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## Structure Reports

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## 4-Carboxypyridinium bromide

Yingchun Wang

Ordered Matter Science Research Center, Southeast University, Nanjing 210096, People's Republic of China

Correspondence e-mail: wyingchun0107@126.com

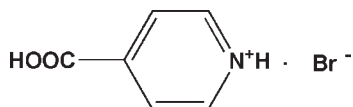
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.006$  Å;  $R$  factor = 0.044;  $wR$  factor = 0.097; data-to-parameter ratio = 18.4.

In the title compound,  $\text{C}_6\text{H}_6\text{NO}_2^+\cdot\text{Br}^-$ , the hydroxy and carbonyl groups make torsion angles of  $164.8$  (4) and  $-17.6$  (6)°, respectively, with the pyridinium ring. Intermolecular  $\text{N}-\text{H}\cdots\text{Br}$ ,  $\text{O}-\text{H}\cdots\text{Br}$  and  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds contribute to the stability of the structure and link the molecules into chains along the  $b$  axis.

## Related literature

For the phase transition of pyridinium tetrachloroiodate(III) studied by X-ray analysis and for dielectric and heat capacity measurements, see: Asaji *et al.* (2007). For the ferroelectric properties of pyridinium perrhenate, see: Wasicki *et al.* (1997). For the structure of 3-carboxypyridinium chloride, see: Slouf (2001).



## Experimental

## Crystal data

 $\text{C}_6\text{H}_6\text{NO}_2^+\cdot\text{Br}^-$  $M_r = 204.03$ Monoclinic,  $P2_1/n$  $a = 7.3179$  (15) Å $b = 7.3433$  (15) Å $c = 13.532$  (3) Å $\beta = 94.37$  (3)° $V = 725.1$  (3) Å<sup>3</sup> $Z = 4$ Mo  $K\alpha$  radiation $\mu = 5.60$  mm<sup>-1</sup>  
 $T = 293$  K

0.20 × 0.20 × 0.20 mm

## Data collection

Rigaku SCXmini diffractometer  
Absorption correction: multi-scan  
(*CrystalClear*; Rigaku, 2005)  
 $T_{\min} = 0.326$ ,  $T_{\max} = 0.339$ 7062 measured reflections  
1670 independent reflections  
1167 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.073$ 

## Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.044$   
 $wR(F^2) = 0.097$   
 $S = 1.06$   
1670 reflections91 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.45$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.33$  e Å<sup>-3</sup>

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O2}-\text{H2A}\cdots\text{Br1}^{\text{i}}$	0.82	2.32	3.127 (3)	170
$\text{N1}-\text{H1A}\cdots\text{Br1}^{\text{ii}}$	0.86	2.45	3.253 (3)	155
$\text{C4}-\text{H4A}\cdots\text{O1}^{\text{iii}}$	0.93	2.39	3.044 (5)	127

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *PRPKAPPA* (Ferguson, 1999) and *PLATON* (Spek, 2009).

The author is grateful to the starter fund of Southeast University for financial support to buy the X-ray diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2263).

## References

- Asaji, T., Eda, K., Fujimori, H., Adachi, T., Shibusawa, T. & Oguni, M. (2007). *J. Mol. Struct.* **826**, 24–28.  
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**supplementary materials**

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## 4-Carboxypyridinium bromide

Y. Wang

### Comment

Some materials have predominant dielectric-ferroelectric performance and they have much applications in many fields. The study of dielectric-ferroelectric materials has received much attention in recent years. PyHX ( $X=ICl_4, ClO_4, IO_4, ReO_4$  etc) (Asaji *et al.*(2007); Wasicki *et al.*(1997)) are representative. As one part of our continuing studies on finding for dielectric-ferroelectric materials, we synthesized the title compound  $C_6H_6NO_2^+Br^-$  unexpected comparing to PyHX, but it has no phase-transition in dielectric-ferroelectric measurement during 93 K to 470 K (m.p. 483 K).

