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2-Amino-5-methylpyridinium 2-hydroxybenzoate

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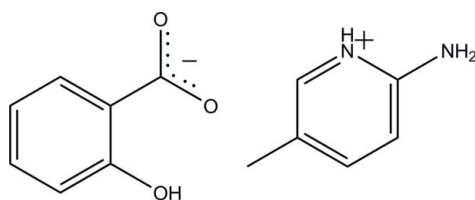
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Key indicators: single-crystal X-ray study; $T = 297$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.043; wR factor = 0.134; data-to-parameter ratio = 17.3.

In the title compound, $\text{C}_6\text{H}_9\text{N}_2^+\cdot\text{C}_7\text{H}_5\text{O}_3^-$, the protonated 2-amino-5-methylpyridinium cation and the 2-hydroxybenzoate anion are both essentially planar, with maximum deviations of 0.026 (2) and 0.034 (1) Å, respectively. The anion is stabilized by an intramolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond, which forms an $S(6)$ ring motif. In the solid state, the anions are linked to the cations *via* pairs of intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds forming $R_2^2(8)$ ring motifs. The crystal structure is further stabilized by $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ interactions which link the molecules into chains along [010]. A $\pi-\pi$ stacking interaction [centroid-centroid-distance = 3.740 (2) Å] is also observed.

Related literature

For background to and the applications of carboxylic acids, see: Miller & Orgel (1974); Kvenvolden *et al.* (1971); Desiraju (1989); MacDonald & Whitesides (1994). For applications of salicylic acid, see: Singh & Vijayan (1974); Patel *et al.* (1988). For related structures, see: Quah *et al.* (2008; 2010*a,b*). For bond-length data, see: Allen *et al.* (1987). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

 $\text{C}_6\text{H}_9\text{N}_2^+\cdot\text{C}_7\text{H}_5\text{O}_3^-$ $M_r = 246.26$

Monoclinic, $P2_1/c$
 $a = 13.211$ (7) Å
 $b = 7.170$ (4) Å
 $c = 14.324$ (7) Å
 $\beta = 104.668$ (11)°
 $V = 1312.6$ (12) Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.09$ mm⁻¹
 $T = 297$ K
 $0.42 \times 0.19 \times 0.10$ mm

Data collection

Bruker SMART APEXII DUO
 CCD area-detector
 diffractometer
 Absorption correction: multi-scan
 (SADABS; Bruker, 2009)
 $T_{\min} = 0.963$, $T_{\max} = 0.991$

14312 measured reflections
 3797 independent reflections
 2233 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.134$
 $S = 1.01$
 3797 reflections

219 parameters
 All H-atom parameters refined
 $\Delta\rho_{\text{max}} = 0.14$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.15$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{N1}-\text{H1N1}\cdots\text{O3}$ | 1.03 (2) | 1.65 (2) | 2.678 (2) | 174.6 (13) |
| $\text{N2}-\text{H1N2}\cdots\text{O2}^i$ | 0.884 (18) | 1.987 (17) | 2.852 (2) | 165.4 (14) |
| $\text{N2}-\text{H2N2}\cdots\text{O2}$ | 0.97 (2) | 1.90 (2) | 2.872 (2) | 179 (2) |
| $\text{O1}-\text{H1O1}\cdots\text{O3}$ | 1.03 (2) | 1.55 (2) | 2.515 (2) | 155 (2) |
| $\text{C5}-\text{H5A}\cdots\text{O1}^{ii}$ | 0.961 (14) | 2.598 (14) | 3.518 (3) | 160.2 (10) |

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

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: BT5314).

