Electronic Supplementary Information for

Isostructurality in three-component crystals achieved by the combination of persistent hydrogen bonding motifs and solvent inclusion

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Section 1. Single Crystal X-ray Diffraction Studies

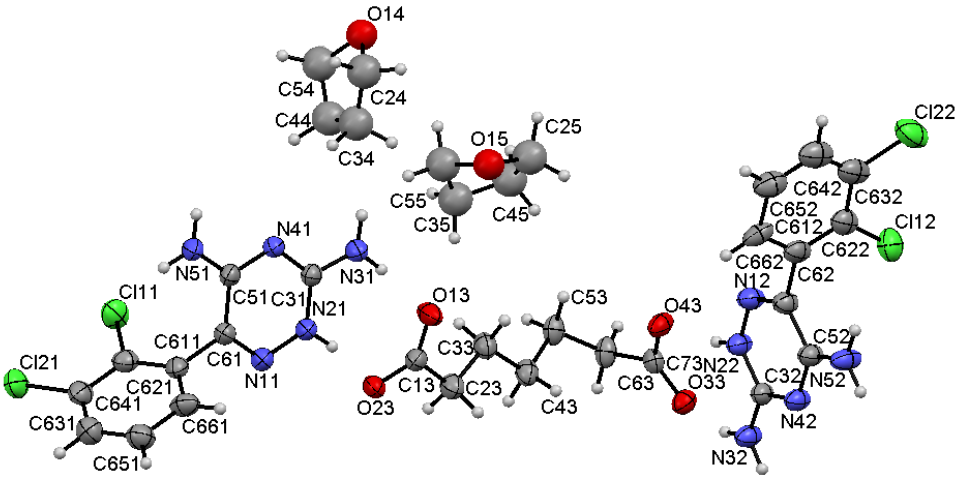

Figure S1 Molecular structure of compound **LMPI-thf** with the atom labeling scheme. Displacement ellipsoids are shown at the 50% probability level. Disordered atoms and displacement ellipsoids of the solvent molecule are not represented for clarity.

Figure S2 Superimposed disordered lamotrigine molecules in **LMPI-thf**, showing the two positions with final occupation factors of 0.93 (blue) and 0.07 (yellow).

Table S1 Hydrogen bond geometries of compound **LMPI-thf** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(21)-H(21)...O(23)#1	0.88	1.87	2.735(3)	166
N(31)-H(31A)...O(13)	0.88	2.10	2.871(4)	146
N(31)-H(31B)...O(13)#1	0.88	1.89	2.770(3)	176
N(51)-H(51A)...O(43)	0.88	2.02	2.857(5)	159
N(51)-H(51B)...O(33)#2	0.88	2.06	2.903(5)	161
N(22)-H(22)...O(43)#3	0.88	1.72	2.577(4)	162
N(32)-H(32A)...O(23)#4	0.88	2.19	3.061(4)	171
N(32)-H(32B)...O(33)#3	0.88	1.98	2.839(5)	164
N(52)-H(52B)...O(23)#1	0.88	2.16	2.865(5)	137
N(52)-H(52A)...N(42)#5	0.88	2.08	2.948(5)	170

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z #2 -x+1,-y+2,-z+1 #3 -x+1,-y+1,-z+1 #4 x-1,y-1,z #5 -x,-y,-z

