

2-Amino-5-chloropyridinium salicylate

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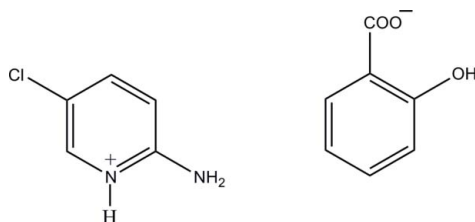
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.001$ Å; R factor = 0.035; wR factor = 0.124; data-to-parameter ratio = 31.4.

In the crystal structure of the title salt, $\text{C}_5\text{H}_6\text{ClN}_2^+ \cdot \text{C}_7\text{H}_5\text{O}_3^-$, the protonated N atom and the 2-amino group of the cation are hydrogen bonded to the carboxylate O atoms *via* a pair of $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds, forming $R_2^2(8)$ ring motifs. These motifs are centrosymmetrically paired *via* $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds, forming a complementary donor–donor–acceptor–acceptor (*DDAA*) array. A typical intramolecular $\text{O}-\text{H} \cdots \text{O}$ hydrogen bond is also observed in the salicylate anion. The crystal structure is further stabilized by weak $\text{C}-\text{H} \cdots \pi$ interactions.

Related literature

For 2-aminopyridines, see: Gellert & Hsu (1988); Banerjee & Murugavel (2004); Bis & Zaworotko (2005); Bis *et al.* (2006) and for salicylic acid, see: Cochran (1953); Singh & Vijayan (1974); Varughese & Kartha (1982). For related structures, see: Hemamalini & Fun (2010*a,b,c*). Pourayoubi *et al.* (2007). For hydrogen-bond motifs, see: Bernstein *et al.* (1995) and for hydrogen-bonding patterns in organic salts, see: Baskar Raj *et al.* (2003). For bond-length data, see: Allen *et al.* (1987). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$\text{C}_5\text{H}_6\text{ClN}_2^+ \cdot \text{C}_7\text{H}_5\text{O}_3^-$
 $M_r = 266.68$

Monoclinic, $P2_1/c$
 $a = 6.7403$ (6) Å

$b = 14.5574$ (12) Å
 $c = 13.2857$ (9) Å
 $\beta = 115.550$ (4)°
 $V = 1176.13$ (16) Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 0.33$ mm⁻¹
 $T = 100$ K
 $0.38 \times 0.34 \times 0.23$ mm

Data collection

Bruker APEXII DUO CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
 $T_{\min} = 0.887$, $T_{\max} = 0.929$

19132 measured reflections
5144 independent reflections
4405 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.124$
 $S = 1.17$
5144 reflections

164 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.66$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.43$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C7–C12 ring.

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N1}-\text{H1} \cdots \text{O2}^i$	0.86	1.83	2.6928 (10)	178
$\text{O1}-\text{H1B} \cdots \text{O2}$	0.82	1.82	2.5483 (11)	147
$\text{N2}-\text{H2A} \cdots \text{O3}^i$	0.86	1.96	2.8181 (11)	178
$\text{N2}-\text{H2B} \cdots \text{O3}^{ii}$	0.86	2.03	2.8321 (13)	154
$\text{C1}-\text{H1A} \cdots \text{Cg1}^{iii}$	0.93	2.57	3.3680 (11)	144

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; 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: SJ5004).

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Banerjee, S. & Murugavel, R. (2004). *Cryst. Growth Des.* **4**, 545–552.
Baskar Raj, S., Stanley, N., Muthiah, P. T., Bocelli, G., Ollá, R. & Cantoni, A. (2003). *Cryst. Growth Des.* **3**, 567–571.
Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bis, J. A., McLaughlin, O. L., Vishweshwar, P. & Zaworotko, M. J. (2006). *Cryst. Growth Des.* **6**, 2648–2650.
Bis, J. A. & Zaworotko, M. A. (2005). *Cryst. Growth Des.* **5**, 1169–1179.
Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cochran, W. (1953). *Acta Cryst.* **6**, 260–268.
Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
Gellert, R. W. & Hsu, I.-N. (1988). *Acta Cryst.* **C44**, 311–313.
Hemamalini, M. & Fun, H.-K. (2010*a*). *Acta Cryst.* **E66**, o464–o465.

