Supporting information

First Snapshot of A Nonpolymeric Hydrogelator Interacting with its Gelling solvents

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Experimental Section

Materials and Methods

All reactants are commercially available (Aldrich) and used without further purification. Microanalyses are performed on a Perkin-Elmer elemental analyzer 2400, Series II. FT-IR and NMR spectra were recorded using Perkin-Elmer SpectrumGX and 200MHzBruker Avance DPX200 spectrometers, respectively. Powder X-ray patterns are recorded on an XPERT Philips (Cu Kα radiation) diffractometer. SEM is performed on a LEO 1430VP. Synthesis of the title compounds were performed following a reported procedure[1] with significant modification.

N,N'-bis(4-pyridyl)urea 1

Analytical Data. mp 200^{0}C. Anal Calcd for $C_{11}H_{12}N_3O.H_2O$: C, 56.89; H, 5.21; N, 24.12. Found: C, 57.69; H, 5.43; N, 24.44. ^{1}H NMR [DMSO (d_6)]: 9.347 (s, 2H, NH), 8.408-8.376 (d, 4H), 7.471-7.440 (d, 4H). FT-IR (cm^{-1}): 3592w, 3400w, 3354w, 3287w, 3183m, 3079w, 3008m, 2947w, 2488w, 2433w, 2348w, 2283w, 2218m, 1942w, 1831w, 1740s, 1639m, 1588s, 1518s, 1422vs, 1332vs, 1285vs, 1245s, 1188vs, 1067m, 1039w, 1002vs, 903m, 836s, 794w, 736s, 645m, 529vs.

N, N'-bis(4-pyridyl)urea monohydrochloride salt 1.HCl

Analytical data. Calcd for $C_{11}H_{12}N_3O.HCl$: C, 52.70; H, 4.42; N, 22.35. Found: C, 52.44; H, 5.41; N, 21.28.

N,N'-bis(3-pyridyl)urea 2

Analytical Data. mp 220^{0}C. Anal Calcd for $C_{11}H_{12}N_3O$: C, 61.6; H, 4.67; N, 26.16. Found: C, 60.78; H, 4.36; N, 25.73. ^{1}H NMR [DMSO (d_6)]: 9.204 (s, 2H, NH), 8.806 (s, 2H), 8.407-8.377 (t, 2H), 8.147-8.085 (m, 2H), 7.569-7.504 (t, 2H). FT-IR (cm^{-1}): 3295w, 3246w, 3218w, 3174w, 3100w, 3038m, 2992m, 2921w, 2864w, 2813w, 2772w, 1942w, 1904w, 1883w, 1843w, 1691vs, 1603s, 1585vs, 1546vs, 1474vs, 1419vs, 1346w, 1327m, 1273vs, 1227s, 1185w, 1132s, 1106w, 1063s, 1047w, 1016m, 970w, 933s, 895s, 834m, 801vs, 703vs, 651m, 617s, 528w, 508s, 407m.

T_{gel} measurement method:

T_{gel} was measured by the drop ball method. A custom-made glass ball weighing 0.19 g was placed on the gel surface, and the gel was heated gradually in an oil bath. The temperature at which the ball fell into the bottom of the test tube was recorded as the gel dissociation temperature (T_{gel}).