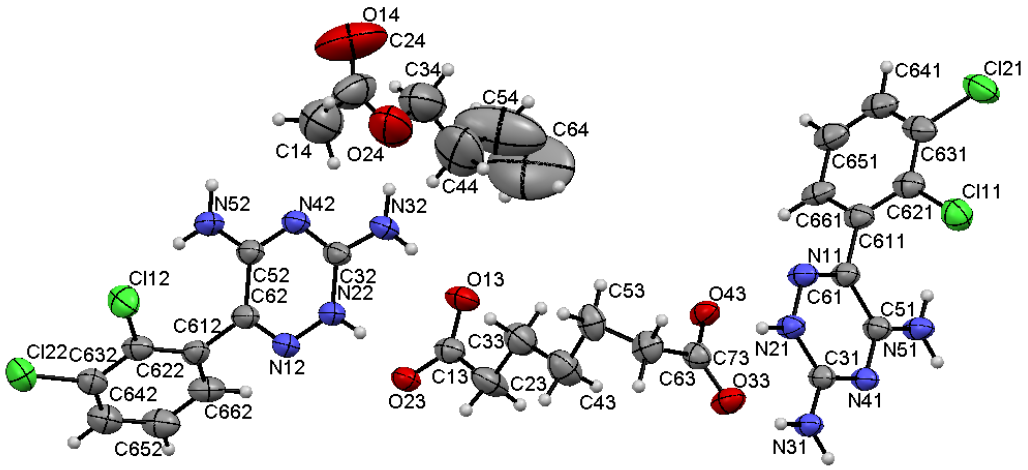

Figure S3 Molecular structure of compound **LMPI-BAc** with the atom labeling scheme. Displacement ellipsoids are shown at the 50% probability level.

Figure S4 Superimposed disordered lamotrigine molecules in **LMPI-BAc**, showing the two positions with final occupation factors of 0.90 (blue) and 0.10 (yellow).

Table S2 Hydrogen bond geometries of compound **LMPI-BAc** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(22)-H(22)...O(23)	0.88	1.88	2.744(4)	168
N(32)-H(32A)...O(13)#3	0.88	2.08	2.858(6)	147
N(32)-H(32B)...O(13)	0.88	1.90	2.780(4)	174
N(52)-H(52A)...O(43)#3	0.88	1.98	2.827(4)	161
N(52)-H(52B)...O(33)#4	0.88	2.03	2.871(5)	158
N(21)-H(21)...O(43)#1	0.88	1.71	2.571(3)	167
N(31)-H(31A)...O(23)#2	0.88	2.16	3.024(3)	167
N(31)-H(31B)...O(33)#1	0.88	1.95	2.808(4)	165
N(51)-H(51B)...O(23)	0.88	2.14	2.834(3)	136
N(51)-H(51A)...N(41)#2	0.88	2.07	2.947(4)	176
Symmetry transformations used to generate equivalent atoms:				
#1 x,y,z-1 #2 -x+1,-y+2,-z+1 #3 -x,-y+1,-z+1 #4 x,y-1,z-1				

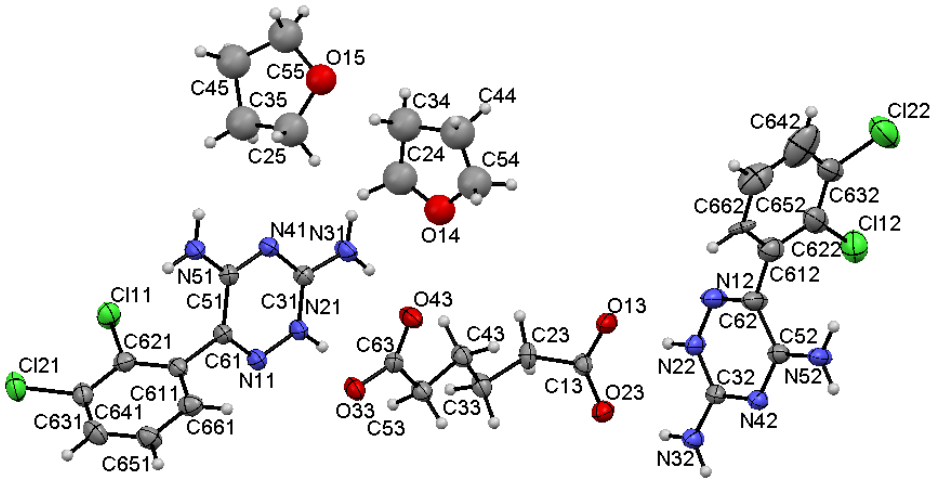

Figure S5 Molecular structure of compound **LMAD-thf** with the atom labeling scheme. Displacement ellipsoids are shown at the 50% probability level. Disordered atoms and displacement ellipsoids of the solvent molecule are not represented for clarity.