Hemamalini, M. & Fun, H.-K. (2010*b*). *Acta Cryst.* **E66**, o557.
Hemamalini, M. & Fun, H.-K. (2010*c*). *Acta Cryst.* **E66**, o783–o784.
Pourayoubi, M., Ghadimi, S. & Ebrahimi Valmoozi, A. A. (2007). *Acta Cryst.* **E63**, o4631.

Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
Singh, T. P. & Vijayan, M. (1974). *Acta Cryst.* **B30**, 557–562.
Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
Varughese, K. I. & Kartha, G. (1982). *Acta Cryst.* **B38**, 301–302.

supplementary materials

Acta Cryst. (2010). E66, o1418-o1419 [doi:10.1107/S1600536810018210]

2-Amino-5-chloropyridinium salicylate

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Comment

2-Aminopyridine is one of the most frequently used synthons in supramolecular chemistry based on hydrogen bonds (Gellert & Hsu, 1988; Banerjee & Murugavel, 2004; Bis & Zaworotko, 2005; Bis *et al.*, 2006). A series of similar complexes formed from 2-amino-5-chloropyridine and carboxylates has been reported previously (Hemamalini & Fun, 2010a,b,c). Salicylic acid (Cochran, 1953) and its derivatives are widely used as analgesic. They are also used for various gastric tympany and externally as antiseptic and antifungal agents for various skin conditions. The crystal structure of salicylic acid and its complexes, for example, antipyrine-salicylic acid (salipyrine) (Singh & Vijayan, 1974) and piperazinedione-salicylic acid (1:2) (Varughese & Kartha, 1982), have been reported in literature. In a continuation of our studies of pyridinium derivatives, the crystal structure determination of the title compound has been undertaken.

The asymmetric unit (Fig. 1) contains one 2-amino-5-chloropyridinium cation and one salicylate anion. The proton transfer from the carboxyl group to atom N1 of 2-amino-5-chloropyridine resulted in the widening of C1—N1—C5 angle of the pyridinium ring to 122.87 (8)°, compared to the corresponding angle of 118.11 (12)° in neutral 2-amino-5-chloropyridine (Pourayoubi *et al.*, 2007). The 2-amino-5-chloropyridinium cation is essentially planar, with a maximum deviation of 0.020 (1) Å for atom Cl. The bond lengths (Allen *et al.*, 1987) and angles are normal.

In the crystal packing (Fig. 2), the protonated N1 atom and the 2-amino group (N2) are hydrogen-bonded to the carboxylate oxygen atoms (O2 and O3) via a pair of intermolecular N1—H1...O2 and N2—H2A...O3 hydrogen bonds forming an $R^2_2(8)$ ring motif (Bernstein *et al.*, 1995). These motifs are centrosymmetrically paired via N—H...O hydrogen bonds, forming a complementary DDAA array (Baskar Raj *et al.* 2003). There is an intramolecular O1—H1B...O2 hydrogen bond in the salicylate anion, which generates an $S(6)$ ring motif. This motif is also observed in the crystal structure of 2-aminopyridinium salicylate (Gellert & Hsu, 1988). The crystal structure is further stabilized by weak C—H... π interactions (Table 1) involving the C7—C12 (centroid Cg1) ring.

Experimental

A hot methanol solution (20 ml) of 2-amino-5-chloropyridine (64 mg, Aldrich) and salicylic acid (69 mg, Merck) were mixed and warmed over a magnetic stirrer hotplate for a few minutes. The resulting solution was allowed to cool slowly at room temperature and crystals of the title compound appeared after a few days.

Refinement

All hydrogen atoms were positioned geometrically [C—H = 0.93 Å, N—H = 0.86 Å and O—H = 0.82 Å] and were refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C}, \text{N})$ or $1.5 U_{\text{eq}}(\text{O})$.

Figures

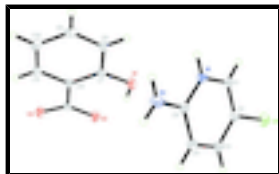


Fig. 1. The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 50% probability level. A dashed line indicates the intramolecular hydrogen bond.

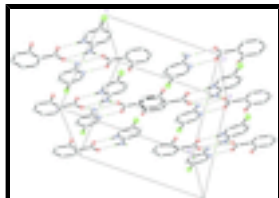
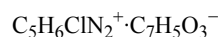


Fig. 2. The crystal packing of the title compound, showing hydrogen-bonded (dashed lines) networks. H atoms not involved in hydrogen bond interactions are omitted for clarity.

