cations into an infinite chain along the *c* axis and these chains are further consolidated by C—H···O hydrogen bonds to form a three-dimensional network. The crystals structure is also influenced by weak π–π interactions [centroid–centroid distance = 3.9055 (9) Å].

3D view



Chemical scheme



Structure description

Pyridine derivatives have been reported for their wide range of applications, such as antimicrobial, analgesic, antihyperglycemic, antiproliferative and antitumor activities (Brandt *et al.*, 2010; El-Sayed *et al.*, 2011). We herein report the synthesis and crystal structure of 2-methylpyridinium 2-carboxy-6-nitrobenzoate (Fig. 1). The geometric parameters are comparable with similar structures reported previously (Divya Bharathi *et al.*, 2015; Sivakumar *et al.*, 2016).

The dihedral angle between the planes of the benzene (C1–C6) and pyridine (N2/C9–C13) rings is 8.45 (9)°. In the anion, the deprotonated carboxylate group (O3/C7/O4) is twisted at an angle of 73.78 (11)° from the attached benzene ring, whereas the carboxy group (O5/C8/O6) is slightly oriented at an angle of 14.98 (10)°. N—H···O and O—H···O hydrogen bonds (Table 1) link the anions and cations into an infinite chain along the *c* axis and these chains are further consolidated by C—H···O contacts (Table 1) to form a three-dimensional network (Fig. 2). The crystal structure is also influenced by a

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O3^{i}	0.88 (1)	1.74 (1)	2.6156 (17)	173 (2)
O6—H6···O4^{ii}	0.82 (1)	1.72 (1)	2.5381 (17)	176 (3)
C4—H4···O6^{iii}	0.93	2.60	3.493 (2)	161
C10—H10···O4^{iv}	0.93	2.50	3.189 (2)	131
C11—H11···O1^{v}	0.93	2.45	3.346 (3)	162
C14—H14C···O5	0.96	2.52	3.428 (3)	158

Symmetry codes: (i) $-x+1, -y+1, -z+2$; (ii) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$; (iv) $x, y, z-1$; (v) $x, -y+\frac{3}{2}, z-\frac{1}{2}$.

weak π–π interaction between the benzene rings [$Cg\cdots Cg^{i}$ distance = 3.9055 (9) Å; symmetry code: (i) $-x, -y+1, -z+2$].

Synthesis and crystallization

When 3-nitrophthalic acid (2.11 g) and 2-methylpyridine (0.931 g) were added to 15 ml of acetone, a white precipitate formed. The precipitate was dissolved in 20 ml of distilled water and kept for slow evaporation at room temperature. Single crystals suitable for X-ray diffraction study were harvested after 45 d.

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.

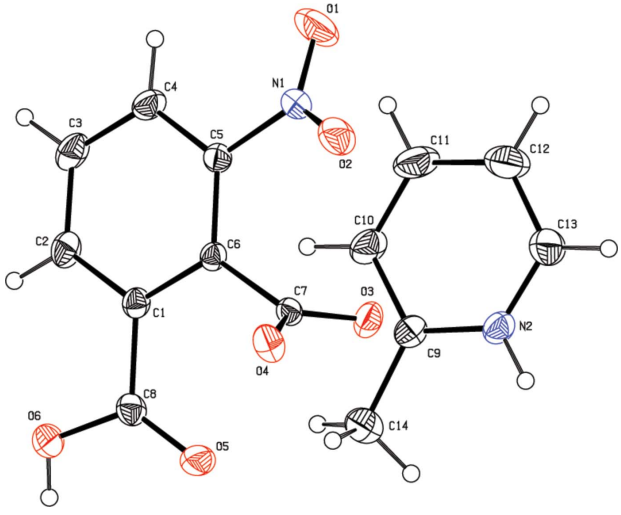


Figure 1
The molecular structure of the title molecular salt, with the atom labelling and 30% probability displacement ellipsoids.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_6H_8N^+\cdot C_8H_4NO_6^-$
M_r	304.26
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	295
a, b, c (Å)	13.1617 (6), 14.1804 (4), 7.4923 (3)
β (°)	98.758 (2)
V (Å^3)	1382.04 (9)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.12
Crystal size (mm)	0.26 × 0.22 × 0.18
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2004)
T_{min}, T_{max}	0.970, 0.979
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	30283, 4541, 3030
R_{int}	0.035
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.733
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.059, 0.163, 1.08
No. of reflections	4541
No. of parameters	207
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.31, −0.27