Supplementary Material (ESI) for Chemical Communications

Single crystal X-ray crystallography

Diffraction data for **1.EG.H_2O**, **1.HCl.xH_2O** and **2** were collected using MoKα (λ= 0.7107 Å) radiation on a SMART APEX diffractometer equipped with charge-coupled device (CCD) area detector. Data for **2.xH_2O** were collected using MoKα (λ= 0.7107 Å) radiation on a CAD-4 diffractometer. Empirical absorption corrections for **1.EG.H_2O**, **1.HCl.xH_2O** and **2** were performed using SADABS provided with the software package of SMART APEX. No absorption corrections were applied to data colleted on CAD-4. Data collection, data reduction, and structure solution/refinement were carried out for **1.EG.H_2O**, **1.HCl.xH_2O** and **2** using the software package of SMART APEX. The corresponding calculations for **2.xH_2O** were performed using CAD4-PC,[1] NRCVAX,[2] and SHELX97.[3] Graphics were generated using MERCURY 1.3.[4]
All structures were solved by direct methods and refined in a routine manner. In all cases, nonhydrogen atoms were treated anisotropically. Whenever possible, the hydrogen atoms were located on a difference Fourier map and refined. In other cases, the hydrogen atoms were geometrically fixed.
For **1.HCl.xH_2O**, the extra electron densities (two peaks at ~1.2e/Å^3) have been assigned as oxygen atoms of some disordered water molecules. The SOF of these two peaks have been refined keeping the x,y,z and temperature factors fixed (at 0.05). After refinement, the refined SOF of the disordered oxygen atoms were fixed and x,y,z and isotropic temperature parameters were refined in the subsequent cycle of refinements.
The crystallographic and hydrogen bonding parameters are listed in Table S1 and Table S2 respectively.

References

1. CAD-4 Software, Version 5.0; Enraf-Nonius: Delft, 1989.
2. I. Gabe, Y. Le. Page, I. P. Charland, F. L. Lee and P. S. While, J. Appl. Crystallogr., 1989, **22**, 384.
3. G. M. Sheldrick, SHELEXL-97, A program for crystal structure solution and refinement; University of Göttingen: Göttingen, Germany, 1993.
4. Mercury 1.3 Supplied with Cambridge Structural Database, Copyright CCDC, 2003-2004.

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Table S1: Crystallographic parameters of compounds reported in the paper.

Crystal data	**1.EG.H_2O**	**1.HCl.xH_2O (x=1.66)**	**2**	**2. xH_2O (x=1.33)**
CCDC Deposit No	CCDC 267563	CCDC 267564	CCDC 267565	CCDC 267566
Empirical formula	$C_{13}H_{18}N_4O4$	$C_{22}H_{28}Cl_2N_8O_{5.32}$	$C_{11}H_{10}N_4O$	$C_{16.50}H_{19}N_6O_{3.50}$
FW	294.31	560.54	214.23	357.38
Crystal size (mm), color	0.66x0.48x0.19, Colourless	0.56 x 0.33 x 0.19, Colourless	0.56x0.43x0.18, Colourless	0.39x0.25x0.12, Pale yellow
Crystal system	Orthorhombic	Triclinic	Orthorhombic	Monoclinic
Space group	P $2_12_12_1$	P -1	A ba2	C 2/c
a/Å	8.1836(7)	9.8236(12)	13.713(6)	13.073(4))
b/Å	10.6011(10)	10.2628(12)	6.977(3)	11.793(7)
c /Å	16.4345(16)	13.9993(17)	10.013(4)	22.678(8)
$\alpha/^0$	90.00	101.696(2)	90.00	90.00
$\beta/^0$	90.00	95.602(2)	90.00	100.03(3)
$\gamma/^0$	90.00	101.734(2)	90.00	90.00
Volume / $Å^{-3}$	1425.8(2)	1338.9(3)	957.9(7)	3443(3)
Z	4	2	4	8
$D_{calc.}$	1.371	1.390	1.485	1.379
F(000)	624	585	448	1504
μ MoKα (mm^{-1})	0.104	0.292	0.102	0.101
Temperature (K)	100(2)	100(2)	100(2)	298(2)
Observed reflections [I > 2 σ(I)]	1807	4359	583	1494
Parameters refined	258	382	94	276
Goodness of fit	1.051	1.113	1.100	0.976
Final R_1 on observed data	0.0360	0.0493	0.0348	0.0420
Final wR_2 on observe data	0.0873	0.1274	0.0860	0.0952
2 θ_{max}	28.29	28.28	28.26	22.45
Electron density max	0.277	0.691	0.252	0.168
Electron density min	-0.215	-0.452	-0.170	-0.272

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Table S2: Hydrogen bonding parameters of the compounds reported in the paper

