

## 2-Amino-5-chloropyridinium hydrogen succinate

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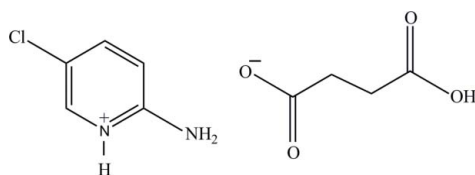
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 Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.038;  $wR$  factor = 0.082; data-to-parameter ratio = 20.8.

In the title salt,  $\text{C}_5\text{H}_6\text{ClN}_2^+\cdot\text{C}_4\text{H}_5\text{O}_4^-$ , the pyridine N atom is protonated. The pyridinium and amino groups associate *via* a pair of  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds to the carboxylate O atoms of the singly deprotonated succinate anion. The hydrogen succinate anions self-assemble *via*  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds into chains along the  $b$  axis. The crystal structure is further stabilized by additional  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds involving the second amino H atoms, as well as  $\text{C}-\text{H}\cdots\text{O}$  contacts, forming a three-dimensional network.

### Related literature

For background to the chemistry of substituted pyridines, see: Pozharski *et al.* (1997); Katritzky *et al.* (1996). For related structures, see: Pourayoubi *et al.* (2007); Akriche & Rzaigui (2005); Zaouali Zgolli *et al.* (2009). For the structure of succinic acid, see: Gopalan *et al.* (2000); Leviel *et al.* (1981). For applications of succinic acid, see: Sauer *et al.* (2008); Song & Lee (2006); Zeikus *et al.* (1999). For details of hydrogen bonding, see: Jeffrey & Saenger (1991); Jeffrey (1997); Scheiner (1997). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



### Experimental

#### Crystal data

 $\text{C}_5\text{H}_6\text{ClN}_2^+\cdot\text{C}_4\text{H}_5\text{O}_4^-$   
 $M_r = 246.65$ 

 Orthorhombic,  $P2_12_12_1$   
 $a = 5.2263$  (1) Å

 $b = 13.5997$  (3) Å  
 $c = 14.9019$  (3) Å  
 $V = 1059.17$  (4) Å<sup>3</sup>  
 $Z = 4$ 

 Mo  $K\alpha$  radiation  
 $\mu = 0.36$  mm<sup>-1</sup>  
 $T = 100$  K  
 $0.41 \times 0.15 \times 0.10$  mm

#### Data collection

 Bruker SMART APEXII CCD  
 area-detector diffractometer  
 Absorption correction: multi-scan  
 (SADABS; Bruker, 2009)  
 $T_{\min} = 0.866$ ,  $T_{\max} = 0.965$ 

 11594 measured reflections  
 3934 independent reflections  
 3581 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.033$ 

#### Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.038$   
 $wR(F^2) = 0.082$   
 $S = 1.02$   
 3934 reflections  
 189 parameters  
 H atoms treated by a mixture of  
 independent and constrained  
 refinement

 $\Delta\rho_{\text{max}} = 0.33$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.27$  e Å<sup>-3</sup>  
 Absolute structure: Flack (1983),  
 1604 Friedel pairs  
 Flack parameter: 0.05 (5)

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O3}-\text{H1O3}\cdots\text{O2}^{\text{i}}$	0.821 (19)	1.819 (19)	2.5891 (15)	156 (2)
$\text{N1}-\text{H1N1}\cdots\text{O2}^{\text{ii}}$	0.86 (2)	1.85 (2)	2.7023 (15)	172.4 (19)
$\text{N2}-\text{H1N2}\cdots\text{O1}^{\text{iii}}$	0.84 (2)	1.95 (2)	2.7814 (15)	177 (2)
$\text{N2}-\text{H2N2}\cdots\text{O1}$	0.826 (19)	2.004 (19)	2.8002 (16)	162 (2)
$\text{C5}-\text{H5}\cdots\text{O4}^{\text{iii}}$	0.964 (17)	2.391 (17)	3.2216 (18)	144.0 (13)

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; 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: SHELXTL and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2616).