2-amino-5-chloropyridinium 2-hydroxybenzoate

Crystal data



$M_r = 266.68$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 6.7403$ (6) Å

$b = 14.5574$ (12) Å

$c = 13.2857$ (9) Å

$\beta = 115.550$ (4)°

$V = 1176.13$ (16) Å³

$Z = 4$

$F(000) = 552$

$D_x = 1.506$ Mg m⁻³

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

Cell parameters from 8071 reflections

$\theta = 2.8$ – 35.0 °

$\mu = 0.33$ mm⁻¹

$T = 100$ K

Block, colourless

$0.38 \times 0.34 \times 0.23$ mm

Data collection

Bruker APEXII DUO CCD area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

φ and ω scans

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

$T_{\min} = 0.887$, $T_{\max} = 0.929$

19132 measured reflections

5144 independent reflections

4405 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\text{max}} = 35.1$ °, $\theta_{\text{min}} = 2.2$ °

$h = -10 \rightarrow 9$

$k = -23 \rightarrow 23$

$l = -21 \rightarrow 21$

Refinement

Refinement on F^2

Least-squares matrix: full

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

$$R[F^2 > 2\sigma(F^2)] = 0.035$$

$$wR(F^2) = 0.124$$

$$S = 1.17$$

5144 reflections

164 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0671P)^2 + 0.2275P]$$

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

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

$$\Delta\rho_{\max} = 0.66 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.43 \text{ e } \text{\AA}^{-3}$$

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	-0.19050 (4)	0.904645 (18)	0.14133 (2)	0.02103 (8)
N1	0.41620 (13)	0.90963 (5)	0.37992 (7)	0.01402 (14)
H1	0.4827	0.8888	0.4469	0.017*
N2	0.74627 (14)	0.97248 (6)	0.40024 (7)	0.01929 (16)
H2A	0.8072	0.9514	0.4672	0.023*
H2B	0.8229	1.0030	0.3741	0.023*
C1	0.19743 (15)	0.89260 (6)	0.32167 (8)	0.01479 (15)
H1A	0.1225	0.8595	0.3544	0.018*
C2	0.08837 (15)	0.92433 (7)	0.21489 (7)	0.01471 (15)
C3	0.20331 (15)	0.97455 (7)	0.16657 (7)	0.01588 (15)
H3	0.1298	0.9965	0.0940	0.019*
C4	0.42261 (15)	0.99101 (7)	0.22608 (7)	0.01550 (15)
H4	0.4992	1.0238	0.1941	0.019*
C5	0.53371 (15)	0.95784 (6)	0.33713 (7)	0.01379 (15)
O1	0.56169 (12)	0.72179 (6)	0.25181 (6)	0.01955 (15)
H1B	0.5299	0.7070	0.1871	0.029*
O2	0.62190 (11)	0.65244 (5)	0.09104 (6)	0.01729 (14)
O3	0.95143 (13)	0.59845 (5)	0.11872 (6)	0.01772 (14)
C7	0.77978 (15)	0.70954 (6)	0.31440 (7)	0.01377 (15)
C8	0.86682 (17)	0.73401 (7)	0.42726 (8)	0.01670 (16)
H8	0.7754	0.7583	0.4567	0.020*

