Electronic Supplementary Material for CrystEngComm

Polymorphism and versatile solvate formation of thiophanate-methyl

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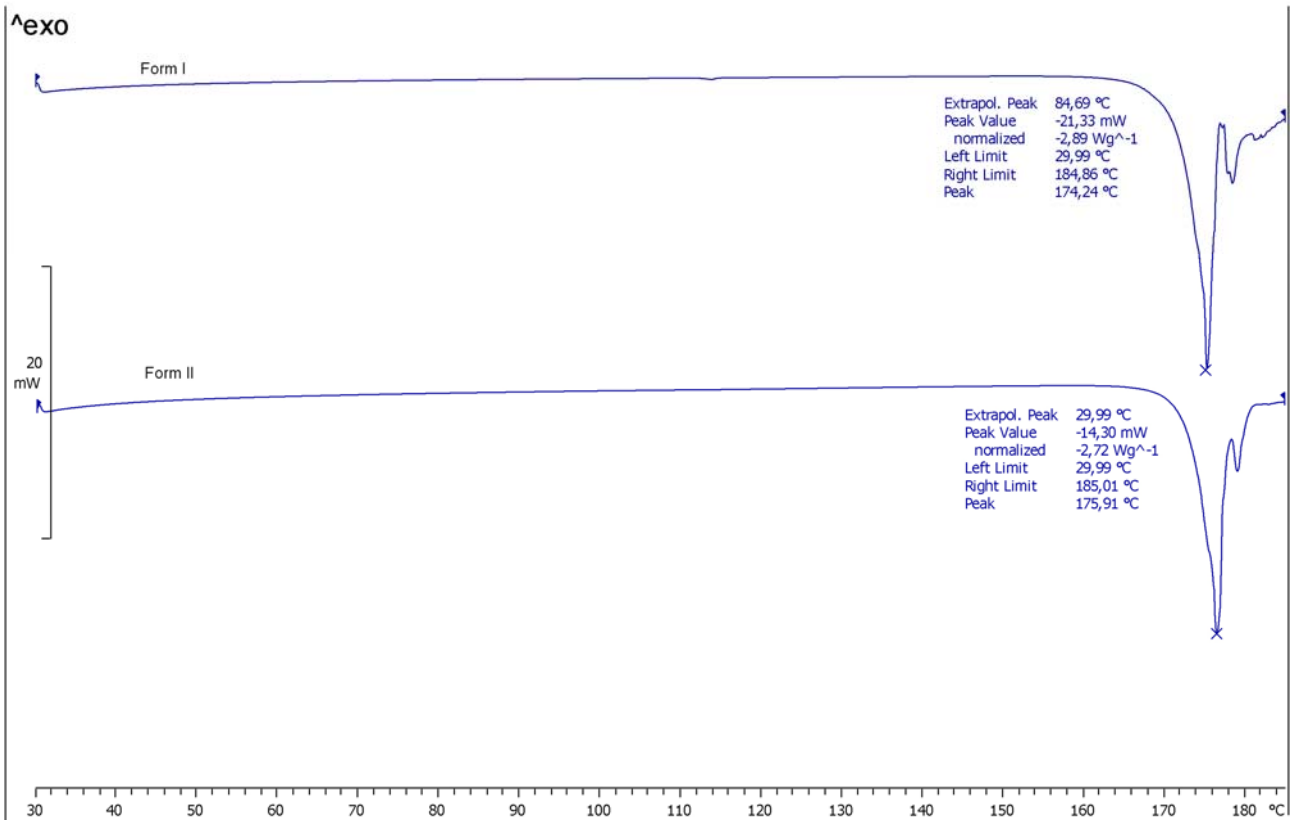
Electronic supplementary information (ESI)

Polymorphs

DSC

Figure I. DSCs of form I and form II (heating rate 5°C/min)