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supplementary materials

Acta Cryst. (2010). E66, o2255-o2256 [doi:10.1107/S1600536810030928]

2-Amino-5-methylpyridinium 2-hydroxybenzoate

C. K. Quah, M. Hemamalini and H.-K. Fun

Comment

Hydrogen bonding has been established as the most effective tool for constructing sophisticated assemblies because of its strength and directionality. Carboxylic acids are believed to have existed in the prebiotic earth (Miller & Orgel, 1974; Kvenvolden *et al.*, 1971) and they exhibit characteristic intermolecular interactions and aggregation patterns. Also carboxyl groups have been used as primary building blocks in the design of crystal structures (Desiraju, 1989; MacDonald & Whitesides, 1994). Salicylic acid, a well known analgesic, and its complexes with a few drug molecules such as antipyrine (Singh & Vijayan, 1974) and sulfadimidine (Patel *et al.*, 1988) were already reported in the literature. The present study is aimed at investigating the supramolecular interactions of the title compound, (I).

The asymmetric unit of title compound (Fig. 1), contains a protonated 2-amino-5-methylpyridinium cation and a 2-hydroxybenzoate anion. In the 2-amino-5-methylpyridinium cation, a wide angle [122.26 (13)°] is subtended at the protonated N1 atom. The 2-amino-5-methylpyridinium cation and 2-hydroxybenzoate anion are essentially planar, with a maximum deviation of 0.026 (2) Å for atom C6 and 0.034 (1) Å for atom O3, respectively. The dihedral angle between these two planes is 4.78 (5)°, indicating they are nearly parallel to each other. The anion is stabilized by an intramolecular O1–H1O1···O3 hydrogen bond, which forms an S(6) ring motif (Bernstein *et al.*, 1995).

In the solid state (Fig. 2), the anions are linked to the cations *via* intermolecular N1–H1N1···O3 and N2–H2N2···O2 hydrogen bonds forming $R_2^2(8)$ ring motifs. The crystal structure is further stabilized by N2–H1N2···O2 and C5–H5A···O1 interactions. The molecules are linked by these interactions into chains along [010]. π – π stacking interactions with short intermolecular distance [3.740 (2) Å] between symmetry-related N1/C1—C5 (centroid Cg1) and C7—C12 (centroid Cg2) [symmetry code: $x, 1 + y, z$] are also observed.

Experimental

A hot methanol solution (20 ml) of 2-amino-5-methylpyridine (54 mg, Aldrich) and salicylic acid (34.5 mg, Merck) was 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 H atoms were located in a difference Fourier map and refined freely.

Figures

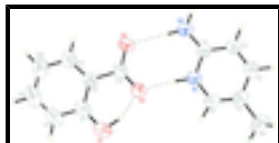


Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids for non-H atoms and the atom-numbering scheme. Intramolecular interactions are shown in dashed lines.

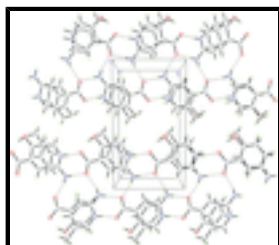
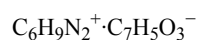


Fig. 2. The crystal structure of the title compound viewed along the *c* axis.

2-Amino-5-methylpyridinium 2-hydroxybenzoate

Crystal data



$$M_r = 246.26$$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$$a = 13.211 (7) \text{ \AA}$$

$$b = 7.170 (4) \text{ \AA}$$

$$c = 14.324 (7) \text{ \AA}$$

$$\beta = 104.668 (11)^\circ$$

$$V = 1312.6 (12) \text{ \AA}^3$$

$$Z = 4$$

$$F(000) = 520$$

$$D_x = 1.246 \text{ Mg m}^{-3}$$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 3026 reflections