D-H…A	**D-H/Å**	**H…A/Å**	**D…A/Å**	**∠D-H…A/^{0}**	**Symmetry operation for A**
1.EG.H_2O					
N(7)-H(7)…O(17)	0.86	2.10	2.864(2)	148.2	-X+1, Y+1/2, -Z+3/2
N(10)-H(10)…O(20)	0.88(3)	1.93(3)	2.805(2)	173(2)	-X+1, Y+1/2, -Z+3/2
O(17)-H(17)…N(1)	0.88(3)	1.83(3)	2.717(2)	179(3)	X, Y, Z
O(20)-H(20)…O(21)	0.87(3)	1.83(3)	2.693(2)	179(3)	X+1/2, -Y+1/2, -Z+2
O(21)-H(21A)…N(14)	0.87(3)	1.90(3)	2.775(2)	176(3)	X, Y, Z
O(21)-H(21B)…O(9)	0.81(4)	2.21(4)	2.945(2)	150(3)	-X+3/2, -Y+1, Z+1/2
1.HCl.xH_2O (x=1.66)					
N(1)-H(1)…N(14')	0.86	1.88	2.736(3)	176.9	-X+1, -Y+2, -Z+2
N(1')-H(1')…N(14)	0.86	1.85	2.712(3)	175.9	-X-1, -Y, -Z+1
N(7')-H(7')…Cl(1)	0.82(3)	2.31(3)	3.116(2)	166(3)	X, Y, Z
N(7)-H(7)…Cl(2)	0.81(3)	2.38(3)	3.151(2)	159(3)	X, Y, Z
N(10)-H(10)…Cl(2)	0.88(4)	2.32(4)	3.164(2)	159(3)	X, Y, Z
N(10')-H(10')…Cl(1)	0.82(4)	2.48(4)	3.249(2)	159(3)	X, Y, Z
O(1)-H(1A)…Cl(1)	0.97(6)	2.30(6)	3.209(3)	156(5)	X, Y, Z
O(1)-H(1B)…O(9')	0.88(4)	1.99(4)	2.856(3)	169(3)	-X, -Y+1, -Z+1
O(2)-H(2A)…O(1)	0.95(5)	1.84(5)	2.776(4)	168(4)	X, Y, Z
O(2)-H(2B)…O(3)	0.82(4)	2.00(4)	2.748(5)	150(3)	X, Y, Z-1
O(3)-H(3A)…Cl(2)	0.79(6)	2.37(6)	3.148(4)	167(5)	X, Y, Z
O(3)-H(3B)…O(2)	0.77(6)	2.07(6)	2.779(5)	153(6)	-X, -Y, -Z+1
2					
N(7)-H(7)…N(1)	0.84(2)	2.23(2)	3.055(2)	168(2)	X, Y-1/2, Z+1/2
2. xH_2O (x=1.33)					
O(1A)-H(1A)…N(17)	0.99(3)	1.88(3)	2.834(3)	164(3)	X, Y, Z
O(1A)-H(1B)…N(15)	0.91(3)	1.99(3)	2.874(3)	164(3)	-X+3/2, -Y+1/2, -Z
O(2A)-H(2A)…O(9)	0.84(3)	2.03(3)	2.858(3)	166(3)	-X+1/2, Y+1/2, -Z+1/2
O(2A)-H(2B)…N(1)	1.01(3)	1.83(3)	2.831(3)	170(2)	X, Y, Z
N(7)-H(7)…O(1A)	0.86(2)	2.28(2)	3.078(3)	154(2)	X-1/2, Y+1/2, Z
N(10)-H(10)…O(1A)	0.82(2)	2.04(2)	2.841(3)	164(2)	X-1/2, Y+1/2, Z
N(23)-H(23)…O(2A)	0.93(2)	1.97(2)	2.852(3)	157.5(19)	-X+1/2, Y-1/2, -Z+1/2