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**supplementary materials**

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## 2-Amino-5-chloropyridinium hydrogen succinate

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### Comment

Pyridine and its derivatives play an important role in heterocyclic chemistry (Pozharski *et al.*, 1997; Katritzky *et al.*, 1996). They are often involved in hydrogen-bonding interactions (Jeffrey & Saenger, 1991; Jeffrey, 1997; Scheiner, 1997). The dicarboxylic acid, succinic acid, is a precursor for many chemicals of industrial importance (Zeikus *et al.*, 1999; Song & Lee, 2006). Succinic acid derivatives are mostly used in chemicals, food and pharmaceuticals (Sauer *et al.*, 2008). The crystal structure of succinic acid has been reported (Gopalan *et al.*, 2000; Leviel *et al.*, 1981). The crystal structures of 2-amino-5-chloropyridine (Pourayoubi *et al.*, 2007), 2-amino-5-chloropyridinium nitrate (Zaouali Zgolli *et al.*, 2009) and bis (2-amino-5-chloropyridinium) dihydrogen diphosphate (Akriche & Rzaigui, 2005) have been reported in literature. In this paper, we present the X-ray single-crystal structure of 2-amino-5-chloropyridinium hydrogen succinate, (I).

The asymmetric unit of (I), Fig. 1, contains a 2-amino-5-chloropyridinium cation and a hydrogen succinate anion, indicating that proton transfer has occurred during the co-crystallisation experiment. In the 2-amino-5-chloropyridinium cation, a wider than normal angle (123.22 (12)°) is subtended at the protonated N1 atom.

In the crystal packing (Fig. 2), the protonated N1 atom and the 2-amino group is hydrogen-bonded to the carboxylate oxygen atoms (O1 and O2) via a pair of N—H···O hydrogen bonds forming a  $R_2^2(8)$  ring motif (Bernstein *et al.* 1995). The hydrogen succinate anions self-assemble via O—H···O hydrogen bonds. The second amino-H atom forms a hydrogen bond with the carboxylate-O1 atom. Furthermore, the crystal structure is stabilized by C—H···O contacts, Table 1, forming a 3D-network.

### Experimental

A hot methanolic solution (10 ml) of 2-amino-5-chloropyridine (32 mg, Aldrich) and a hot aqueous solution (10 ml) of succinic acid (29 mg, Merck) were mixed and warmed over a water bath for 10 minutes. The resulting solution was allowed to cool slowly at room temperature. Single crystals of (I) appeared from the mother liquor after a few days.

### Refinement

All the H atoms were located in a difference Fourier map and allowed to refine freely [N—H = 0.83 (2) - 0.86 (2) Å, C—H = 0.944 (18) - 1.047 (19) Å, O—H = 0.822 (19) Å ].

## Figures

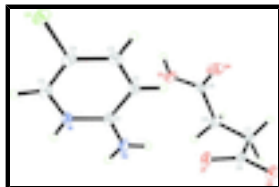


Fig. 1. The asymmetric unit of (I) showing atom labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

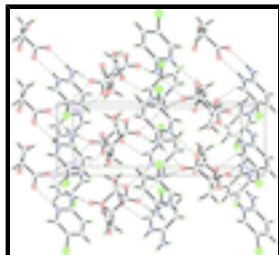
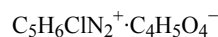


Fig. 2. The crystal packing of (I), showing intermolecular interactions as dashed lines.

## 2-Amino-5-chloropyridinium hydrogen succinate

### Crystal data



$M_r = 246.65$

Orthorhombic,  $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 5.2263$  (1) Å

$b = 13.5997$  (3) Å

$c = 14.9019$  (3) Å

$V = 1059.17$  (4) Å<sup>3</sup>

$Z = 4$

$F(000) = 512$

$D_x = 1.547$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 3633 reflections

$\theta = 2.7\text{--}33.2^\circ$

$\mu = 0.36$  mm<sup>-1</sup>

$T = 100$  K

Block, yellow

$0.41 \times 0.15 \times 0.10$  mm

### Data collection

Bruker SMART APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

graphite

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan (SADABS; Bruker, 2009)