$$\theta = 3.2\text{--}26.8^\circ$$

$$\mu = 0.09 \text{ mm}^{-1}$$

$$T = 297 \text{ K}$$

Block, yellow

$$0.42 \times 0.19 \times 0.10 \text{ mm}$$

Data collection

Bruker SMART APEXII DUO CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

graphite

φ and ω scans

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

$$T_{\min} = 0.963, T_{\max} = 0.991$$

14312 measured reflections

3797 independent reflections

2233 reflections with $I > 2\sigma(I)$

$$R_{\text{int}} = 0.028$$

$$\theta_{\max} = 30.0^\circ, \theta_{\min} = 2.9^\circ$$

$$h = -18 \rightarrow 18$$

$$k = -10 \rightarrow 10$$

$$l = -20 \rightarrow 19$$

Refinement

Refinement on F^2

Least-squares matrix: full

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

| | |
|---------------------------------|--|
| $R[F^2 > 2\sigma(F^2)] = 0.043$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.134$ | All H-atom parameters refined |
| $S = 1.01$ | $w = 1/[\sigma^2(F_o^2) + (0.0607P)^2 + 0.0959P]$ |
| 3797 reflections | where $P = (F_o^2 + 2F_c^2)/3$ |
| 219 parameters | $(\Delta/\sigma)_{\max} < 0.001$ |
| 0 restraints | $\Delta\rho_{\max} = 0.14 \text{ e } \text{\AA}^{-3}$ |
| | $\Delta\rho_{\min} = -0.15 \text{ e } \text{\AA}^{-3}$ |

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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| N1 | 0.25056 (7) | 0.79968 (17) | 0.30963 (8) | 0.0491 (3) |
| N2 | 0.07534 (9) | 0.7373 (2) | 0.28908 (10) | 0.0664 (4) |
| C1 | 0.15649 (8) | 0.84904 (19) | 0.32288 (9) | 0.0485 (3) |
| C2 | 0.15072 (10) | 1.0168 (2) | 0.37198 (9) | 0.0542 (3) |
| C3 | 0.23752 (10) | 1.1242 (2) | 0.40264 (10) | 0.0561 (3) |
| C4 | 0.33511 (10) | 1.0709 (2) | 0.38749 (9) | 0.0544 (3) |
| C5 | 0.33759 (9) | 0.9075 (2) | 0.34103 (9) | 0.0523 (3) |
| C6 | 0.43050 (14) | 1.1912 (3) | 0.41915 (16) | 0.0791 (5) |
| O1 | 0.40974 (7) | 0.27586 (19) | 0.17167 (9) | 0.0806 (4) |
| O2 | 0.10956 (7) | 0.41138 (14) | 0.18462 (8) | 0.0703 (3) |
| O3 | 0.27788 (7) | 0.48394 (15) | 0.21915 (9) | 0.0710 (3) |
| C7 | 0.32912 (10) | 0.1574 (2) | 0.13606 (10) | 0.0581 (4) |
| C8 | 0.35051 (15) | -0.0109 (3) | 0.09641 (12) | 0.0760 (5) |
| C9 | 0.27204 (17) | -0.1348 (3) | 0.05976 (13) | 0.0830 (5) |
| C10 | 0.17009 (17) | -0.0959 (3) | 0.06012 (13) | 0.0799 (5) |
| C11 | 0.14807 (12) | 0.0712 (2) | 0.09921 (11) | 0.0635 (4) |
| C12 | 0.22624 (9) | 0.19952 (19) | 0.13827 (9) | 0.0494 (3) |
| C13 | 0.20156 (9) | 0.37630 (19) | 0.18311 (10) | 0.0529 (3) |
| H2A | 0.0850 (11) | 1.050 (2) | 0.3827 (10) | 0.067 (4)* |
| H3A | 0.2348 (12) | 1.246 (3) | 0.4373 (11) | 0.074 (5)* |
| H5A | 0.3970 (10) | 0.854 (2) | 0.3237 (9) | 0.053 (3)* |
| H6A | 0.4887 (16) | 1.146 (3) | 0.3935 (14) | 0.107 (7)* |
| H6B | 0.4150 (17) | 1.318 (4) | 0.3879 (17) | 0.131 (9)* |
| H6C | 0.4491 (16) | 1.208 (3) | 0.4862 (19) | 0.123 (8)* |

