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2-Amino-5-bromopyridinium trifluoroacetate

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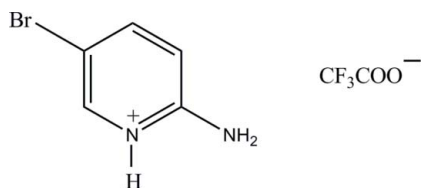
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; disorder in main residue; R factor = 0.039; wR factor = 0.099; data-to-parameter ratio = 16.5.

In the title compound, $\text{C}_5\text{H}_6\text{BrN}_2^+ \cdot \text{C}_2\text{F}_3\text{O}_2^-$, the F atoms of the anion are disordered over two sets of sites, with occupancies of 0.59 (2):0.41 (2). In the crystal structure, the anions and cations are linked into a two-dimensional network parallel to (100) by $\text{N}-\text{H} \cdots \text{O}$ and $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds. Within this network, the $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds generate $R_2^2(8)$ ring motifs.

Related literature

For background to the chemistry of substituted pyridines, see: Pozharski *et al.* (1997); Katritzky *et al.* (1996). For related structures, see: Goubitz *et al.* (2001); Vaday & Foxman (1999). For details of hydrogen bonding, see: Jeffrey & Saenger (1991); Jeffrey (1997); Scheiner (1997). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$\text{C}_5\text{H}_6\text{BrN}_2^+ \cdot \text{C}_2\text{F}_3\text{O}_2^-$
 $M_r = 287.05$
Orthorhombic, $Pna2_1$
 $a = 17.5852$ (13) Å
 $b = 11.3010$ (9) Å
 $c = 5.1264$ (4) Å
 $V = 1018.77$ (14) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 4.06$ mm⁻¹
 $T = 296$ K
 $0.73 \times 0.41 \times 0.09$ mm

Data collection

Bruker SMART APEXII CCD
area-detector diffractometer
Absorption correction: multi-scan
(*SADABS*; Bruker, 2009)
 $T_{\min} = 0.156$, $T_{\max} = 0.709$
8343 measured reflections
2899 independent reflections
1547 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.056$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.099$
 $S = 0.93$
2899 reflections
176 parameters
56 restraints
H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.46$ e Å⁻³
 $\Delta\rho_{\min} = -0.28$ e Å⁻³
Absolute structure: Flack (1983),
1254 Friedel pairs
Flack parameter: 0.024 (12)

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

| $D-\text{H} \cdots A$ | $D-\text{H}$ | $\text{H} \cdots A$ | $D \cdots A$ | $D-\text{H} \cdots A$ |
|---|--------------|---------------------|--------------|-----------------------|
| $\text{N1}-\text{H1N1} \cdots \text{O1}^i$ | 0.93 (3) | 1.80 (3) | 2.720 (5) | 171 (3) |
| $\text{N2}-\text{H1N2} \cdots \text{O1}^{ii}$ | 0.83 (4) | 2.05 (4) | 2.870 (4) | 176 (5) |
| $\text{N2}-\text{H2N2} \cdots \text{O2}^i$ | 0.83 (4) | 2.03 (4) | 2.849 (5) | 170 (4) |
| $\text{C1}-\text{H1A} \cdots \text{O2}^{iii}$ | 0.93 | 2.34 | 3.245 (4) | 164 |

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

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: CI5042).

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supplementary materials

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2-Amino-5-bromopyridinium trifluoroacetate

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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-bond interactions (Jeffrey & Saenger, 1991; Jeffrey, 1997; Scheiner, 1997). The crystal structures of 2-amino-5-bromopyridine (Goubitz *et al.*, 2001) and 2-amino-5-bromopyridinium propynoate (Vaday & Foxman, 1999) have been reported. In order to study hydrogen bonding interactions, the title salt was prepared and its crystal structure is reported here.

The asymmetric unit of (I) (Fig. 1) contains one 2-amino-5-bromopyridinium cation and one trifluoroacetate anion, indicating that proton transfer has occurred during the co-crystallisation. The 2-amino-5-methylpyridinium cation is essentially planar, with a maximum deviation of 0.016 (4) Å for atom C1; As a result of protonation, the C1—N1—C5 angle is widened to 122.5 (4)°. The bond lengths and angles are normal (Allen *et al.*, 1987).