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

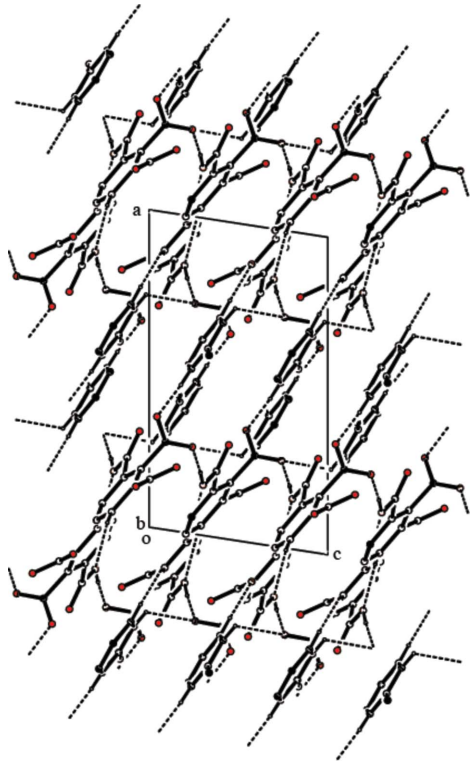


Figure 2
A packing diagram of the title compound, viewed along the b axis Hydrogen bonds are shown as dashed lines and C-bound H atoms which are not involved in the interactions have been omitted for clarity.

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full crystallographic data

IUCrData (2016). **1**, x161104 [https://doi.org/10.1107/S2414314616011044]

2-Methylpyridinium 2-carboxy-6-nitrobenzoate

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Crystal data

$C_6H_8N^+·C_8H_4NO_6^-$
M_r = 304.26
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 13.1617 (6) Å
b = 14.1804 (4) Å
c = 7.4923 (3) Å
β = 98.758 (2)°
V = 1382.04 (9) Å^3
Z = 4
$F(000)$ = 632
D_x = 1.462 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8089 reflections
θ = 2.4–30.4°
μ = 0.12 mm^{-1}
T = 295 K
Block, colourless
0.26 × 0.22 × 0.18 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} = 0.970, T_{max} = 0.979
30283 measured reflections
4541 independent reflections
3030 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
θ_{max} = 31.4°, θ_{min} = 2.1°
h = −18→19
k = −20→20
l = −10→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.163
S = 1.08
4541 reflections
207 parameters
2 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0726P)^2 + 0.3878P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 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	0.14459 (11)	0.37567 (10)	0.85916 (19)	0.0288 (3)
C2	0.05285 (13)	0.37663 (12)	0.7378 (2)	0.0379 (4)
H2	0.0297	0.3214	0.6781	0.045*
C3	−0.00370 (14)	0.45810 (14)	0.7053 (2)	0.0430 (4)
H3	−0.0651	0.4573	0.6254	0.052*
C4	0.03003 (13)	0.54042 (12)	0.7901 (2)	0.0382 (4)
H4	−0.0066	0.5962	0.7657	0.046*
C5	0.12005 (11)	0.53859 (10)	0.9131 (2)	0.0301 (3)
C6	0.17868 (11)	0.45788 (10)	0.95374 (18)	0.0259 (3)
C7	0.27615 (11)	0.45897 (9)	1.09188 (19)	0.0269 (3)
C8	0.20863 (13)	0.28803 (11)	0.8768 (2)	0.0332 (3)
C9	0.40945 (12)	0.51335 (12)	0.6703 (2)	0.0337 (3)
C10	0.32040 (14)	0.55589 (14)	0.5859 (3)	0.0471 (5)
H10	0.2695	0.5200	0.5178	0.057*
C11	0.30748 (17)	0.65092 (16)	0.6028 (3)	0.0605 (6)
H11	0.2471	0.6795	0.5479	0.073*
C12	0.38325 (19)	0.70445 (15)	0.7007 (3)	0.0655 (7)
H12	0.3751	0.7692	0.7120	0.079*
C13	0.47059 (16)	0.66071 (14)	0.7808 (3)	0.0533 (5)
H13	0.5229	0.6957	0.8474	0.064*
C14	0.42969 (16)	0.41122 (13)	0.6643 (3)	0.0472 (4)
H14A	0.5019	0.4008	0.6656	0.071*
H14B	0.3919	0.3850	0.5559	0.071*
H14C	0.4085	0.3813	0.7675	0.071*
N1	0.15079 (11)	0.62778 (10)	1.0041 (2)	0.0419 (4)
N2	0.48092 (10)	0.56815 (10)	0.76378 (19)	0.0366 (3)
O1	0.12179 (15)	0.70028 (10)	0.9258 (3)	0.0865 (7)
O2	0.20205 (12)	0.62608 (9)	1.1529 (2)	0.0536 (4)
O3	0.35201 (8)	0.49864 (9)	1.04405 (16)	0.0389 (3)
O4	0.27360 (10)	0.42200 (8)	1.24116 (15)	0.0392 (3)
O5	0.29721 (10)	0.28674 (8)	0.94647 (19)	0.0488 (4)
O6	0.15868 (10)	0.21431 (9)	0.8020 (2)	0.0511 (4)
H2A	0.5366 (11)	0.5419 (14)	0.822 (3)	0.053 (6)*
H6	0.1968 (18)	0.1700 (14)	0.787 (4)	0.079*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0275 (7)	0.0311 (7)	0.0266 (6)	−0.0022 (6)	0.0001 (5)	−0.0017 (5)
C2	0.0329 (8)	0.0446 (9)	0.0328 (8)	−0.0056 (7)	−0.0055 (6)	−0.0061 (7)