supplementary materials

| | | | | |
|------|-------------|------------|-------------|------------|
| H8A | 0.4216 (15) | -0.033 (3) | 0.1009 (13) | 0.097 (6)* |
| H9A | 0.2895 (14) | -0.256 (3) | 0.0343 (13) | 0.098 (6)* |
| H10A | 0.1156 (15) | -0.181 (3) | 0.0375 (14) | 0.102 (6)* |
| H11A | 0.0773 (12) | 0.101 (2) | 0.1003 (10) | 0.068 (4)* |
| H1N1 | 0.2564 (11) | 0.678 (3) | 0.2733 (11) | 0.073 (4)* |
| H1N2 | 0.0141 (13) | 0.771 (2) | 0.2980 (12) | 0.078 (5)* |
| H2N2 | 0.0862 (13) | 0.626 (3) | 0.2540 (13) | 0.087 (5)* |
| H1O1 | 0.3730 (16) | 0.382 (3) | 0.1984 (15) | 0.116 (7)* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|-------------|--------------|
| N1 | 0.0397 (5) | 0.0494 (7) | 0.0589 (6) | 0.0009 (5) | 0.0137 (4) | -0.0009 (5) |
| N2 | 0.0401 (5) | 0.0620 (9) | 0.0988 (9) | -0.0039 (5) | 0.0209 (6) | -0.0157 (7) |
| C1 | 0.0396 (5) | 0.0504 (8) | 0.0560 (7) | 0.0017 (5) | 0.0131 (5) | 0.0018 (6) |
| C2 | 0.0480 (6) | 0.0565 (9) | 0.0592 (7) | 0.0039 (6) | 0.0158 (6) | -0.0028 (6) |
| C3 | 0.0614 (7) | 0.0537 (9) | 0.0520 (7) | -0.0011 (7) | 0.0121 (6) | -0.0041 (7) |
| C4 | 0.0524 (7) | 0.0579 (9) | 0.0508 (7) | -0.0090 (6) | 0.0092 (5) | 0.0044 (6) |
| C5 | 0.0401 (6) | 0.0607 (9) | 0.0574 (7) | -0.0017 (6) | 0.0143 (5) | 0.0045 (7) |
| C6 | 0.0653 (9) | 0.0833 (14) | 0.0848 (12) | -0.0264 (10) | 0.0118 (9) | -0.0071 (11) |
| O1 | 0.0495 (5) | 0.0882 (9) | 0.1105 (9) | 0.0064 (5) | 0.0323 (5) | -0.0146 (7) |
| O2 | 0.0473 (5) | 0.0544 (7) | 0.1169 (8) | 0.0028 (4) | 0.0349 (5) | -0.0095 (6) |
| O3 | 0.0502 (5) | 0.0530 (6) | 0.1159 (8) | -0.0031 (5) | 0.0324 (5) | -0.0166 (6) |
| C7 | 0.0549 (7) | 0.0635 (10) | 0.0597 (7) | 0.0154 (7) | 0.0216 (6) | 0.0049 (7) |
| C8 | 0.0784 (10) | 0.0775 (13) | 0.0775 (10) | 0.0292 (10) | 0.0297 (8) | -0.0028 (9) |
| C9 | 0.1128 (15) | 0.0655 (12) | 0.0739 (10) | 0.0248 (11) | 0.0296 (10) | -0.0121 (9) |
| C10 | 0.0967 (13) | 0.0645 (12) | 0.0772 (11) | -0.0022 (10) | 0.0198 (9) | -0.0197 (9) |
| C11 | 0.0634 (8) | 0.0604 (10) | 0.0672 (9) | 0.0032 (7) | 0.0177 (7) | -0.0063 (7) |
| C12 | 0.0505 (6) | 0.0480 (8) | 0.0521 (6) | 0.0086 (6) | 0.0176 (5) | 0.0059 (6) |
| C13 | 0.0471 (6) | 0.0451 (8) | 0.0719 (8) | 0.0040 (6) | 0.0252 (6) | 0.0047 (7) |