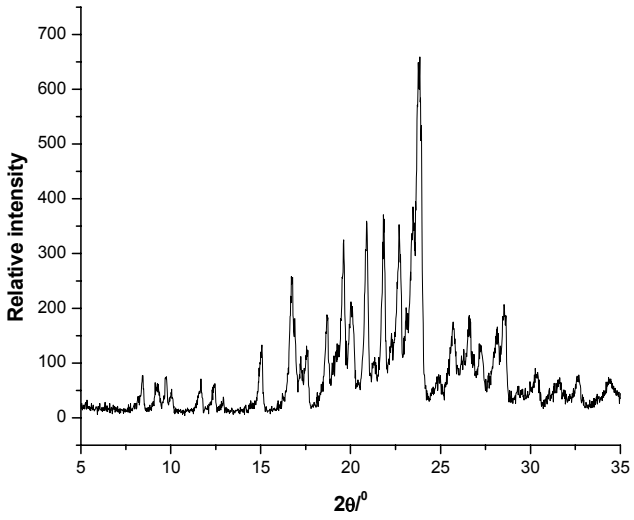

Figure S1: XRPD of xerogel of **1** (1 wt %, 10% EG in water) recorded after 6 hrs of drying at 120 ºC.

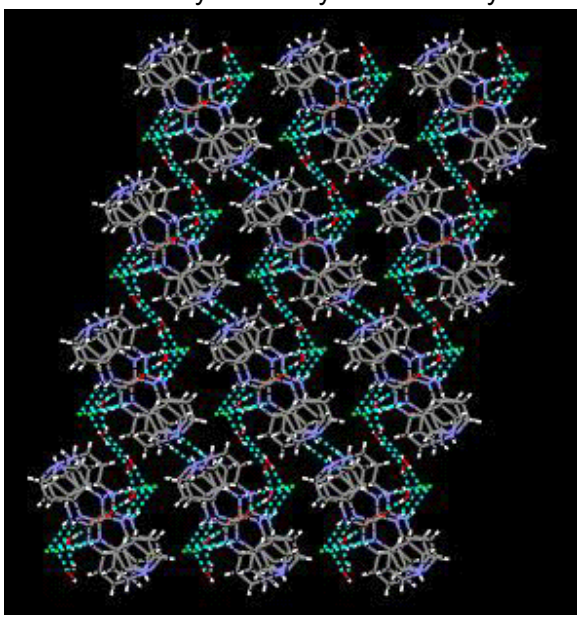

Figure S2: Molecular packing and hydrogen bonding interactions in the crystal structure of **1.HCl.xH_2O** viewed down c-axis. Disordered oxygen atoms are omitted for the sake of clarity.

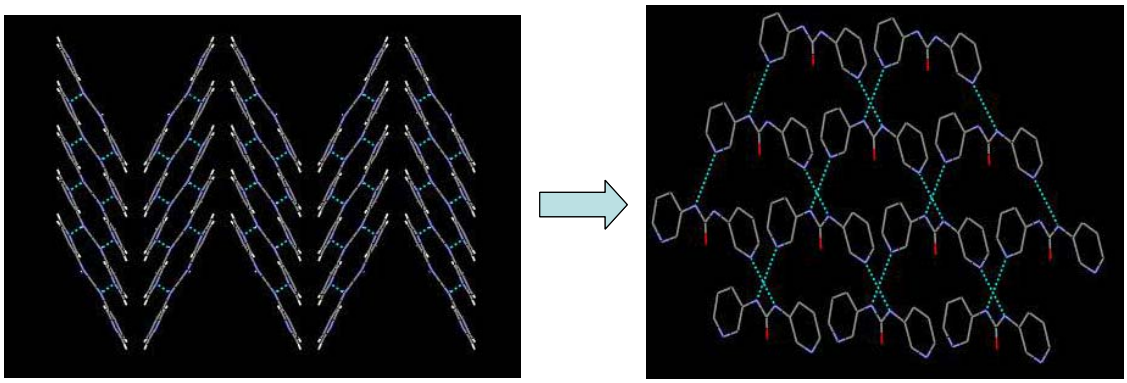

Figure S3: Left: Herringbone packing arrangement of **2**; right: hydrogen bonding interactions in one of the non-planar 2-D sheets in **2**.