The asymmetric unit of the title compound contains one 4-Carboxypyridinium basic ion and one bromide negative ion (Fig 1). In contrast to the planar 3-carboxypyridinium chloride (Slouf, 2001), the carboxyl group in the title molecule is slightly rotated with torsion angles of  $164.8 (4)^\circ$  and  $-17.6 (6)^\circ$ . In the planar 3-carboxypyridinium chloride structure, N—H $\cdots$ O hydrogen bonds form chains along the *c* axis, whereas in the title structure, 4-Carboxypyridinium basic ions and bromide ions are linked into chains along *b* through hydrogen bonds (Table 1, Fig 2). Crystallographic details of the title structure were examined with PLATON (Spek, 2009).

### Experimental

Methyl benzoate 0.685 g (5 mmol) in ethanol (30 ml), and 1.01 g hydrobromic acid (40%, 5 mmol) was added. The mixed solution was filtrated and the crystals suitable for structure determination were grown by slow evaporation of the solution at room temperature for five days.

### Refinement

Positional parameters of all the H atoms were calculated geometrically and were allowed to ride on the C atoms to which they are bonded, with C—H = 0.93 Å, N—H = 0.75–0.86 Å; with  $U_{iso}(H) = 1.2U_{eq}(C)$ , with  $U_{iso}(H) = 1.2-1.5U_{eq}(N)$ .

### Figures

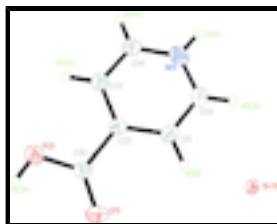


Fig. 1. The molecular structure of the title compound, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

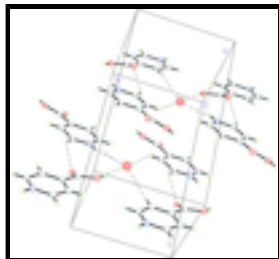


Fig. 2. A view of a packing section of the title compound. Dashed lines indicate hydrogen bonds.

## 4-Carboxypyridinium bromide

### Crystal data

$C_6H_6NO_2^+ \cdot Br^-$	$F(000) = 400$
$M_r = 204.03$	$D_x = 1.869 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: $-P\ 2_1/n$	Cell parameters from 0 reflections
$a = 7.3179 (15) \text{ \AA}$	$\theta = 3.0\text{--}27.5^\circ$
$b = 7.3433 (15) \text{ \AA}$	$\mu = 5.60 \text{ mm}^{-1}$
$c = 13.532 (3) \text{ \AA}$	$T = 293 \text{ K}$
$\beta = 94.37 (3)^\circ$	Prism, colorless
$V = 725.1 (3) \text{ \AA}^3$	$0.20 \times 0.20 \times 0.20 \text{ mm}$
$Z = 4$	

### Data collection

Rigaku SCXmini diffractometer	1670 independent reflections
Radiation source: fine-focus sealed tube graphite	1167 reflections with $I > 2\sigma(I)$
Detector resolution: $13.6612 \text{ pixels mm}^{-1}$	$R_{\text{int}} = 0.073$
CCD_Profile_fitting scans	$\theta_{\text{max}} = 27.5^\circ$ , $\theta_{\text{min}} = 3.0^\circ$
Absorption correction: multi-scan ( <i>CrystalClear</i> ; Rigaku, 2005)	$h = -9 \rightarrow 9$
$T_{\text{min}} = 0.326$ , $T_{\text{max}} = 0.339$	$k = -9 \rightarrow 9$
7062 measured reflections	$l = -17 \rightarrow 17$

### Refinement

Refinement on $F^2$	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.044$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.097$	H-atom parameters constrained
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.0363P)^2]$
1670 reflections	where $P = (F_o^2 + 2F_c^2)/3$
	$(\Delta/\sigma)_{\text{max}} < 0.001$