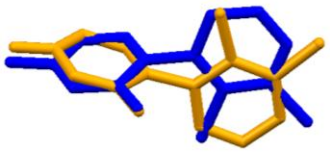

Figure S6 Superimposed disordered lamotrigine molecules in **LMAD-thf**, showing the two positions with final occupation factors of 0.80 (blue) and 0.20 (yellow).

Table S3 Hydrogen bond geometries of compound **LMAD-thf** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(21)-H(21)...O(33)	0.88	1.86	2.712(4)	164
N(31)-H(31A)...O(43)#1	0.88	2.04	2.863(4)	155
N(31)-H(31B)...O(43)	0.88	1.93	2.810(4)	173
N(51)-H(51A)...O(13)#1	0.88	1.98	2.822(4)	161
N(51)-H(51B)...O(23)#2	0.88	2.17	3.020(4)	161
N(22)-H(22)...O(13)#3	0.88	1.78	2.626(5)	160
N(32)-H(32A)...O(33)#4	0.88	2.32	3.192(10)	173
N(32)-H(32B)...O(23)#3	0.88	1.96	2.832(10)	168
N(52)-H(52B)...O(33)	0.88	2.15	2.884(5)	141
N(52)-H(52A)...N(42)#4	0.88	2.05	2.930(9)	177
Symmetry transformations used to generate equivalent atoms:				
#1 -x,-y+1,-z+1 #2 x,y-1,z-1 #3 x,y,z-1 #4 -x+1,-y+2,-z+1				

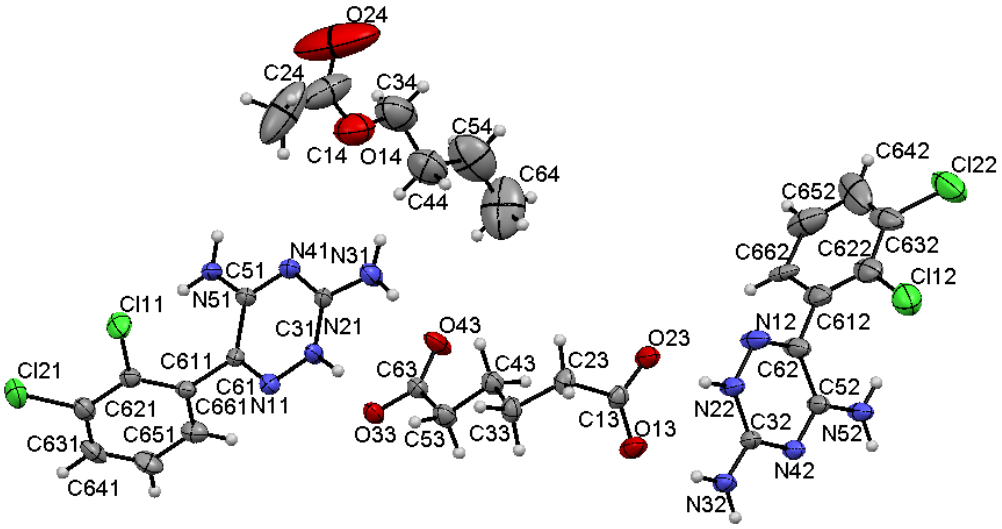

Figure S7 Molecular structure of compound **LMAD-BAc** with the atom labeling scheme. Displacement ellipsoids are shown at the 50% probability level. Disordered atoms are not represented for clarity.

Figure S8 Superimposed disordered lamotrigine molecules in **LMAD-BAc**, showing the two positions with final occupation factors of 0.83 (blue) and 0.17(yellow).