TG/DTA

Figure II. TG/DTA of form I

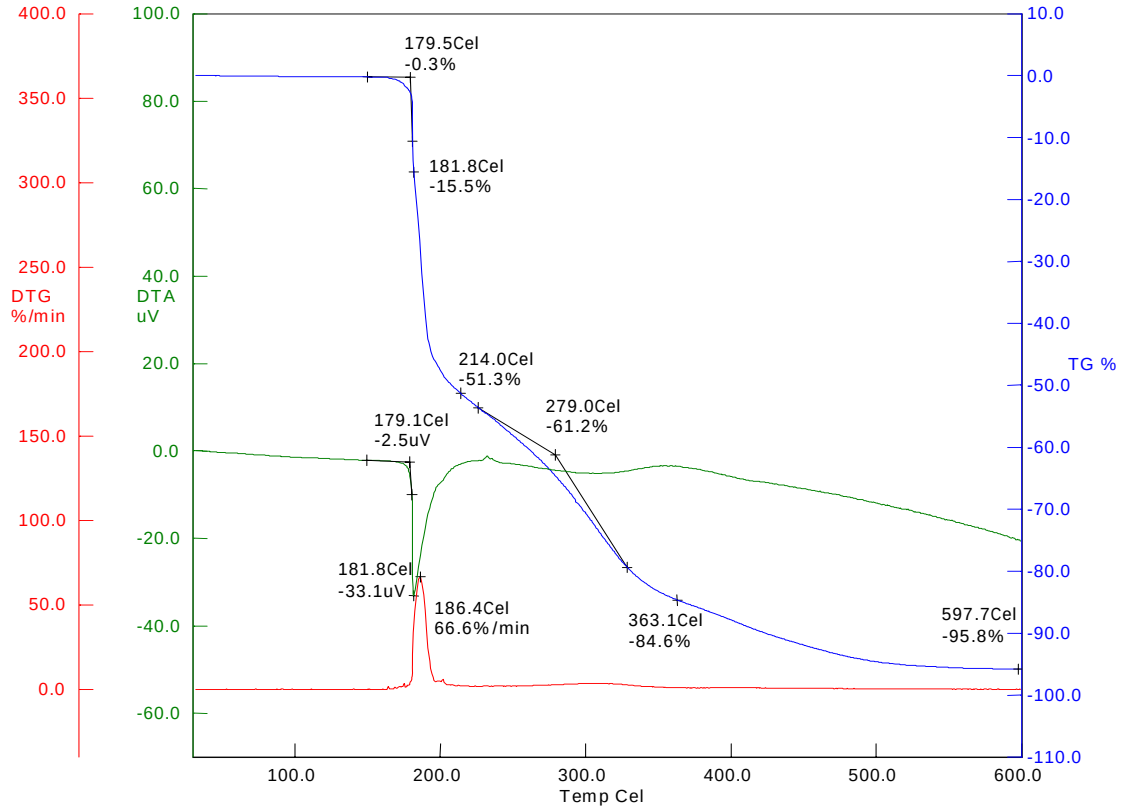