$T_{\min} = 0.866$ ,  $T_{\max} = 0.965$

11594 measured reflections

3934 independent reflections

3581 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\max} = 33.2^\circ$ ,  $\theta_{\min} = 2.0^\circ$

$h = -8 \rightarrow 6$

$k = -17 \rightarrow 20$

$l = -21 \rightarrow 22$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

$$R[F^2 > 2\sigma(F^2)] = 0.038$$

$$wR(F^2) = 0.082$$

$$S = 1.02$$

3934 reflections

189 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0404P)^2 + 0.0588P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

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

$$\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack (1983), 1604 Friedel pairs

Flack parameter: 0.05 (5)

### Special details

**Experimental.** The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

**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  $F^2 > 2\sigma(F^2)$  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 ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	-0.16471 (6)	0.66417 (3)	0.01385 (3)	0.02344 (8)
N1	0.3976 (2)	0.47974 (9)	-0.04334 (8)	0.0152 (2)
N2	0.5510 (2)	0.33552 (9)	0.01762 (9)	0.0194 (2)
C1	0.3838 (2)	0.40861 (10)	0.02044 (9)	0.0152 (2)
C2	0.1897 (3)	0.41668 (10)	0.08661 (9)	0.0170 (2)
C3	0.0245 (3)	0.49419 (11)	0.08409 (10)	0.0183 (3)
C4	0.0469 (2)	0.56603 (10)	0.01630 (10)	0.0180 (2)
C5	0.2340 (3)	0.55775 (10)	-0.04688 (10)	0.0168 (2)
O1	0.42571 (19)	0.16607 (8)	0.11491 (6)	0.0208 (2)
O2	0.24386 (19)	0.03548 (7)	0.17729 (7)	0.0184 (2)
O3	0.8289 (2)	0.36179 (8)	0.25630 (8)	0.0232 (2)
O4	0.4478 (2)	0.29887 (8)	0.29328 (8)	0.0277 (3)
C6	0.4118 (2)	0.10302 (9)	0.17571 (9)	0.0142 (2)
C7	0.6061 (3)	0.10441 (10)	0.25145 (10)	0.0179 (3)
C8	0.7907 (2)	0.19017 (10)	0.24860 (10)	0.0181 (3)
C9	0.6663 (3)	0.28792 (10)	0.26836 (8)	0.0158 (2)
H2	0.180 (3)	0.3686 (13)	0.1322 (11)	0.020 (4)*
H3	-0.110 (3)	0.4991 (12)	0.1279 (11)	0.020 (4)*
H5	0.262 (3)	0.6021 (12)	-0.0964 (12)	0.016 (4)*
H7A	0.713 (4)	0.0395 (14)	0.2466 (13)	0.029 (5)*