Table S4 Hydrogen bond geometries of compound **LMAD-BAc** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(21)-H(21)...O(33)#1	0.86	1.88	2.721(5)	166
N(31)-H(31A)...O(43)	0.86	2.05	2.845(4)	153
N(31)-H(31B)...O(43)#1	0.86	1.94	2.803(5)	177
N(51)-H(51A)...O(23)	0.86	2.02	2.832(6)	158
N(51)-H(51B)...O(13)#2	0.86	2.29	3.114(8)	160
N(22)-H(22)...O(23)#3	0.86	1.74	2.577(4)	166
N(32)-H(32A)...O(33)#4	0.86	2.19	3.046(4)	172
N(32)-H(32B)...O(13)#3	0.86	1.97	2.815(5)	170
N(52)-H(52B)...O(33)	0.86	2.14	2.832(4)	137
N(52)-H(52A)...N(42)#4	0.86	2.08	2.943(5)	177
Symmetry transformations used to generate equivalent atoms:				
#1 -x+1,-y+2,-z+1 #2 -x+1,-y+1,-z #3 x,y,z+1 #4 -x,-y+1,-z+1				

Section 2. Thermal analyses

For the solvated LMDC-guest crystalline phases the thermal analyses are characterized by two main processes. A first broad endothermic peak in the DSC is associated with a determined fast weight loss in the TGA, which corresponds to a desolvation process by evaporation of the solvent molecules in the structure upon heating. After that, a second endothermic sharp peak is observed in the DSC, corresponding to the melting of the desolvated salt. This second endothermic peak is also associated with a smoother but continuous weight loss in the TGA, related with the degradation of the sample.

Table S5 Summary of thermal events shown in the DSC and TGA curves of the LMDC-guest compounds **LMPI-thf**, **LMPI-BAc**, **LMAD-thf** and **LMAD-BAc**.

LMDC Compound	DSC desolvation onset (°C)	TGA desolvation weight loss (%)	DSC melting onset (°C)	DSC melting peak (°C)	Literature DC melting point (°C)*
LMPI-thf	120	17.2	184	190	103-105
LMPI-BAc	114	14.0	184	188	103-105
LMAD-thf	112	15.4	198	203	151-154
LMAD-BAc	125	14.2	199	206	151-154

(*) The DC melting points where obtained from the Sigma-Aldrich catalogue.

Section 3. Infrared spectroscopy

The FTIR-ATR spectra of powder samples of all the LMDC-guest compounds are characterized by the presence of broad bands between 3300 and 2200 cm^{-1}, corresponding to stretching vibrations of $N-H^{+}$ of amine hydrogen bonded salts, and also by the shifting to lower frequencies of the C=O characteristic band of the dicarboxylic acid, which indicates the carboxylate anion formation[1] (Table S5). Morover the FTIR-ATR depict the solvent guest molecule content showing the characteristic bands corresponding to the guest molecules included in each particular case. The fact that these samples do not show any peak of the neutral DC also indicates that the samples do not contain any nanocrystalline or amorphous unreacted material of the initial neutral species.

1. Silverstein, R. M. & Webster, F. X. *Spectrometric Identification of Organic Compounds*, 6th ed. Wiley, New York, 1998; Chapter *3*, pp 71-143.

Table S6 Table with the IR-ATR selected characteristic absorption bands observed in the isostructural LMDC-guest compounds **LMPI-thf**, **LMPI-BAc**, **LMAD-thf** and **LMAD-BAc** (cm^{-1}).

LMDC-guest Compound	Included guest bands in LMDC-guest	Hydrogen bonded $N^{(+)}$-H bands in LMDC-guest	C=O shifted bands of $COO^{(-)}$ in LMDC-guest	C=O bands of the COOH groups in the neutral DC
LMPI-thf	1059, 907	3287, 2959, 2853	1651	1682
LMPI-BAc	1733,1250,1058	3288, 2954	1652	1682
LMAD-thf	1059, 916	3279, 2960	1650	1683
LMAD-BAc	1732,1245,1057	3282, 2954	1660	1683