In the crystal packing (Fig. 2), the cations and anions are linked via N—H···O hydrogen bonds to form $R_2^2(8)$ ring motifs (Bernstein *et al.*, 1995). The ionic units are linked into a two-dimensional network parallel to the (100) by N—H···O and C—H···O hydrogen bonds (Table 1).

Experimental

To a hot methanol solution (20 ml) of 2-amino-5-bromopyridine (44 mg, Aldrich) was added a few drops of trifluoroacetic acid. The solution was warmed over a water bath for a few minutes. The resulting solution was allowed to cool slowly to room temperature. Crystals of the title compound appeared after a few days.

Refinement

Atoms H1N1, H1N2 and H2N2 were located in a difference Fourier map and refined; the N—H distances of the NH₂ group were restrained to be equal. The remaining H atoms were positioned geometrically [C—H = 0.93 Å] and were refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The F atoms of the anion are disordered over two positions with occupancies of 0.59 (2):0.41 (2). The C—F distances were restrained to be equal and the U^{ij} components of F atoms were restrained to an approximate isotropic behaviour.

Figures

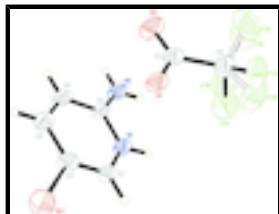


Fig. 1. The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 30% probability level. Both disorder components are shown.

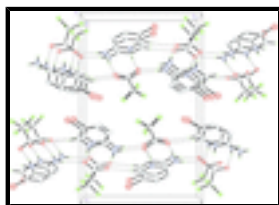
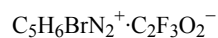


Fig. 2. The crystal packing of the title compound, showing hydrogen-bonded (dashed lines) networks.

2-Amino-5-bromopyridinium trifluoroacetate

Crystal data



$M_r = 287.05$

Orthorhombic, $Pna2_1$

Hall symbol: P 2c -2n

$a = 17.5852(13) \text{ \AA}$

$b = 11.3010(9) \text{ \AA}$

$c = 5.1264(4) \text{ \AA}$

$V = 1018.77(14) \text{ \AA}^3$

$Z = 4$

$F(000) = 560$

$D_x = 1.871 \text{ Mg m}^{-3}$

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

Cell parameters from 1994 reflections

$\theta = 2.9\text{--}22.5^\circ$

$\mu = 4.06 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Plate, colourless

$0.73 \times 0.41 \times 0.09 \text{ mm}$

Data collection

Bruker SMART APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

φ and ω scans

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

$T_{\min} = 0.156$, $T_{\max} = 0.709$

8343 measured reflections

2899 independent reflections

1547 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.056$

$\theta_{\max} = 30.1^\circ$, $\theta_{\min} = 2.1^\circ$

$h = -24 \rightarrow 24$

$k = -14 \rightarrow 15$

$l = -7 \rightarrow 7$

Refinement

Refinement on F^2

Least-squares matrix: full

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

$$R[F^2 > 2\sigma(F^2)] = 0.039$$

$$wR(F^2) = 0.099$$

$$S = 0.93$$

2899 reflections

176 parameters

56 restraints

Primary atom site location: structure-invariant direct methods

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0247P)^2]$$

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

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

$$\Delta\rho_{\max} = 0.46 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack (1983), 1254 Friedel pairs

Flack parameter: 0.024 (12)