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

| | | | |
|---------|-------------|----------|-------------|
| N1—C1 | 1.3510 (15) | C6—H6C | 0.94 (3) |
| N1—C5 | 1.3638 (17) | O1—C7 | 1.3567 (19) |
| N1—H1N1 | 1.030 (18) | O1—H1O1 | 1.03 (2) |
| N2—C1 | 1.3279 (18) | O2—C13 | 1.2467 (15) |
| N2—H1N2 | 0.884 (18) | O3—C13 | 1.2710 (16) |
| N2—H2N2 | 0.97 (2) | C7—C8 | 1.393 (2) |
| C1—C2 | 1.405 (2) | C7—C12 | 1.4006 (18) |
| C2—C3 | 1.359 (2) | C8—C9 | 1.365 (3) |
| C2—H2A | 0.950 (15) | C8—H8A | 0.938 (19) |
| C3—C4 | 1.413 (2) | C9—C10 | 1.377 (3) |
| C3—H3A | 1.011 (18) | C9—H9A | 0.99 (2) |
| C4—C5 | 1.352 (2) | C10—C11 | 1.384 (2) |
| C4—C6 | 1.500 (2) | C10—H10A | 0.94 (2) |
| C5—H5A | 0.960 (13) | C11—C12 | 1.391 (2) |
| C6—H6A | 0.99 (2) | C11—H11A | 0.962 (15) |
| C6—H6B | 1.01 (3) | C12—C13 | 1.494 (2) |

| | | | |
|--------------|--------------|-----------------|--------------|
| C1—N1—C5 | 122.26 (13) | H6A—C6—H6C | 113.4 (17) |
| C1—N1—H1N1 | 118.8 (8) | H6B—C6—H6C | 108 (2) |
| C5—N1—H1N1 | 118.9 (8) | C7—O1—H1O1 | 101.7 (11) |
| C1—N2—H1N2 | 117.6 (11) | O1—C7—C8 | 118.34 (13) |
| C1—N2—H2N2 | 118.2 (10) | O1—C7—C12 | 122.04 (13) |
| H1N2—N2—H2N2 | 124.1 (15) | C8—C7—C12 | 119.62 (15) |
| N2—C1—N1 | 118.50 (13) | C9—C8—C7 | 120.52 (16) |
| N2—C1—C2 | 123.91 (12) | C9—C8—H8A | 124.5 (13) |
| N1—C1—C2 | 117.58 (11) | C7—C8—H8A | 114.8 (13) |
| C3—C2—C1 | 119.91 (12) | C8—C9—C10 | 121.02 (18) |
| C3—C2—H2A | 122.5 (9) | C8—C9—H9A | 119.2 (11) |
| C1—C2—H2A | 117.6 (9) | C10—C9—H9A | 119.8 (11) |
| C2—C3—C4 | 121.70 (14) | C9—C10—C11 | 118.87 (18) |
| C2—C3—H3A | 121.2 (9) | C9—C10—H10A | 122.2 (13) |
| C4—C3—H3A | 117.1 (9) | C11—C10—H10A | 118.9 (13) |
| C5—C4—C3 | 116.52 (12) | C10—C11—C12 | 121.65 (15) |
| C5—C4—C6 | 121.61 (14) | C10—C11—H11A | 120.0 (10) |
| C3—C4—C6 | 121.86 (16) | C12—C11—H11A | 118.3 (9) |
| C4—C5—N1 | 122.02 (12) | C11—C12—C7 | 118.32 (13) |
| C4—C5—H5A | 126.5 (8) | C11—C12—C13 | 120.92 (12) |
| N1—C5—H5A | 111.4 (8) | C7—C12—C13 | 120.75 (12) |
| C4—C6—H6A | 111.8 (13) | O2—C13—O3 | 123.17 (13) |
| C4—C6—H6B | 108.9 (13) | O2—C13—C12 | 119.90 (12) |
| H6A—C6—H6B | 102.8 (18) | O3—C13—C12 | 116.93 (11) |
| C4—C6—H6C | 111.5 (14) | | |
| C5—N1—C1—N2 | 179.21 (12) | C8—C9—C10—C11 | -0.5 (3) |
| C5—N1—C1—C2 | -0.82 (18) | C9—C10—C11—C12 | -0.3 (3) |
| N2—C1—C2—C3 | -178.87 (13) | C10—C11—C12—C7 | 1.0 (2) |
| N1—C1—C2—C3 | 1.16 (19) | C10—C11—C12—C13 | -177.95 (14) |
| C1—C2—C3—C4 | -0.7 (2) | O1—C7—C12—C11 | 179.29 (13) |
| C2—C3—C4—C5 | -0.1 (2) | C8—C7—C12—C11 | -0.8 (2) |
| C2—C3—C4—C6 | 178.54 (15) | O1—C7—C12—C13 | -1.8 (2) |
| C3—C4—C5—N1 | 0.46 (19) | C8—C7—C12—C13 | 178.09 (13) |
| C6—C4—C5—N1 | -178.17 (14) | C11—C12—C13—O2 | -1.0 (2) |
| C1—N1—C5—C4 | 0.00 (19) | C7—C12—C13—O2 | -179.86 (12) |
| O1—C7—C8—C9 | 179.92 (15) | C11—C12—C13—O3 | 178.39 (13) |
| C12—C7—C8—C9 | 0.0 (2) | C7—C12—C13—O3 | -0.49 (19) |
| C7—C8—C9—C10 | 0.7 (3) | | |