91 parameters

$$\Delta\rho_{\max} = 0.45 \text{ e } \text{\AA}^{-3}$$

0 restraints

$$\Delta\rho_{\min} = -0.33 \text{ e } \text{\AA}^{-3}$$

### Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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  $F^2 > \sigma(F^2)$  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 ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.05149 (7)	0.81361 (5)	0.25911 (3)	0.0471 (2)
O2	0.7136 (4)	-0.0655 (4)	-0.06801 (19)	0.0495 (8)
H2A	0.6581	-0.1279	-0.1107	0.074*
C2	0.7434 (6)	0.2225 (5)	0.0056 (3)	0.0351 (9)
O1	0.5215 (4)	0.1518 (4)	-0.1253 (2)	0.0534 (9)
N1	0.8996 (5)	0.4472 (5)	0.1454 (3)	0.0501 (10)
H1A	0.9504	0.5186	0.1897	0.060*
C1	0.7207 (6)	0.4094 (5)	-0.0030 (3)	0.0470 (11)
H1B	0.6524	0.4587	-0.0573	0.056*
C5	0.7998 (6)	0.5208 (6)	0.0693 (3)	0.0495 (12)
H5A	0.7840	0.6463	0.0653	0.059*
C3	0.8476 (6)	0.1523 (5)	0.0853 (3)	0.0450 (12)
H3A	0.8657	0.0273	0.0912	0.054*
C6	0.6474 (6)	0.0997 (5)	-0.0713 (3)	0.0375 (10)
C4	0.9248 (7)	0.2683 (6)	0.1562 (3)	0.0498 (12)
H4A	0.9938	0.2226	0.2113	0.060*

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.0633 (4)	0.0335 (2)	0.0427 (3)	0.0000 (2)	-0.0077 (2)	0.0051 (2)
O2	0.067 (2)	0.0397 (17)	0.0395 (17)	0.0007 (15)	-0.0115 (16)	-0.0047 (14)
C2	0.034 (2)	0.039 (2)	0.033 (2)	0.0015 (17)	0.0009 (18)	0.0023 (18)
O1	0.049 (2)	0.061 (2)	0.0477 (19)	0.0024 (15)	-0.0130 (17)	-0.0010 (15)
N1	0.054 (3)	0.050 (2)	0.046 (2)	-0.0040 (19)	-0.0036 (19)	-0.0168 (19)
C1	0.053 (3)	0.041 (2)	0.046 (3)	0.008 (2)	-0.006 (2)	0.004 (2)
C5	0.053 (3)	0.035 (2)	0.060 (3)	0.000 (2)	0.000 (3)	0.003 (2)
C3	0.057 (3)	0.038 (2)	0.039 (3)	-0.001 (2)	-0.006 (2)	0.0000 (19)
C6	0.044 (3)	0.041 (2)	0.027 (2)	-0.001 (2)	-0.001 (2)	0.0008 (18)
C4	0.060 (3)	0.048 (3)	0.040 (3)	0.005 (2)	-0.012 (2)	-0.002 (2)

## supplementary materials

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### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

