Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Piperazinediium pyridine-2,5-dicarboxylate dihydrate

Shabnam Sheshmani,[a] Hossein Aghabozorg[b]* and Mohammad Ghadermazi[c]

[a]Department of Chemistry, Islamic Azad University, Shahr-e Rey Branch, Tehran, Iran, [b]Department of Chemistry, Teacher Training University, Tehran, Iran, and [c]Department of Chemistry, Faculty of Science, Kurdistan University, Sanandaj, Iran
Correspondence e-mail: haghabozorg@yahoo.com

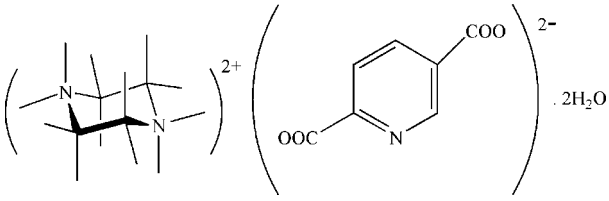
Received 24 April 2007; accepted 1 May 2007

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.038; wR factor = 0.114; data-to-parameter ratio = 17.7.

In the title compound, $C_4H_{12}N_2^{2+}\cdot C_7H_3NO_4^{2-}\cdot 2H_2O$, intermolecular N—H···O and O—H···O hydrogen bonds and C—H···π interactions between piperazinediium and the aromatic ring of pyridine-2,5-dicarboxylate are responsible for extending the structure into a three-dimensional supramolecular network.

Related literature

For general background, see: Aghabozorg *et al.* (2006); Moghimi *et al.* (2005); Sheshmani *et al.* (2006); Allen *et al.* (1987); Cremer & Pople (1975).



Experimental

Crystal data

$C_4H_{12}N_2^{2+}\cdot C_7H_3NO_4^{2-}\cdot 2H_2O$
M_r = 289.29
Triclinic, $P\overline{1}$
a = 7.0673 (6) Å
b = 9.9909 (9) Å
c = 11.2827 (10) Å
α = 64.181 (2)°
β = 77.479 (2)°
γ = 69.794 (2)°
V = 670.92 (10) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 100 (2) K
0.24 × 0.22 × 0.19 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.971, T_{max} = 0.976
6675 measured reflections
3200 independent reflections
2716 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.114
S = 0.99
3200 reflections
181 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2*NA*···O3^{i}	0.87	1.82	2.686 (2)	173
N2—H2*NB*···O1*S*	0.87	1.86	2.719 (1)	169
N3—H3*NA*···O1^{ii}	0.87	1.87	2.736 (2)	174
N3—H3*NB*···O4^{iii}	0.87	1.91	2.770 (1)	168
O1*S*—H1*SA*···O2*S*	0.82	1.89	2.701 (2)	172
O1*S*—H1*SB*···O2	0.82	1.94	2.735 (1)	164
O2*S*—H2*SB*···O2^{ii}	0.82	1.92	2.709 (1)	161
O2*S*—H2*SA*···O3^{iv}	0.82	1.98	2.730 (2)	152

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

Data collection: *APEXII* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2005); software used to prepare material for publication: *SHELXTL*.

We are grateful to Islamic Azad University, Shahr-e Rey Branch, for financial support of this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2240).

References

Aghabozorg, H., Ghadermazi, M. & Sadr Khanlou, E. (2006). *Anal. Sci.* **22**, x253–x254.
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.
Bruker (2005). *APEXII* (Version 2.0-1), *SAINT* (Version 7.23A), *SADABS* (Version 2004/1) and *SHELXTL* (Version 6.1). Bruker AXS Inc., Madison, Wisconsin, USA.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Moghimi, A., Sheshmani, S., Shokrollahi, A., Shamsipur, M., Kickelbick, G. & Aghabozorg, H. (2005). *Z. Anorg. Allg. Chem.* **631**, 160–169.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheshmani, S., Ghadermazi, M. & Aghabozorg, H. (2006). *Acta Cryst.* E**62**, o3620–o3622.

supplementary materials

Acta Cryst. (2007). E**63**, o2869 [**doi:10.1107/S1600536807021538**]

Piperazinediium pyridine-2,5-dicarboxylate dihydrate

S. Sheshmani, H. Aghabozorg and M. Ghadermazi

Comment

Proton transfer is highly important in physics, chemistry and biochemistry. In order to develop new types of proton transfer compounds and hydrogen bonding systems, our research group has already synthesized proton transfer compounds with different proton donors and acceptors (Aghabozorg *et al.*, 2006; Moghimi *et al.*, 2005; Sheshmani *et al.*, 2006). We herein report the crystal structure of the title compound, (I).