## supplementary materials

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H7B	0.504 (4)	0.1041 (13)	0.3078 (13)	0.033 (5)*
H8A	0.925 (4)	0.1818 (13)	0.2917 (12)	0.026 (5)*
H8B	0.883 (4)	0.1978 (13)	0.1893 (12)	0.023 (5)*
H1O3	0.764 (4)	0.4144 (14)	0.2709 (13)	0.026 (5)*
H1N1	0.517 (4)	0.4729 (13)	-0.0823 (13)	0.026 (5)*
H1N2	0.667 (4)	0.3364 (14)	-0.0209 (13)	0.029 (5)*
H2N2	0.538 (4)	0.2904 (14)	0.0544 (13)	0.027 (5)*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C11	0.01978 (14)	0.01782 (15)	0.03271 (18)	0.00423 (12)	0.00071 (13)	-0.00177 (14)
N1	0.0162 (5)	0.0134 (5)	0.0162 (5)	-0.0010 (4)	0.0012 (4)	0.0015 (4)
N2	0.0200 (5)	0.0154 (5)	0.0227 (6)	0.0009 (5)	0.0046 (5)	0.0071 (5)
C1	0.0156 (5)	0.0133 (5)	0.0168 (6)	-0.0035 (4)	-0.0024 (4)	0.0009 (5)
C2	0.0188 (6)	0.0168 (6)	0.0154 (6)	-0.0038 (5)	0.0007 (5)	0.0013 (5)
C3	0.0177 (6)	0.0193 (6)	0.0180 (6)	-0.0033 (5)	0.0013 (5)	-0.0030 (5)
C4	0.0176 (5)	0.0154 (6)	0.0209 (6)	0.0001 (5)	-0.0026 (5)	-0.0021 (5)
C5	0.0175 (5)	0.0124 (6)	0.0205 (7)	-0.0014 (5)	-0.0030 (5)	0.0008 (5)
O1	0.0257 (5)	0.0174 (5)	0.0194 (5)	-0.0048 (4)	-0.0037 (4)	0.0068 (4)
O2	0.0197 (4)	0.0132 (4)	0.0222 (5)	-0.0027 (4)	-0.0035 (4)	0.0039 (4)
O3	0.0242 (5)	0.0129 (5)	0.0326 (6)	-0.0011 (4)	0.0082 (5)	-0.0048 (4)
O4	0.0192 (5)	0.0251 (6)	0.0387 (6)	-0.0001 (4)	0.0062 (4)	-0.0112 (5)
C6	0.0153 (5)	0.0118 (5)	0.0154 (6)	0.0024 (4)	0.0000 (4)	-0.0013 (5)
C7	0.0226 (6)	0.0140 (6)	0.0169 (6)	-0.0011 (5)	-0.0027 (5)	0.0027 (5)
C8	0.0169 (6)	0.0156 (6)	0.0218 (7)	0.0014 (5)	-0.0023 (5)	-0.0016 (5)
C9	0.0184 (5)	0.0153 (6)	0.0138 (6)	0.0011 (5)	-0.0014 (5)	-0.0017 (5)

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

C11—C4	1.7336 (13)	C5—H5	0.965 (17)
N1—C1	1.3580 (17)	O1—C6	1.2496 (16)
N1—C5	1.3636 (18)	O2—C6	1.2708 (16)
N1—H1N1	0.86 (2)	O3—C9	1.3281 (17)
N2—C1	1.3242 (17)	O3—H1O3	0.822 (19)
N2—H1N2	0.83 (2)	O4—C9	1.2100 (17)
N2—H2N2	0.83 (2)	C6—C7	1.5183 (19)
C1—C2	1.4189 (18)	C7—C8	1.5141 (19)
C2—C3	1.363 (2)	C7—H7A	1.047 (19)
C2—H2	0.944 (18)	C7—H7B	0.99 (2)
C3—C4	1.410 (2)	C8—C9	1.5090 (19)
C3—H3	0.961 (17)	C8—H8A	0.959 (19)
C4—C5	1.362 (2)	C8—H8B	1.010 (18)
C1—N1—C5	123.22 (12)	N1—C5—H5	115.0 (10)
C1—N1—H1N1	115.7 (12)	C9—O3—H1O3	110.9 (14)
C5—N1—H1N1	121.0 (12)	O1—C6—O2	123.33 (12)
C1—N2—H1N2	119.3 (14)	O1—C6—C7	119.44 (11)
C1—N2—H2N2	118.7 (13)	O2—C6—C7	117.21 (11)