Special details

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> | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|------|--------------|-------------|--------------|----------------------------------|-----------|
| Br1 | 0.93625 (2) | 0.38997 (4) | 0.26064 (12) | 0.0770 (2) | |
| N1 | 0.80785 (16) | 0.5888 (2) | 0.7575 (9) | 0.0462 (6) | |
| N2 | 0.7800 (2) | 0.7862 (3) | 0.8112 (8) | 0.0631 (11) | |
| C1 | 0.8432 (2) | 0.4973 (3) | 0.6357 (8) | 0.0489 (8) | |
| H1A | 0.8355 | 0.4204 | 0.6947 | 0.059* | |
| C2 | 0.8889 (2) | 0.5166 (4) | 0.4322 (8) | 0.0540 (9) | |
| C3 | 0.9016 (2) | 0.6353 (4) | 0.3492 (8) | 0.0585 (11) | |
| H3A | 0.9342 | 0.6507 | 0.2106 | 0.070* | |
| C4 | 0.8661 (2) | 0.7253 (4) | 0.4722 (8) | 0.0563 (10) | |
| H4A | 0.8743 | 0.8029 | 0.4183 | 0.068* | |
| C5 | 0.81681 (19) | 0.7018 (3) | 0.6821 (7) | 0.0474 (9) | |
| O1 | 0.70895 (14) | 0.5277 (2) | 0.1425 (6) | 0.0589 (7) | |
| O2 | 0.67948 (17) | 0.7148 (2) | 0.2175 (8) | 0.0751 (9) | |
| F1A | 0.6204 (5) | 0.5331 (17) | 0.6225 (16) | 0.120 (4) | 0.59 (2) |
| F2A | 0.5460 (5) | 0.6483 (7) | 0.419 (3) | 0.104 (3) | 0.59 (2) |
| F3A | 0.5673 (5) | 0.4758 (8) | 0.273 (3) | 0.095 (3) | 0.59 (2) |
| F1B | 0.5407 (6) | 0.6290 (16) | 0.294 (4) | 0.115 (5) | 0.41 (2) |
| F2B | 0.5819 (10) | 0.4561 (7) | 0.392 (4) | 0.105 (5) | 0.41 (2) |
| F3B | 0.6028 (10) | 0.6030 (19) | 0.6312 (19) | 0.113 (5) | 0.41 (2) |
| C6 | 0.5992 (2) | 0.5688 (3) | 0.3866 (8) | 0.0636 (11) | |
| C7 | 0.66887 (19) | 0.6091 (3) | 0.2336 (9) | 0.0510 (9) | |
| H1N1 | 0.7730 (19) | 0.576 (3) | 0.891 (7) | 0.041 (9)* | |

supplementary materials

| | | | | |
|------|-----------|-----------|------------|-------------|
| H1N2 | 0.785 (2) | 0.856 (3) | 0.767 (11) | 0.060 (11)* |
| H2N2 | 0.748 (2) | 0.773 (4) | 0.927 (7) | 0.067 (14)* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| Br1 | 0.0861 (3) | 0.0606 (3) | 0.0842 (3) | 0.0050 (2) | 0.0152 (3) | -0.0136 (3) |
| N1 | 0.0546 (15) | 0.0281 (14) | 0.0561 (15) | -0.0047 (11) | 0.002 (2) | -0.004 (2) |
| N2 | 0.085 (2) | 0.0291 (17) | 0.075 (3) | 0.0045 (18) | 0.014 (2) | 0.0079 (18) |
| C1 | 0.058 (2) | 0.0280 (18) | 0.061 (2) | -0.0045 (16) | -0.0053 (18) | -0.0018 (17) |
| C2 | 0.059 (2) | 0.040 (2) | 0.063 (2) | 0.0022 (17) | -0.0031 (18) | -0.0071 (18) |
| C3 | 0.061 (2) | 0.054 (3) | 0.061 (3) | -0.007 (2) | 0.0016 (18) | 0.0057 (19) |
| C4 | 0.067 (2) | 0.037 (2) | 0.064 (2) | -0.0068 (19) | -0.004 (2) | 0.013 (2) |
| C5 | 0.0519 (18) | 0.0322 (19) | 0.058 (2) | -0.0045 (16) | -0.0059 (16) | 0.0088 (16) |
| O1 | 0.0679 (15) | 0.0319 (14) | 0.0768 (16) | 0.0077 (12) | 0.0135 (14) | 0.0109 (13) |
| O2 | 0.0987 (19) | 0.0303 (14) | 0.096 (3) | 0.0012 (13) | 0.0185 (18) | 0.0044 (18) |
| F1A | 0.115 (5) | 0.166 (9) | 0.078 (4) | -0.013 (5) | 0.011 (3) | 0.046 (5) |
| F2A | 0.093 (4) | 0.080 (4) | 0.139 (8) | 0.018 (3) | 0.040 (4) | -0.019 (4) |
| F3A | 0.083 (3) | 0.082 (4) | 0.119 (6) | -0.036 (3) | 0.008 (4) | -0.011 (5) |
| F1B | 0.069 (5) | 0.143 (8) | 0.132 (9) | 0.030 (5) | 0.009 (6) | -0.004 (7) |
| F2B | 0.119 (7) | 0.062 (6) | 0.133 (9) | -0.011 (5) | 0.047 (7) | -0.001 (5) |
| F3B | 0.130 (8) | 0.121 (9) | 0.088 (6) | -0.024 (6) | 0.036 (5) | -0.009 (6) |
| C6 | 0.065 (3) | 0.045 (2) | 0.080 (3) | 0.002 (2) | 0.005 (2) | -0.007 (2) |
| C7 | 0.062 (2) | 0.037 (2) | 0.054 (2) | 0.0022 (16) | -0.005 (2) | 0.001 (2) |