The molecule of the title compound, (I), contains one cation, one anion and also two water molecules (Fig. 1). The bond lengths and angles are within normal ranges (Allen *et al.*, 1987). The piperazine ring: A (N2/N3/C8—C11) is not planar, having total puckering amplitude, Q_T of 1.104 (3) Å and chair conformation [φ = -151.67 (4)°, θ = 122.13 (3)°] (Cremer & Pople, 1975).

In the title compound, protons from one carboxylic acid unit are transferred to N atoms of the piperazine. The non-covalent interactions have an important role in self-association of the crystal system. As can be seen from the packing diagram (Fig. 2), the intermolecular N—H···O and O—H···O hydrogen bonds (Table 1) and C—H···π interactions between piperazinediium and aromatic ring of pyridine-2,5-dicarboxylate (Fig. 3) are responsible for extending the structure into three dimension resulting in a supramolecular network.

Experimental

The title compound was synthesized by a reaction between pyridine-2,5-dicarboxylic acid (2,5-pydcH_2) and piperazine (pipz) in a 1:1 molar ratio. A solution of pipz (430 mg, 5 mmol) in tetrahydrofuran (10 ml) was added to a solution of 2,5-pydcH_2 (835 mg, 5 mmol) in tetrahydrofuran (10 ml). The resulting powder was dissolved in water to give colorless crystals of (I) (yield; 80%).

Refinement

H atoms were positioned geometrically, with O—H = 0.82 Å (for OH_2), N—H = 0.87 Å (for NH_2) and C—H = 0.95 and 0.99 Å for aromatic and methylene H, respectively, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C,O,N)$.

Figures

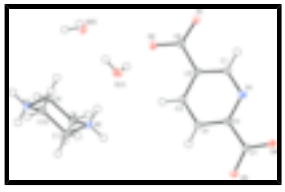


Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

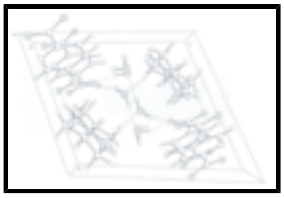


Fig. 2. A packing diagram for (I). Hydrogen bonds are shown as dashed lines.

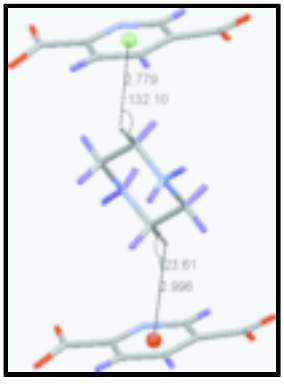


Fig. 3. Intermolecular C—H···π interaction between piperazinediium and aromatic ring of pyridine-2,5-dicarboxylate.

Piperazinediium pyridine-2,5-dicarboxylate dihydrate

Crystal data

$C_4H_{12}N_2^{2+}·C_7H_3NO_4^{2-}·2H_2O$	$Z = 2$
$M_r = 289.29$	$F_{000} = 308$
Triclinic, $P\overline{1}$	$D_x = 1.432$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 7.0673$ (6) Å	Cell parameters from 189 reflections
$b = 9.9909$ (9) Å	$\theta = 3$–28º
$c = 11.2827$ (10) Å	$\mu = 0.12$ mm^{-1}
$\alpha = 64.181$ (2)º	$T = 100$ (2) K
$\beta = 77.479$ (2)º	Prism, colorless
$\gamma = 69.794$ (2)º	0.24 × 0.22 × 0.19 mm
$V = 670.92$ (10) Å^3	

Data collection

Bruker APEXII CCD area-detector diffractometer	3200 independent reflections
Radiation source: fine-focus sealed tube	2716 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.022$
$T = 100(2)$ K	$\theta_{max} = 28.0$º
ω scans	$\theta_{min} = 2.0$º
Absorption correction: multi-scan (SADABS; Bruker, 2005)	$h = -9 \rightarrow 9$
$T_{min} = 0.971$, $T_{max} = 0.976$	$k = -13 \rightarrow 13$
6675 measured reflections	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