C3	0.0305 (8)	0.0566 (11)	0.0374 (9)	−0.0006 (8)	−0.0086 (7)	0.0036 (8)
C4	0.0303 (8)	0.0409 (9)	0.0414 (9)	0.0055 (7)	−0.0016 (6)	0.0102 (7)
C5	0.0285 (7)	0.0280 (7)	0.0326 (7)	−0.0015 (6)	0.0009 (6)	0.0040 (6)
C6	0.0240 (6)	0.0281 (7)	0.0245 (6)	−0.0017 (5)	0.0003 (5)	0.0031 (5)
C7	0.0278 (7)	0.0227 (6)	0.0278 (7)	−0.0020 (5)	−0.0040 (5)	0.0002 (5)
C8	0.0356 (8)	0.0314 (8)	0.0315 (7)	−0.0027 (6)	0.0014 (6)	−0.0053 (6)
C9	0.0323 (8)	0.0401 (8)	0.0280 (7)	0.0019 (6)	0.0024 (6)	−0.0004 (6)
C10	0.0381 (9)	0.0525 (11)	0.0450 (10)	0.0061 (8)	−0.0122 (7)	−0.0087 (8)
C11	0.0508 (12)	0.0596 (13)	0.0636 (13)	0.0228 (10)	−0.0156 (10)	−0.0056 (10)
C12	0.0685 (15)	0.0424 (11)	0.0782 (16)	0.0159 (10)	−0.0126 (12)	−0.0103 (10)
C13	0.0499 (11)	0.0426 (10)	0.0617 (12)	−0.0012 (9)	−0.0094 (9)	−0.0071 (9)
C14	0.0537 (11)	0.0395 (9)	0.0474 (10)	0.0018 (8)	0.0049 (8)	−0.0008 (8)
N1	0.0356 (7)	0.0270 (7)	0.0613 (10)	−0.0008 (6)	0.0015 (7)	0.0022 (6)
N2	0.0296 (7)	0.0414 (7)	0.0365 (7)	0.0014 (6)	−0.0019 (5)	0.0027 (6)
O1	0.0902 (14)	0.0297 (7)	0.1243 (16)	−0.0004 (8)	−0.0329 (12)	0.0156 (8)
O2	0.0592 (9)	0.0382 (7)	0.0583 (9)	−0.0027 (6)	−0.0076 (7)	−0.0118 (6)
O3	0.0269 (6)	0.0467 (7)	0.0408 (6)	−0.0058 (5)	−0.0024 (5)	0.0093 (5)
O4	0.0495 (7)	0.0361 (6)	0.0285 (5)	−0.0101 (5)	−0.0054 (5)	0.0065 (4)
O5	0.0402 (7)	0.0359 (6)	0.0636 (8)	0.0062 (5)	−0.0132 (6)	−0.0091 (6)
O6	0.0388 (7)	0.0353 (7)	0.0764 (10)	−0.0018 (5)	−0.0002 (6)	−0.0223 (6)

Geometric parameters (Å, º)

C1—C2	1.397 (2)	C9—C10	1.383 (2)
C1—C6	1.4021 (19)	C9—C14	1.474 (3)
C1—C8	1.496 (2)	C10—C11	1.366 (3)
C2—C3	1.376 (3)	C10—H10	0.9300
C2—H2	0.9300	C11—C12	1.373 (3)
C3—C4	1.370 (3)	C11—H11	0.9300
C3—H3	0.9300	C12—C13	1.362 (3)
C4—C5	1.386 (2)	C12—H12	0.9300
C4—H4	0.9300	C13—N2	1.328 (2)
C5—C6	1.388 (2)	C13—H13	0.9300
C5—N1	1.465 (2)	C14—H14A	0.9600
C6—C7	1.5208 (19)	C14—H14B	0.9600
C7—O4	1.2403 (18)	C14—H14C	0.9600
C7—O3	1.2453 (19)	N1—O2	1.212 (2)
C8—O5	1.203 (2)	N1—O1	1.216 (2)
C8—O6	1.3141 (19)	N2—H2A	0.876 (9)
C9—N2	1.334 (2)	O6—H6	0.822 (10)
C2—C1—C6	119.96 (14)	C10—C9—C14	123.99 (16)
C2—C1—C8	119.03 (13)	C11—C10—C9	119.77 (17)
C6—C1—C8	120.88 (13)	C11—C10—H10	120.1
C3—C2—C1	120.95 (15)	C9—C10—H10	120.1
C3—C2—H2	119.5	C10—C11—C12	120.28 (18)
C1—C2—H2	119.5	C10—C11—H11	119.9
C4—C3—C2	120.33 (15)	C12—C11—H11	119.9