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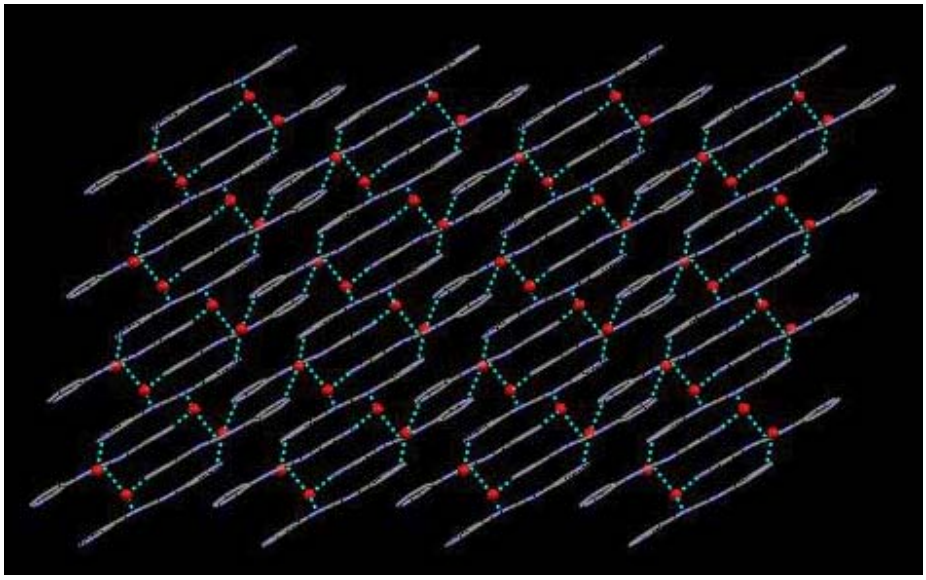

Figure S4: 3-D hydrogen bonding network involving the urea and water molecule (red ball) in **2.xH_2O**. Hydrogen atoms are not shown for clarity.

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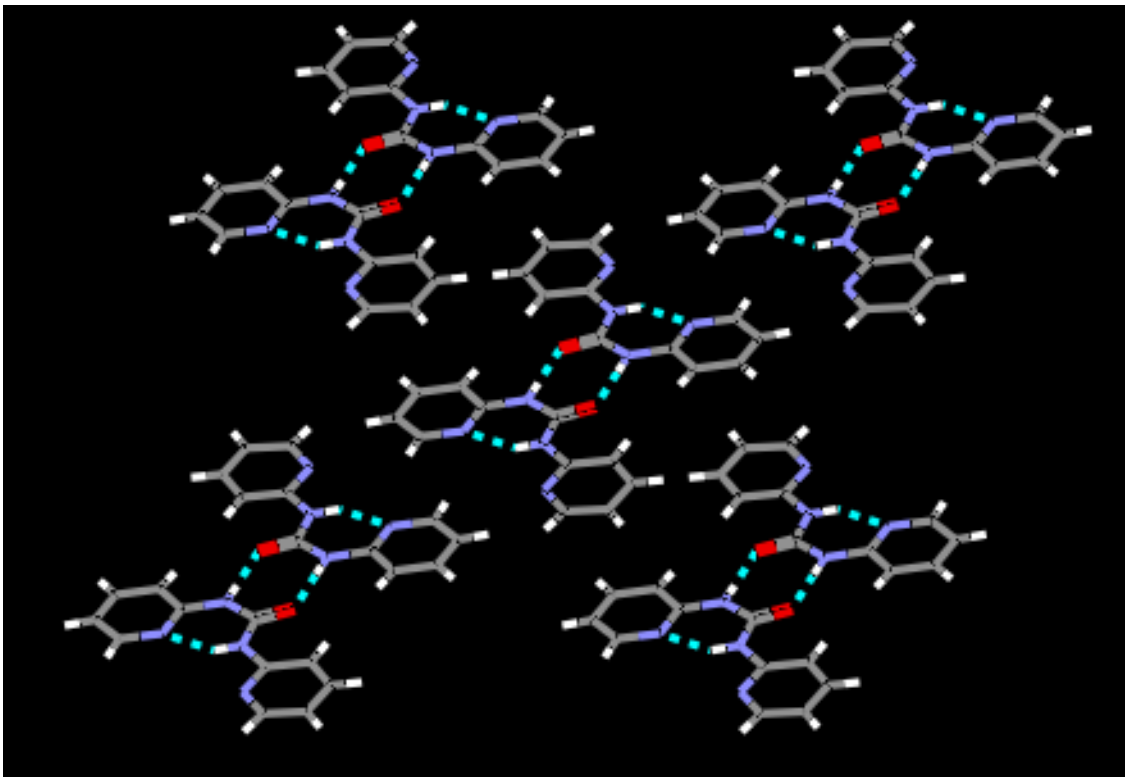