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|----------------------------------|------------|-------------|-------------|---------------|
| N1—H1N1 \cdots O3 | 1.03 (2) | 1.65 (2) | 2.678 (2) | 174.6 (13) |
| N2—H1N2 \cdots O2 ⁱ | 0.884 (18) | 1.987 (17) | 2.852 (2) | 165.4 (14) |
| N2—H2N2 \cdots O2 | 0.97 (2) | 1.90 (2) | 2.872 (2) | 179 (2) |
| O1—H1O1 \cdots O3 | 1.03 (2) | 1.55 (2) | 2.515 (2) | 155 (2) |
| C5—H5A \cdots O1 ⁱⁱ | 0.961 (14) | 2.598 (14) | 3.518 (3) | 160.2 (10) |

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

Fig. 1

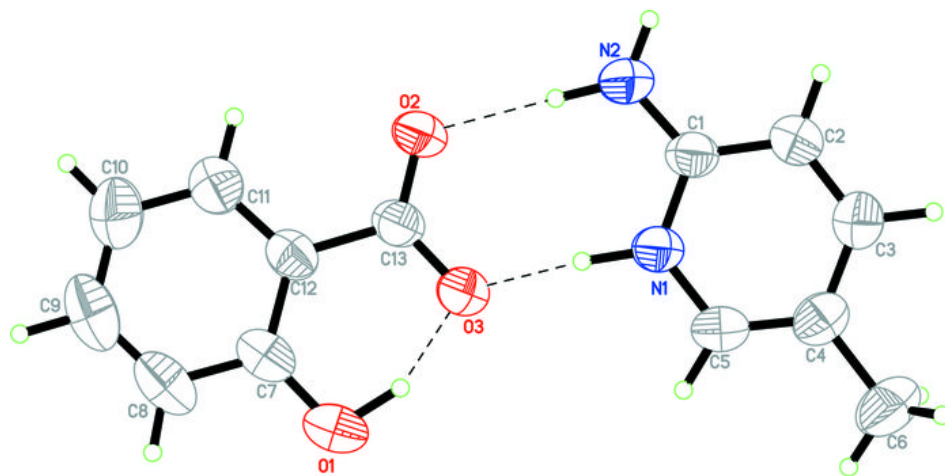


Fig. 2