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

$wR(F^2) = 0.114$

$S = 0.99$

3200 reflections

181 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0683P)^2 + 0.2024P]$ where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.41$ e Å^{-3}

$\Delta\rho_{min} = -0.31$ e Å^{-3}

Extinction correction: none

Special details

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.72069 (13)	0.42146 (11)	0.10061 (9)	0.0179 (2)
O2	0.68360 (13)	0.35887 (10)	0.31757 (9)	0.0172 (2)
O3	1.71752 (12)	−0.03466 (10)	0.33147 (8)	0.0153 (2)
O4	1.74763 (13)	0.08585 (10)	0.11263 (9)	0.0181 (2)
N1	1.33832 (15)	0.21315 (12)	0.10751 (10)	0.0139 (2)
C1	1.13793 (18)	0.27830 (14)	0.10828 (12)	0.0138 (2)
H1A	1.0800	0.3353	0.0257	0.017*
C2	1.00909 (17)	0.26795 (13)	0.22219 (12)	0.0122 (2)
C3	1.09484 (18)	0.18307 (14)	0.34258 (12)	0.0140 (2)
H3A	1.0123	0.1716	0.4230	0.017*
C4	1.30236 (18)	0.11520 (13)	0.34412 (12)	0.0138 (2)
H4A	1.3640	0.0576	0.4254	0.017*
C5	1.41866 (17)	0.13292 (13)	0.22462 (12)	0.0119 (2)
C6	0.78624 (17)	0.35448 (13)	0.21273 (12)	0.0124 (2)
C7	1.64623 (17)	0.05751 (13)	0.22069 (12)	0.0125 (2)
N2	0.92925 (15)	0.22547 (12)	0.71808 (10)	0.0131 (2)
H2NA	1.0383	0.1590	0.7023	0.016*