Figure S5: Hydrogen bonded dimers in the crystal structure of **3** generated using the cif deposited in Cambridge Structural Database (REFCODE – XERDIH)

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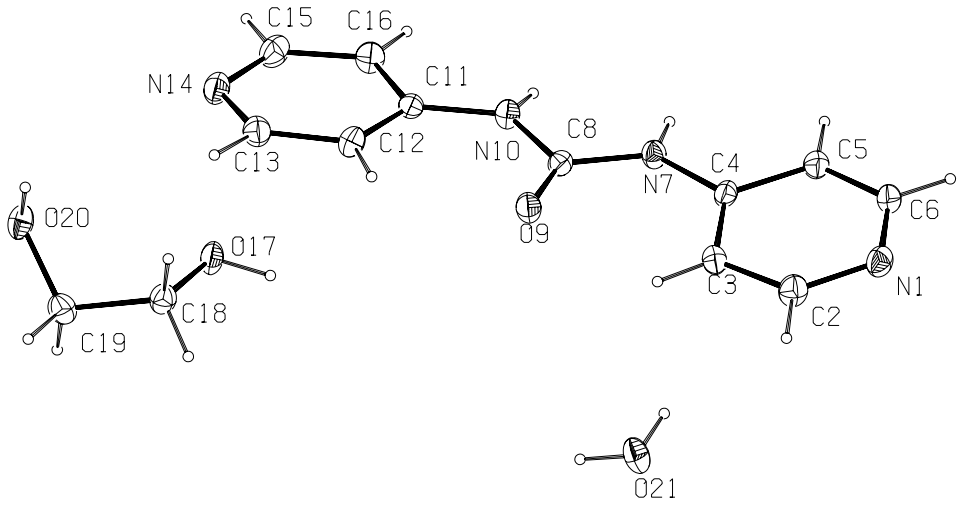
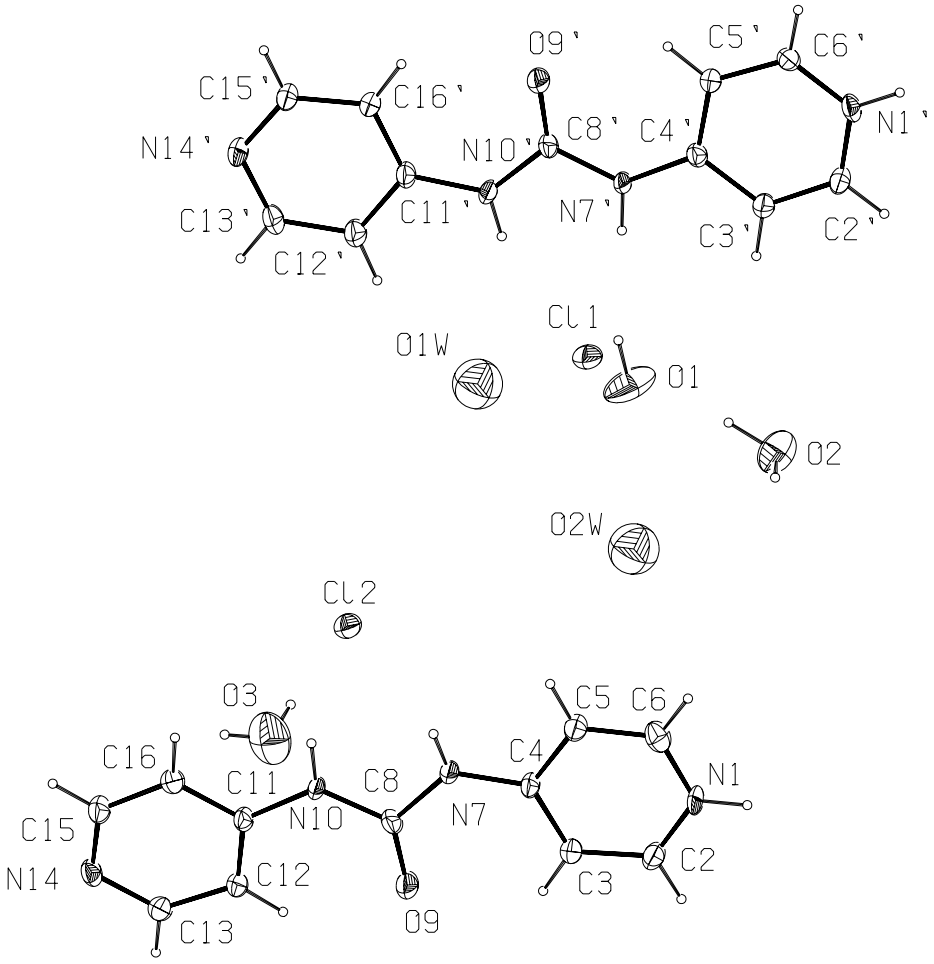
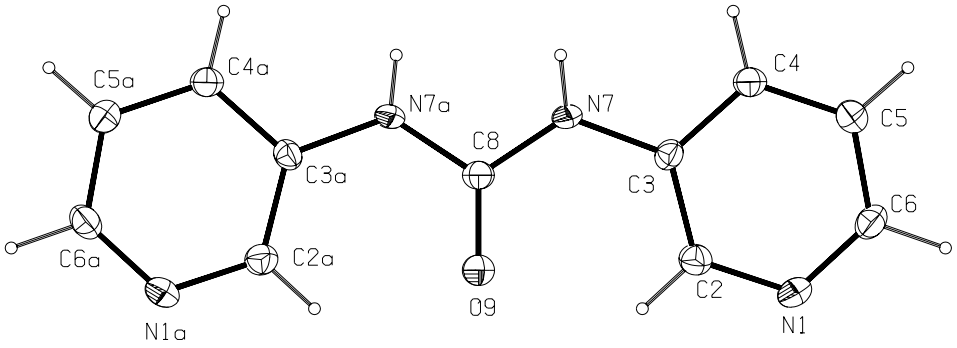
ORTEP DIGRAMS (probability 50%)