H1N2—N2—H2N2	122.0 (19)	C8—C7—C6	114.51 (11)
N2—C1—N1	118.52 (12)	C8—C7—H7A	107.9 (10)
N2—C1—C2	123.49 (12)	C6—C7—H7A	107.2 (10)
N1—C1—C2	117.99 (12)	C8—C7—H7B	111.6 (11)
C3—C2—C1	119.57 (13)	C6—C7—H7B	105.6 (12)
C3—C2—H2	121.4 (11)	H7A—C7—H7B	109.9 (15)
C1—C2—H2	119.0 (11)	C9—C8—C7	113.48 (11)
C2—C3—C4	120.21 (13)	C9—C8—H8A	106.9 (11)
C2—C3—H3	119.8 (10)	C7—C8—H8A	110.9 (11)
C4—C3—H3	119.9 (10)	C9—C8—H8B	106.5 (10)
C5—C4—C3	119.81 (12)	C7—C8—H8B	114.0 (10)
C5—C4—C11	120.47 (11)	H8A—C8—H8B	104.4 (14)
C3—C4—C11	119.71 (11)	O4—C9—O3	123.52 (13)
C4—C5—N1	119.20 (13)	O4—C9—C8	125.11 (13)
C4—C5—H5	125.8 (10)	O3—C9—C8	111.36 (12)
C5—N1—C1—N2	179.59 (12)	C11—C4—C5—N1	-179.96 (10)
C5—N1—C1—C2	-0.30 (18)	C1—N1—C5—C4	0.21 (19)
N2—C1—C2—C3	-179.60 (13)	O1—C6—C7—C8	4.56 (19)
N1—C1—C2—C3	0.29 (18)	O2—C6—C7—C8	-176.50 (12)
C1—C2—C3—C4	-0.2 (2)	C6—C7—C8—C9	69.12 (16)
C2—C3—C4—C5	0.1 (2)	C7—C8—C9—O4	7.3 (2)
C2—C3—C4—C11	179.95 (11)	C7—C8—C9—O3	-173.70 (12)
C3—C4—C5—N1	-0.10 (19)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H1O3 $\cdots$ O2 <sup>i</sup>	0.821 (19)	1.819 (19)	2.5891 (15)	156 (2)
N1—H1N1 $\cdots$ O2 <sup>ii</sup>	0.86 (2)	1.85 (2)	2.7023 (15)	172.4 (19)
N2—H1N2 $\cdots$ O1 <sup>ii</sup>	0.84 (2)	1.95 (2)	2.7814 (15)	177 (2)
N2—H2N2 $\cdots$ O1	0.826 (19)	2.004 (19)	2.8002 (16)	162 (2)
C5—H5 $\cdots$ O4 <sup>iii</sup>	0.964 (17)	2.391 (17)	3.2216 (18)	144.0 (13)

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



Fig. 1

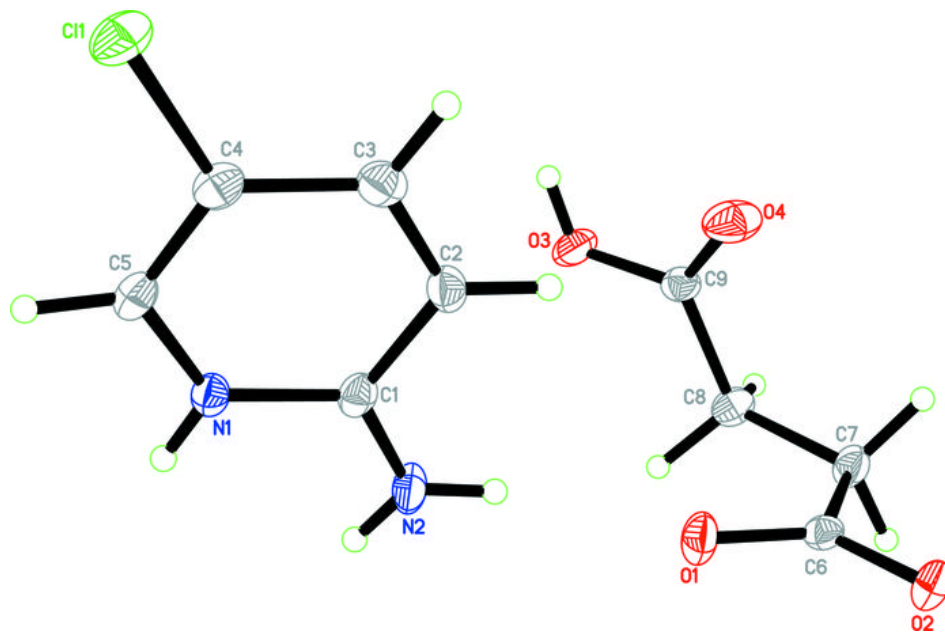


Fig. 2