H2NB	0.9062	0.3013	0.6413	0.016*
N3	0.62060 (14)	0.34644 (11)	0.88677 (10)	0.0125 (2)
H3NA	0.5147	0.4194	0.8957	0.015*
H3NB	0.6435	0.2692	0.9629	0.015*
C8	0.76465 (18)	0.15153 (14)	0.78825 (12)	0.0151 (2)
H8A	0.8089	0.0667	0.8736	0.018*
H8B	0.7345	0.1062	0.7345	0.018*
C9	0.57630 (18)	0.27015 (14)	0.81250 (12)	0.0153 (2)
H9A	0.5247	0.3495	0.7269	0.018*
H9B	0.4702	0.2186	0.8635	0.018*
C10	0.78693 (17)	0.41821 (13)	0.81741 (11)	0.0132 (2)
H10A	0.8168	0.4641	0.8708	0.016*
H10B	0.7448	0.5023	0.7313	0.016*
C11	0.97483 (17)	0.29762 (14)	0.79543 (12)	0.0143 (2)
H11A	1.0839	0.3469	0.7470	0.017*
H11B	1.0221	0.2168	0.8816	0.017*
O1S	0.82858 (14)	0.44226 (10)	0.47339 (9)	0.0197 (2)
H1SA	0.7424	0.5214	0.4750	0.024*
H1SB	0.7827	0.4028	0.4401	0.024*
O2S	0.56303 (15)	0.71798 (11)	0.45834 (9)	0.0232 (2)
H2SB	0.4951	0.7101	0.5286	0.028*
H2SA	0.5919	0.7966	0.4441	0.028*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0134 (4)	0.0224 (4)	0.0144 (4)	0.0020 (3)	−0.0028 (3)	−0.0087 (4)
O2	0.0124 (4)	0.0223 (5)	0.0148 (4)	−0.0014 (3)	0.0009 (3)	−0.0092 (4)
O3	0.0118 (4)	0.0162 (4)	0.0132 (4)	0.0003 (3)	−0.0021 (3)	−0.0045 (3)
O4	0.0127 (4)	0.0191 (4)	0.0142 (4)	−0.0003 (3)	0.0009 (3)	−0.0032 (3)
N1	0.0117 (5)	0.0146 (5)	0.0127 (5)	−0.0017 (4)	−0.0007 (4)	−0.0047 (4)
C1	0.0128 (5)	0.0148 (5)	0.0125 (6)	−0.0013 (4)	−0.0025 (4)	−0.0055 (4)
C2	0.0106 (5)	0.0118 (5)	0.0146 (6)	−0.0017 (4)	−0.0007 (4)	−0.0069 (4)
C3	0.0142 (6)	0.0150 (5)	0.0117 (5)	−0.0028 (4)	0.0012 (4)	−0.0065 (4)
C4	0.0141 (6)	0.0135 (5)	0.0122 (5)	−0.0004 (4)	−0.0033 (4)	−0.0053 (4)
C5	0.0110 (5)	0.0107 (5)	0.0140 (5)	−0.0017 (4)	−0.0009 (4)	−0.0059 (4)
C6	0.0114 (5)	0.0114 (5)	0.0149 (6)	−0.0022 (4)	−0.0009 (4)	−0.0065 (4)
C7	0.0114 (5)	0.0105 (5)	0.0153 (6)	−0.0017 (4)	−0.0011 (4)	−0.0058 (4)
N2	0.0118 (5)	0.0139 (5)	0.0111 (5)	−0.0003 (4)	−0.0004 (4)	−0.0055 (4)
N3	0.0109 (5)	0.0139 (5)	0.0109 (5)	−0.0014 (4)	−0.0004 (4)	−0.0052 (4)
C8	0.0146 (5)	0.0141 (5)	0.0177 (6)	−0.0030 (4)	−0.0008 (4)	−0.0083 (5)
C9	0.0113 (5)	0.0189 (6)	0.0180 (6)	−0.0034 (4)	−0.0014 (4)	−0.0098 (5)
C10	0.0144 (5)	0.0128 (5)	0.0119 (5)	−0.0038 (4)	−0.0001 (4)	−0.0048 (4)
C11	0.0115 (5)	0.0181 (6)	0.0142 (6)	−0.0044 (4)	0.0004 (4)	−0.0075 (5)
O1S	0.0254 (5)	0.0179 (4)	0.0166 (5)	−0.0043 (4)	−0.0047 (4)	−0.0075 (4)
O2S	0.0313 (5)	0.0206 (5)	0.0188 (5)	−0.0112 (4)	0.0070 (4)	−0.0098 (4)

Geometric parameters (Å, °)

O1—C6	1.2511 (15)	N3—C10	1.4843 (15)
O2—C6	1.2563 (15)	N3—C9	1.4887 (15)
O3—C7	1.2705 (15)	N3—H3NA	0.8698
O4—C7	1.2413 (15)	N3—H3NB	0.8695
N1—C1	1.3387 (15)	C8—C9	1.5120 (16)
N1—C5	1.3413 (15)	C8—H8A	0.9900
C1—C2	1.3905 (16)	C8—H8B	0.9900
C1—H1A	0.9500	C9—H9A	0.9900
C2—C3	1.3892 (16)	C9—H9B	0.9900
C2—C6	1.5137 (15)	C10—C11	1.5128 (16)
C3—C4	1.3874 (16)	C10—H10A	0.9900
C3—H3A	0.9500	C10—H10B	0.9900
C4—C5	1.3918 (16)	C11—H11A	0.9900
C4—H4A	0.9500	C11—H11B	0.9900
C5—C7	1.5223 (16)	O1S—H1SA	0.8197
N2—C8	1.4868 (16)	O1S—H1SB	0.8197
N2—C11	1.4885 (15)	O2S—H2SB	0.8199
N2—H2NA	0.8699	O2S—H2SA	0.8195
N2—H2NB	0.8695		
C1—N1—C5	117.45 (10)	C9—N3—H3NA	110.7
N1—C1—C2	124.22 (11)	C10—N3—H3NB	117.0
N1—C1—H1A	117.9	C9—N3—H3NB	100.3
C2—C1—H1A	117.9	H3NA—N3—H3NB	109.6
C3—C2—C1	117.48 (11)	N2—C8—C9	110.20 (10)
C3—C2—C6	122.09 (10)	N2—C8—H8A	109.6
C1—C2—C6	120.33 (10)	C9—C8—H8A	109.6
C4—C3—C2	119.28 (11)	N2—C8—H8B	109.6
C4—C3—H3A	120.4	C9—C8—H8B	109.6
C2—C3—H3A	120.4	H8A—C8—H8B	108.1
C3—C4—C5	118.90 (11)	N3—C9—C8	110.65 (9)
C3—C4—H4A	120.6	N3—C9—H9A	109.5
C5—C4—H4A	120.6	C8—C9—H9A	109.5
N1—C5—C4	122.66 (11)	N3—C9—H9B	109.5
N1—C5—C7	116.24 (10)	C8—C9—H9B	109.5
C4—C5—C7	121.08 (10)	H9A—C9—H9B	108.1
O1—C6—O2	125.15 (11)	N3—C10—C11	110.20 (9)
O1—C6—C2	117.55 (10)	N3—C10—H10A	109.6
O2—C6—C2	117.22 (10)	C11—C10—H10A	109.6
O4—C7—O3	124.71 (11)	N3—C10—H10B	109.6
O4—C7—C5	119.37 (10)	C11—C10—H10B	109.6
O3—C7—C5	115.90 (10)	H10A—C10—H10B	108.1
C8—N2—C11	110.78 (9)	N2—C11—C10	109.79 (9)
C8—N2—H2NA	111.4	N2—C11—H11A	109.7
C11—N2—H2NA	110.0	C10—C11—H11A	109.7
C8—N2—H2NB	117.1	N2—C11—H11B	109.7
C11—N2—H2NB	103.1	C10—C11—H11B	109.7