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

| | | | |
|--------------|-----------|------------|------------|
| Br1—C2 | 1.875 (4) | C4—C5 | 1.407 (5) |
| N1—C5 | 1.344 (4) | C4—H4A | 0.93 |
| N1—C1 | 1.358 (5) | O1—C7 | 1.250 (4) |
| N1—H1N1 | 0.93 (4) | O2—C7 | 1.212 (4) |
| N2—C5 | 1.330 (5) | F1A—C6 | 1.329 (6) |
| N2—H1N2 | 0.82 (3) | F2A—C6 | 1.307 (6) |
| N2—H2N2 | 0.84 (3) | F3A—C6 | 1.327 (6) |
| C1—C2 | 1.334 (5) | F1B—C6 | 1.321 (7) |
| C1—H1A | 0.93 | F2B—C6 | 1.310 (7) |
| C2—C3 | 1.425 (6) | F3B—C6 | 1.314 (7) |
| C3—C4 | 1.349 (6) | C6—C7 | 1.524 (6) |
| C3—H3A | 0.93 | | |
| C5—N1—C1 | 122.5 (4) | N2—C5—N1 | 118.8 (3) |
| C5—N1—H1N1 | 116 (2) | N2—C5—C4 | 123.0 (4) |
| C1—N1—H1N1 | 121 (2) | N1—C5—C4 | 118.1 (4) |
| C5—N2—H1N2 | 120 (4) | F2B—C6—F3B | 106.2 (8) |
| C5—N2—H2N2 | 124 (3) | F2B—C6—F1B | 109.0 (10) |
| H1N2—N2—H2N2 | 116 (5) | F3B—C6—F1B | 103.2 (9) |
| C2—C1—N1 | 120.7 (4) | F2A—C6—F3A | 107.3 (7) |
| C2—C1—H1A | 119.6 | F2A—C6—F1A | 107.2 (6) |
| N1—C1—H1A | 119.6 | F3A—C6—F1A | 106.1 (6) |