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C9	1.08961 (17)	0.72202 (7)	0.49541 (8)	0.01810 (17)
H9	1.1464	0.7380	0.5704	0.022*
C10	1.22897 (16)	0.68615 (7)	0.45190 (8)	0.01796 (17)
H10	1.3782	0.6787	0.4975	0.022*
C11	1.14261 (15)	0.66179 (6)	0.34034 (8)	0.01524 (15)
H11	1.2353	0.6382	0.3113	0.018*
C12	0.91805 (14)	0.67199 (6)	0.27039 (7)	0.01249 (14)
C13	0.82718 (15)	0.63875 (6)	0.15205 (7)	0.01318 (15)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.01164 (11)	0.02568 (13)	0.02128 (12)	-0.00140 (7)	0.00287 (8)	-0.00279 (8)
N1	0.0125 (3)	0.0153 (3)	0.0128 (3)	-0.0010 (2)	0.0041 (2)	0.0018 (2)
N2	0.0127 (3)	0.0256 (4)	0.0160 (3)	-0.0046 (3)	0.0029 (3)	0.0045 (3)
C1	0.0129 (3)	0.0144 (4)	0.0164 (4)	-0.0011 (3)	0.0057 (3)	-0.0001 (3)
C2	0.0116 (3)	0.0160 (4)	0.0147 (3)	-0.0002 (3)	0.0039 (3)	-0.0016 (3)
C3	0.0148 (4)	0.0178 (4)	0.0127 (3)	0.0013 (3)	0.0038 (3)	0.0009 (3)
C4	0.0150 (4)	0.0173 (4)	0.0136 (3)	-0.0003 (3)	0.0056 (3)	0.0025 (3)
C5	0.0122 (3)	0.0149 (4)	0.0131 (3)	-0.0006 (3)	0.0044 (3)	0.0007 (3)
O1	0.0123 (3)	0.0292 (4)	0.0164 (3)	0.0026 (2)	0.0054 (2)	-0.0033 (3)
O2	0.0128 (3)	0.0237 (3)	0.0128 (3)	0.0018 (2)	0.0031 (2)	-0.0024 (2)
O3	0.0176 (3)	0.0215 (3)	0.0145 (3)	0.0046 (2)	0.0074 (3)	-0.0015 (2)
C7	0.0133 (3)	0.0146 (3)	0.0134 (3)	-0.0001 (3)	0.0057 (3)	-0.0004 (3)
C8	0.0184 (4)	0.0189 (4)	0.0139 (3)	0.0001 (3)	0.0079 (3)	-0.0016 (3)
C9	0.0209 (4)	0.0187 (4)	0.0117 (3)	-0.0012 (3)	0.0042 (3)	-0.0008 (3)
C10	0.0158 (4)	0.0181 (4)	0.0150 (4)	0.0010 (3)	0.0019 (3)	0.0000 (3)
C11	0.0133 (3)	0.0153 (4)	0.0155 (3)	0.0012 (3)	0.0047 (3)	-0.0005 (3)
C12	0.0123 (3)	0.0130 (3)	0.0116 (3)	0.0004 (3)	0.0047 (3)	-0.0001 (3)
C13	0.0138 (3)	0.0135 (3)	0.0118 (3)	0.0004 (3)	0.0052 (3)	0.0004 (3)

Geometric parameters (\AA , $^\circ$)

C11—C2	1.7280 (9)	O1—H1B	0.8200
N1—C5	1.3534 (12)	O2—C13	1.2821 (11)
N1—C1	1.3603 (12)	O3—C13	1.2496 (11)
N1—H1	0.8600	C7—C8	1.4002 (13)
N2—C5	1.3285 (12)	C7—C12	1.4069 (12)
N2—H2A	0.8600	C8—C9	1.3901 (14)
N2—H2B	0.8600	C8—H8	0.9300
C1—C2	1.3662 (13)	C9—C10	1.3992 (14)
C1—H1A	0.9300	C9—H9	0.9300
C2—C3	1.4057 (13)	C10—C11	1.3846 (13)
C3—C4	1.3635 (13)	C10—H10	0.9300
C3—H3	0.9300	C11—C12	1.4012 (13)
C4—C5	1.4204 (12)	C11—H11	0.9300
C4—H4	0.9300	C12—C13	1.5001 (12)
O1—C7	1.3527 (11)		