H2NA—N2—H2NB	103.9	H11A—C11—H11B	108.2
C10—N3—C9	111.45 (9)	H1SA—O1S—H1SB	108.3
C10—N3—H3NA	107.6	H2SB—O2S—H2SA	98.1
C5—N1—C1—C2	0.01 (18)	C3—C2—C6—O2	6.44 (17)
N1—C1—C2—C3	−0.63 (18)	C1—C2—C6—O2	−169.99 (11)
N1—C1—C2—C6	175.95 (11)	N1—C5—C7—O4	7.27 (16)
C1—C2—C3—C4	0.93 (17)	C4—C5—C7—O4	−174.20 (11)
C6—C2—C3—C4	−175.59 (11)	N1—C5—C7—O3	−171.12 (10)
C2—C3—C4—C5	−0.64 (18)	C4—C5—C7—O3	7.41 (16)
C1—N1—C5—C4	0.32 (17)	C11—N2—C8—C9	58.08 (12)
C1—N1—C5—C7	178.83 (10)	C10—N3—C9—C8	56.11 (12)
C3—C4—C5—N1	0.00 (18)	N2—C8—C9—N3	−56.11 (13)
C3—C4—C5—C7	−178.44 (10)	C9—N3—C10—C11	−56.94 (12)
C3—C2—C6—O1	−176.57 (11)	C8—N2—C11—C10	−58.93 (12)
C1—C2—C6—O1	7.01 (17)	N3—C10—C11—N2	57.86 (12)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2NA···O3^{i}	0.87	1.82	2.686 (2)	173
N2—H2NB···O1S	0.87	1.86	2.719 (1)	169
N3—H3NA···O1^{ii}	0.87	1.87	2.736 (2)	174
N3—H3NB···O4^{iii}	0.87	1.91	2.770 (1)	168
O1S—H1SA···O2S	0.82	1.89	2.701 (2)	172
O1S—H1SB···O2	0.82	1.94	2.735 (1)	164
O2S—H2SB···O2^{ii}	0.82	1.92	2.709 (1)	161
O2S—H2SA···O3^{iv}	0.82	1.98	2.730 (2)	152

Symmetry codes: (i) −*x*+3, −*y*, −*z*+1; (ii) −*x*+1, −*y*+1, −*z*+1; (iii) *x*−1, *y*, *z*+1; (iv) *x*−1, *y*+1, *z*.