| | | | |
|--------------|------------|--------------|-------------|
| C1—C2—C3 | 118.8 (4) | F2A—C6—C7 | 115.8 (6) |
| C1—C2—Br1 | 120.6 (3) | F2B—C6—C7 | 119.1 (7) |
| C3—C2—Br1 | 120.6 (3) | F3B—C6—C7 | 111.4 (7) |
| C4—C3—C2 | 119.8 (4) | F1B—C6—C7 | 106.8 (8) |
| C4—C3—H3A | 120.1 | F3A—C6—C7 | 110.4 (6) |
| C2—C3—H3A | 120.1 | F1A—C6—C7 | 109.5 (5) |
| C3—C4—C5 | 120.0 (4) | O2—C7—O1 | 127.8 (4) |
| C3—C4—H4A | 120.0 | O2—C7—C6 | 116.9 (4) |
| C5—C4—H4A | 120.0 | O1—C7—C6 | 115.2 (3) |
| C5—N1—C1—C2 | -0.2 (6) | F2B—C6—C7—O2 | 174.5 (14) |
| N1—C1—C2—C3 | 1.7 (5) | F3B—C6—C7—O2 | -61.4 (13) |
| N1—C1—C2—Br1 | -178.9 (3) | F1B—C6—C7—O2 | 50.6 (12) |
| C1—C2—C3—C4 | -1.6 (6) | F3A—C6—C7—O2 | 142.0 (8) |
| Br1—C2—C3—C4 | 179.0 (3) | F1A—C6—C7—O2 | -101.5 (10) |
| C2—C3—C4—C5 | 0.1 (6) | F2A—C6—C7—O1 | -161.2 (9) |
| C1—N1—C5—N2 | 179.8 (3) | F2B—C6—C7—O1 | -6.5 (14) |
| C1—N1—C5—C4 | -1.4 (6) | F3B—C6—C7—O1 | 117.6 (12) |
| C3—C4—C5—N2 | -179.8 (4) | F1B—C6—C7—O1 | -130.4 (12) |
| C3—C4—C5—N1 | 1.4 (5) | F3A—C6—C7—O1 | -39.0 (8) |
| F2A—C6—C7—O2 | 19.8 (10) | F1A—C6—C7—O1 | 77.5 (10) |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|-----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N1—H1N1 \cdots O1 ⁱ | 0.93 (3) | 1.80 (3) | 2.720 (5) | 171 (3) |
| N2—H1N2 \cdots O1 ⁱⁱ | 0.83 (4) | 2.05 (4) | 2.870 (4) | 176 (5) |
| N2—H2N2 \cdots O2 ⁱ | 0.83 (4) | 2.03 (4) | 2.849 (5) | 170 (4) |
| C1—H1A \cdots O2 ⁱⁱⁱ | 0.93 | 2.34 | 3.245 (4) | 164 |

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

Fig. 1

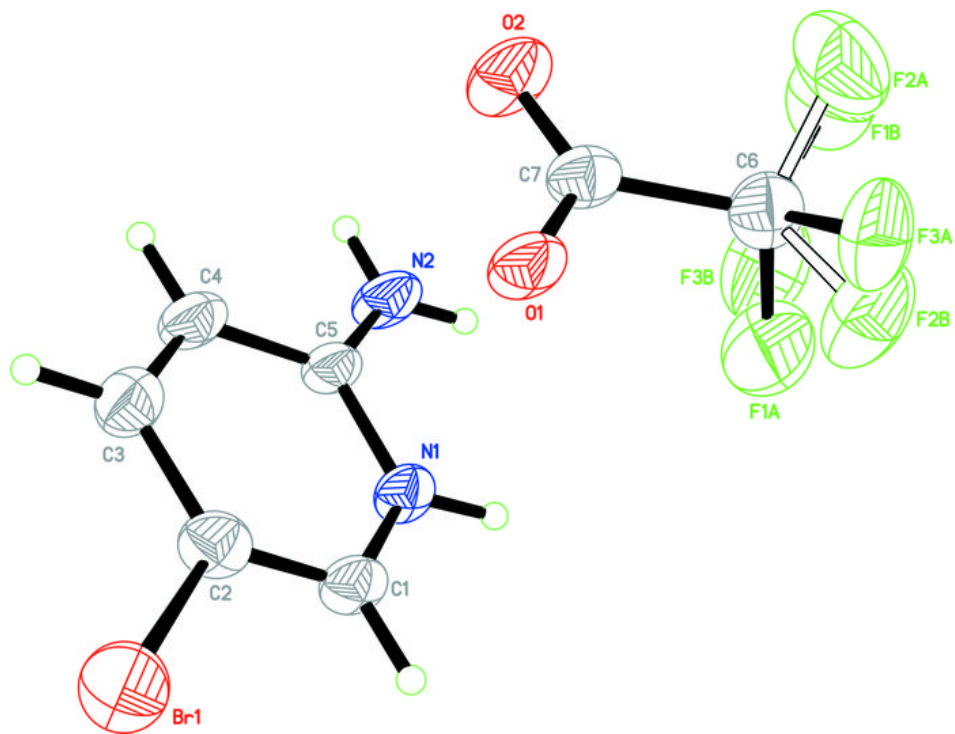


Fig. 2