C5—N1—C1	122.87 (8)	O1—C7—C8	117.84 (8)
C5—N1—H1	118.6	O1—C7—C12	122.33 (8)
C1—N1—H1	118.6	C8—C7—C12	119.81 (8)
C5—N2—H2A	120.0	C9—C8—C7	120.10 (8)
C5—N2—H2B	120.0	C9—C8—H8	119.9
H2A—N2—H2B	120.0	C7—C8—H8	119.9
N1—C1—C2	119.66 (8)	C8—C9—C10	120.45 (8)
N1—C1—H1A	120.2	C8—C9—H9	119.8
C2—C1—H1A	120.2	C10—C9—H9	119.8
C1—C2—C3	119.63 (8)	C11—C10—C9	119.39 (9)
C1—C2—C11	119.87 (7)	C11—C10—H10	120.3
C3—C2—C11	120.48 (7)	C9—C10—H10	120.3
C4—C3—C2	119.98 (8)	C10—C11—C12	121.20 (8)
C4—C3—H3	120.0	C10—C11—H11	119.4
C2—C3—H3	120.0	C12—C11—H11	119.4
C3—C4—C5	119.78 (8)	C11—C12—C7	119.03 (8)
C3—C4—H4	120.1	C11—C12—C13	119.80 (8)
C5—C4—H4	120.1	C7—C12—C13	121.11 (8)
N2—C5—N1	119.03 (8)	O3—C13—O2	123.67 (8)
N2—C5—C4	122.89 (8)	O3—C13—C12	119.32 (8)
N1—C5—C4	118.08 (8)	O2—C13—C12	117.00 (7)
C7—O1—H1B	109.5		
C5—N1—C1—C2	0.46 (14)	C8—C9—C10—C11	-0.61 (15)
N1—C1—C2—C3	-0.25 (14)	C9—C10—C11—C12	-0.31 (15)
N1—C1—C2—C11	-178.88 (7)	C10—C11—C12—C7	1.35 (14)
C1—C2—C3—C4	0.27 (14)	C10—C11—C12—C13	-175.67 (9)
C11—C2—C3—C4	178.89 (7)	O1—C7—C12—C11	179.72 (8)
C2—C3—C4—C5	-0.47 (14)	C8—C7—C12—C11	-1.48 (13)
C1—N1—C5—N2	179.07 (9)	O1—C7—C12—C13	-3.30 (14)
C1—N1—C5—C4	-0.64 (13)	C8—C7—C12—C13	175.51 (8)
C3—C4—C5—N2	-179.05 (9)	C11—C12—C13—O3	3.25 (13)
C3—C4—C5—N1	0.64 (13)	C7—C12—C13—O3	-173.71 (8)
O1—C7—C8—C9	179.44 (9)	C11—C12—C13—O2	-177.95 (8)
C12—C7—C8—C9	0.58 (14)	C7—C12—C13—O2	5.09 (13)
C7—C8—C9—C10	0.47 (15)		

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

Cg1 is the centroid of the C7—C12 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O2 ⁱ	0.86	1.83	2.6928 (10)	178.
O1—H1B \cdots O2	0.82	1.82	2.5483 (11)	147.
N2—H2A \cdots O3 ⁱ	0.86	1.96	2.8181 (11)	178.
N2—H2B \cdots O3 ⁱⁱ	0.86	2.03	2.8321 (13)	154.
C1—H1A \cdots Cg1 ⁱⁱⁱ	0.93	2.57	3.3680 (11)	144.

Symmetry codes: (i) $x, -y+3/2, z+1/2$; (ii) $-x+2, y+1/2, -z+1/2$; (iii) $x-1, y, z$.

Fig. 1

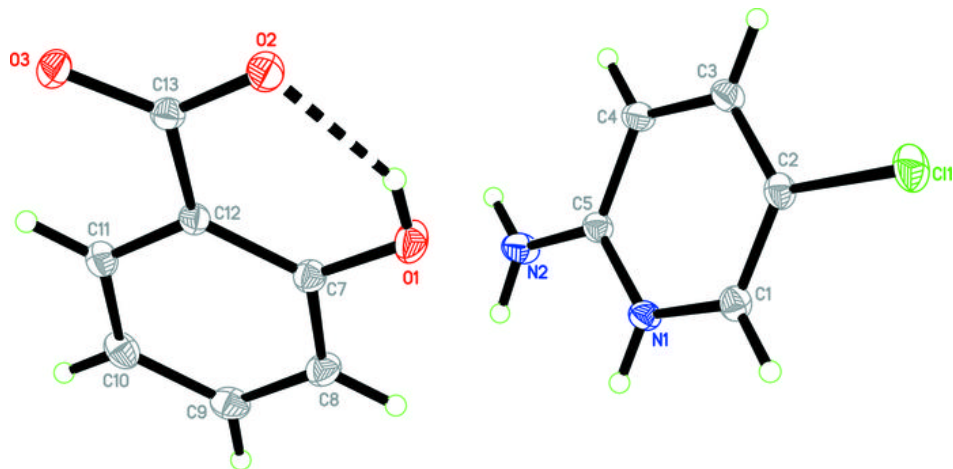


Fig. 2