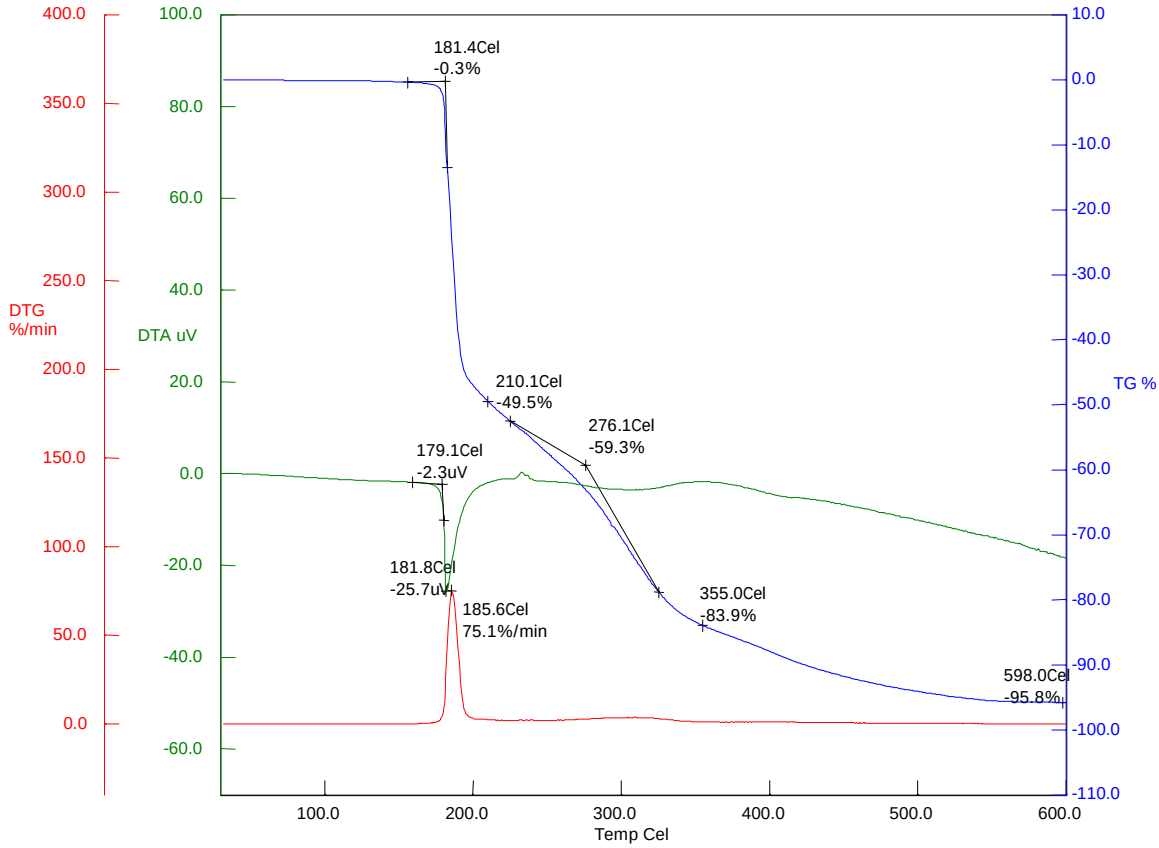
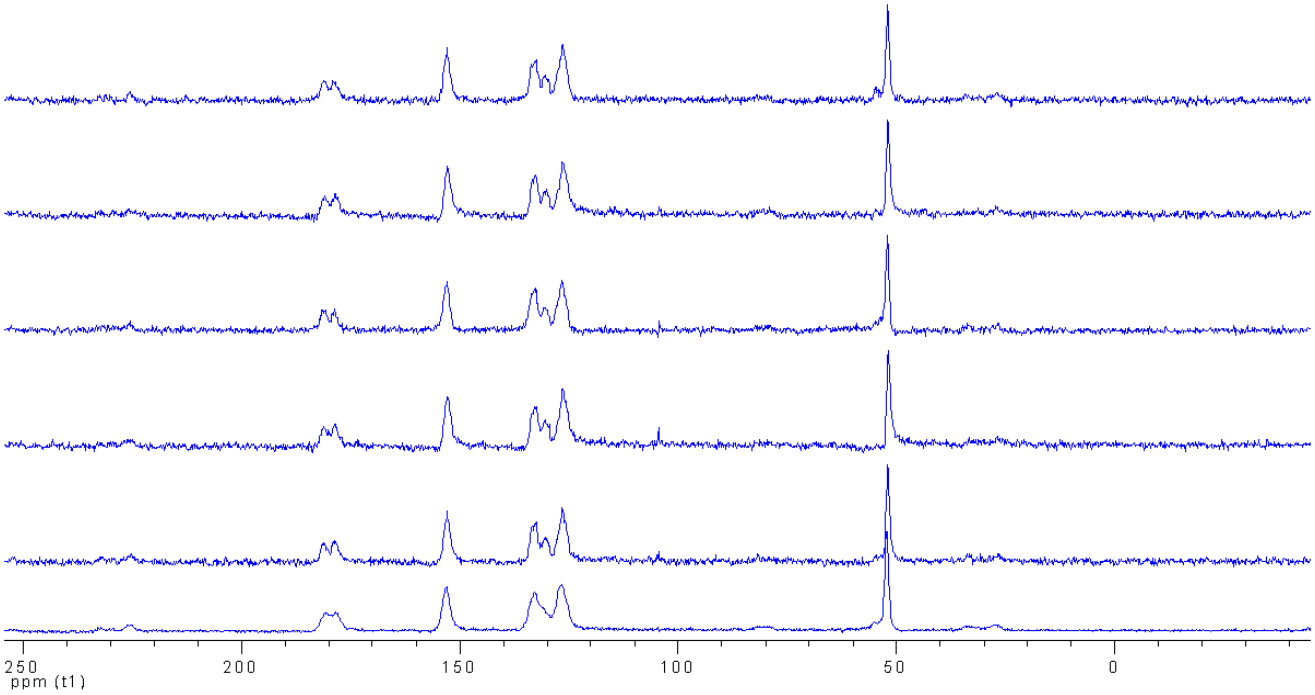