C4—C3—H3	119.8	C13—C12—C11	118.62 (19)
C2—C3—H3	119.8	C13—C12—H12	120.7
C3—C4—C5	118.43 (15)	C11—C12—H12	120.7
C3—C4—H4	120.8	N2—C13—C12	119.97 (18)
C5—C4—H4	120.8	N2—C13—H13	120.0
C4—C5—C6	123.49 (14)	C12—C13—H13	120.0
C4—C5—N1	116.18 (14)	C9—C14—H14A	109.5
C6—C5—N1	120.32 (13)	C9—C14—H14B	109.5
C5—C6—C1	116.75 (13)	H14A—C14—H14B	109.5
C5—C6—C7	121.62 (13)	C9—C14—H14C	109.5
C1—C6—C7	121.62 (12)	H14A—C14—H14C	109.5
O4—C7—O3	125.69 (13)	H14B—C14—H14C	109.5
O4—C7—C6	118.26 (13)	O2—N1—O1	123.40 (16)
O3—C7—C6	116.04 (12)	O2—N1—C5	119.14 (13)
O5—C8—O6	124.19 (15)	O1—N1—C5	117.45 (16)
O5—C8—C1	123.15 (14)	C13—N2—C9	123.51 (16)
O6—C8—C1	112.61 (13)	C13—N2—H2A	117.5 (14)
N2—C9—C10	117.84 (16)	C9—N2—H2A	118.9 (14)
N2—C9—C14	118.17 (15)	C8—O6—H6	113 (2)

C6—C1—C2—C3	1.8 (3)	C1—C6—C7—O3	105.86 (16)
C8—C1—C2—C3	−174.11 (17)	C2—C1—C8—O5	163.55 (17)
C1—C2—C3—C4	0.9 (3)	C6—C1—C8—O5	−12.4 (2)
C2—C3—C4—C5	−2.2 (3)	C2—C1—C8—O6	−14.0 (2)
C3—C4—C5—C6	0.7 (3)	C6—C1—C8—O6	170.11 (15)
C3—C4—C5—N1	−178.05 (16)	N2—C9—C10—C11	−1.1 (3)
C4—C5—C6—C1	1.9 (2)	C14—C9—C10—C11	178.4 (2)
N1—C5—C6—C1	−179.33 (14)	C9—C10—C11—C12	1.1 (4)
C4—C5—C6—C7	−179.05 (15)	C10—C11—C12—C13	−0.5 (4)
N1—C5—C6—C7	−0.3 (2)	C11—C12—C13—N2	−0.2 (4)
C2—C1—C6—C5	−3.2 (2)	C4—C5—N1—O2	152.73 (17)
C8—C1—C6—C5	172.70 (14)	C6—C5—N1—O2	−26.1 (2)
C2—C1—C6—C7	177.83 (14)	C4—C5—N1—O1	−26.3 (2)
C8—C1—C6—C7	−6.3 (2)	C6—C5—N1—O1	154.86 (19)
C5—C6—C7—O4	106.09 (17)	C12—C13—N2—C9	0.2 (3)
C1—C6—C7—O4	−74.96 (19)	C10—C9—N2—C13	0.5 (3)
C5—C6—C7—O3	−73.09 (19)	C14—C9—N2—C13	−179.03 (19)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O3^{i}	0.88 (1)	1.74 (1)	2.6156 (17)	173 (2)
O6—H6···O4^{ii}	0.82 (1)	1.72 (1)	2.5381 (17)	176 (3)
C4—H4···O6^{iii}	0.93	2.60	3.493 (2)	161
C10—H10···O4^{iv}	0.93	2.50	3.189 (2)	131

C11—H11···O1^{v}	0.93	2.45	3.346 (3)	162
C14—H14*C*···O5	0.96	2.52	3.428 (3)	158

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+2; (ii) *x*, −*y*+1/2, *z*−1/2; (iii) −*x*, *y*+1/2, −*z*+3/2; (iv) *x*, *y*, *z*−1; (v) *x*, −*y*+3/2, *z*−1/2.