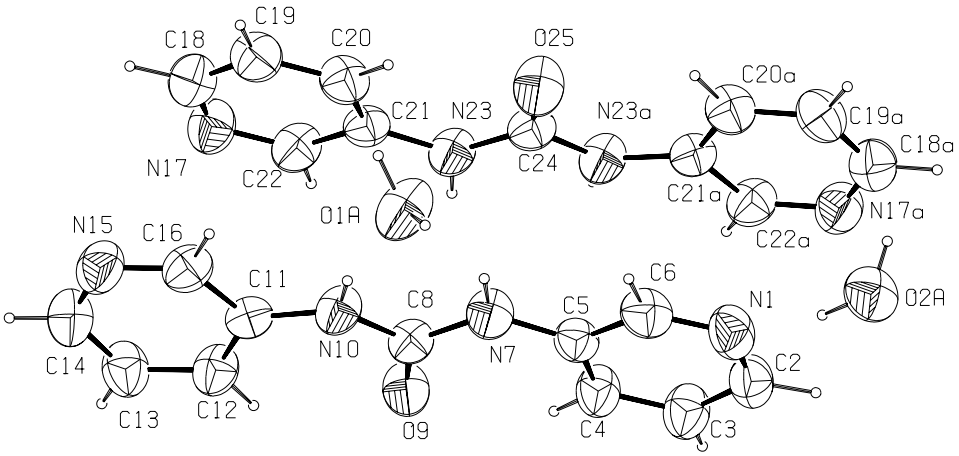
1.EG.H_2O



1.HCL.xH_2O



2



2.xH_2O