Fig. 1

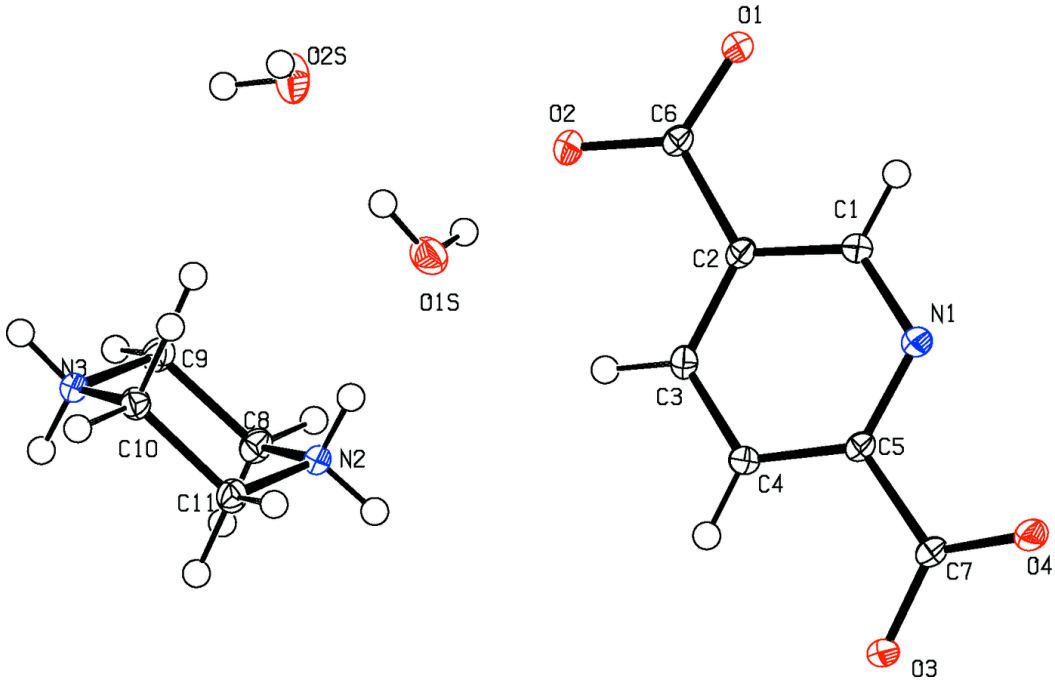


Fig. 2

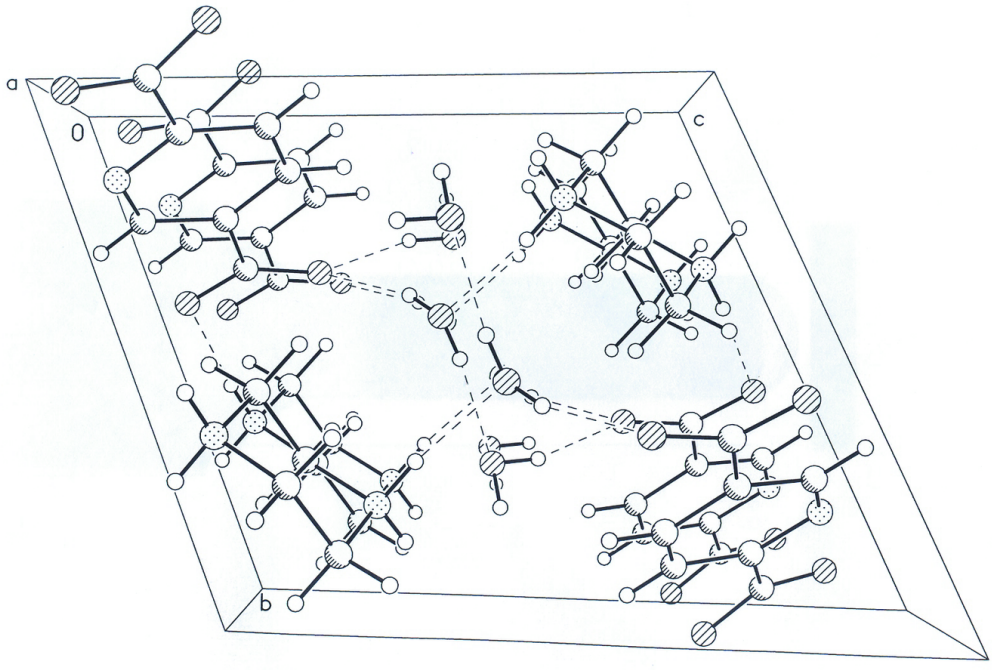


Fig. 3