O2—C6	1.306 (5)	N1—H1A	0.8600
O2—H2A	0.8200	C1—C5	1.369 (6)
C2—C3	1.373 (5)	C1—H1B	0.9300
C2—C1	1.386 (5)	C5—H5A	0.9300
C2—C6	1.508 (5)	C3—C4	1.372 (6)
O1—C6	1.195 (5)	C3—H3A	0.9300
N1—C5	1.330 (5)	C4—H4A	0.9300
N1—C4	1.333 (5)		
C6—O2—H2A	109.5	N1—C5—H5A	120.4
C3—C2—C1	119.6 (4)	C1—C5—H5A	120.4
C3—C2—C6	121.2 (3)	C4—C3—C2	119.4 (4)
C1—C2—C6	119.2 (4)	C4—C3—H3A	120.3
C5—N1—C4	123.3 (4)	C2—C3—H3A	120.3
C5—N1—H1A	118.4	O1—C6—O2	125.8 (4)
C4—N1—H1A	118.4	O1—C6—C2	121.8 (4)
C5—C1—C2	119.3 (4)	O2—C6—C2	112.3 (4)
C5—C1—H1B	120.3	N1—C4—C3	119.2 (4)
C2—C1—H1B	120.3	N1—C4—H4A	120.4
N1—C5—C1	119.2 (4)	C3—C4—H4A	120.4
C3—C2—C1—C5	-1.2 (6)	C3—C2—C6—O1	160.3 (4)
C6—C2—C1—C5	176.6 (4)	C1—C2—C6—O1	-17.6 (6)
C4—N1—C5—C1	-1.2 (7)	C3—C2—C6—O2	-17.4 (6)
C2—C1—C5—N1	1.2 (7)	C1—C2—C6—O2	164.8 (4)
C1—C2—C3—C4	1.2 (7)	C5—N1—C4—C3	1.2 (7)
C6—C2—C3—C4	-176.6 (4)	C2—C3—C4—N1	-1.2 (7)

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2A $\cdots$ Br1 <sup>i</sup>	0.82	2.32	3.127 (3)	170.
N1—H1A $\cdots$ Br1 <sup>ii</sup>	0.86	2.45	3.253 (3)	155.
C4—H4A $\cdots$ O1 <sup>iii</sup>	0.93	2.39	3.044 (5)	127.

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

Fig. 1

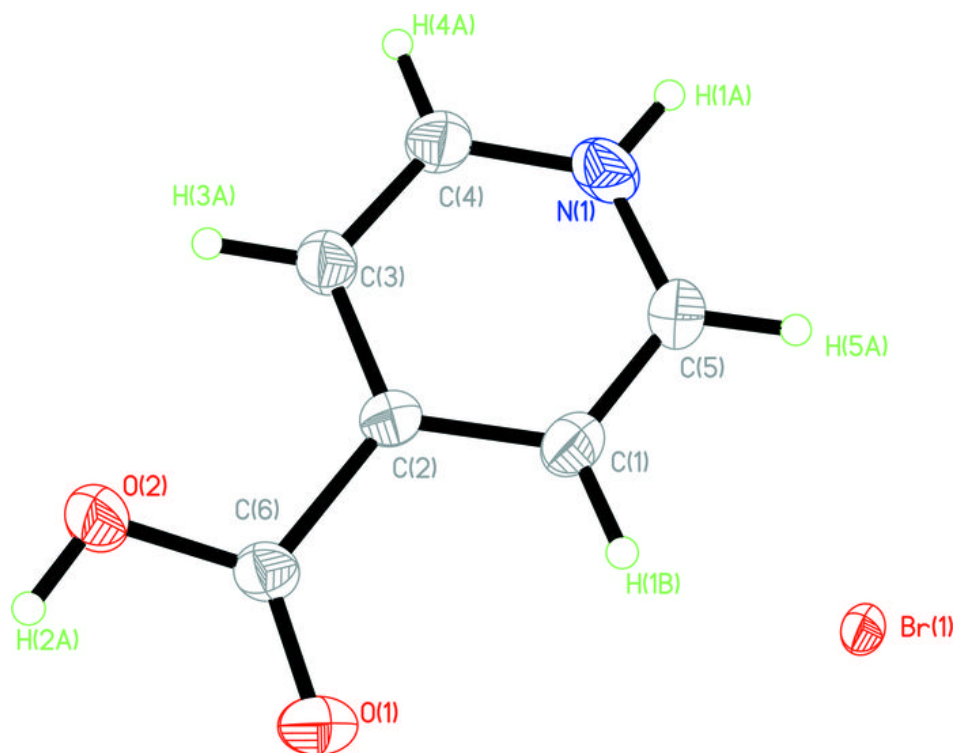


Fig. 2