Figure III. TG/DTA of form II



CP/MAS NMR

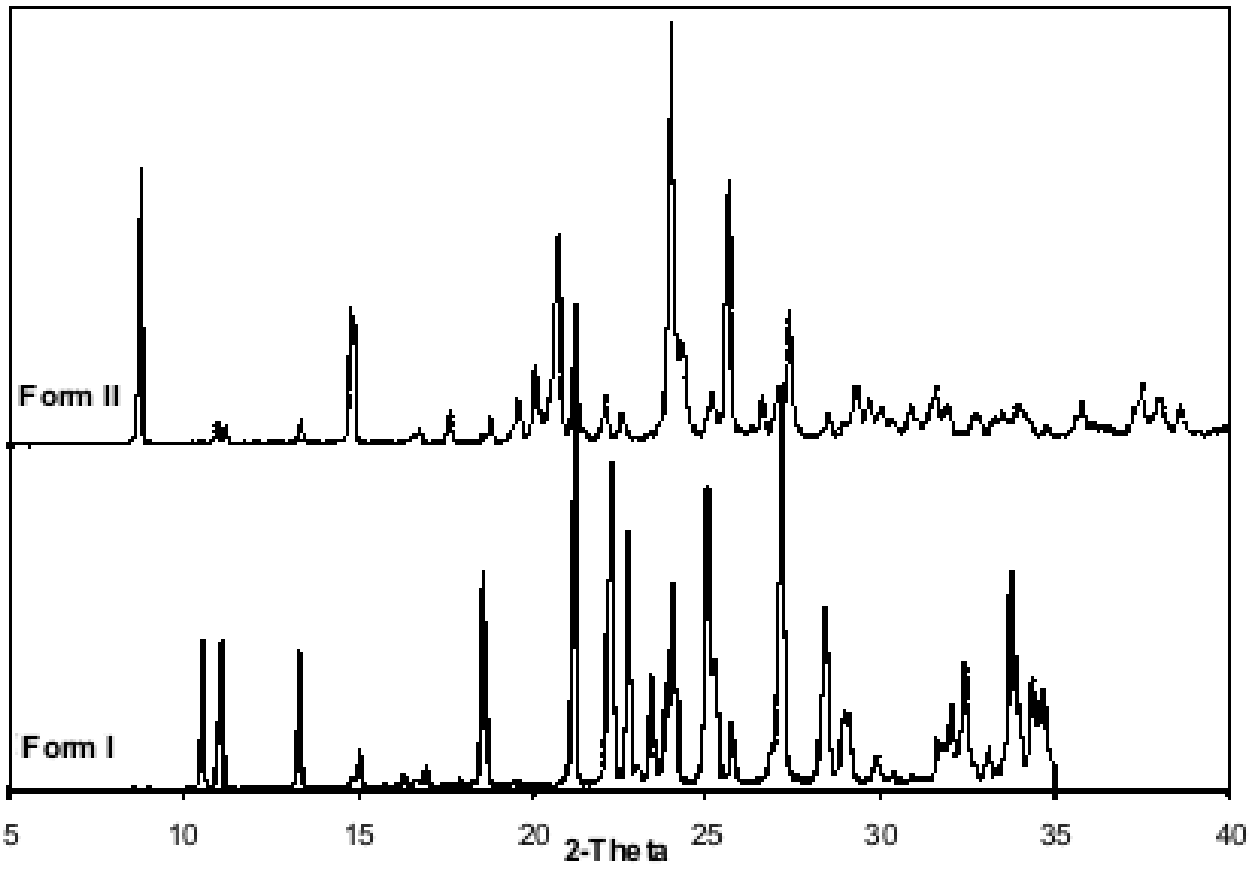
Figure IV. ^{13}C CP/MAS NMR spectra of form II at rising temperatures (RT-100°C)



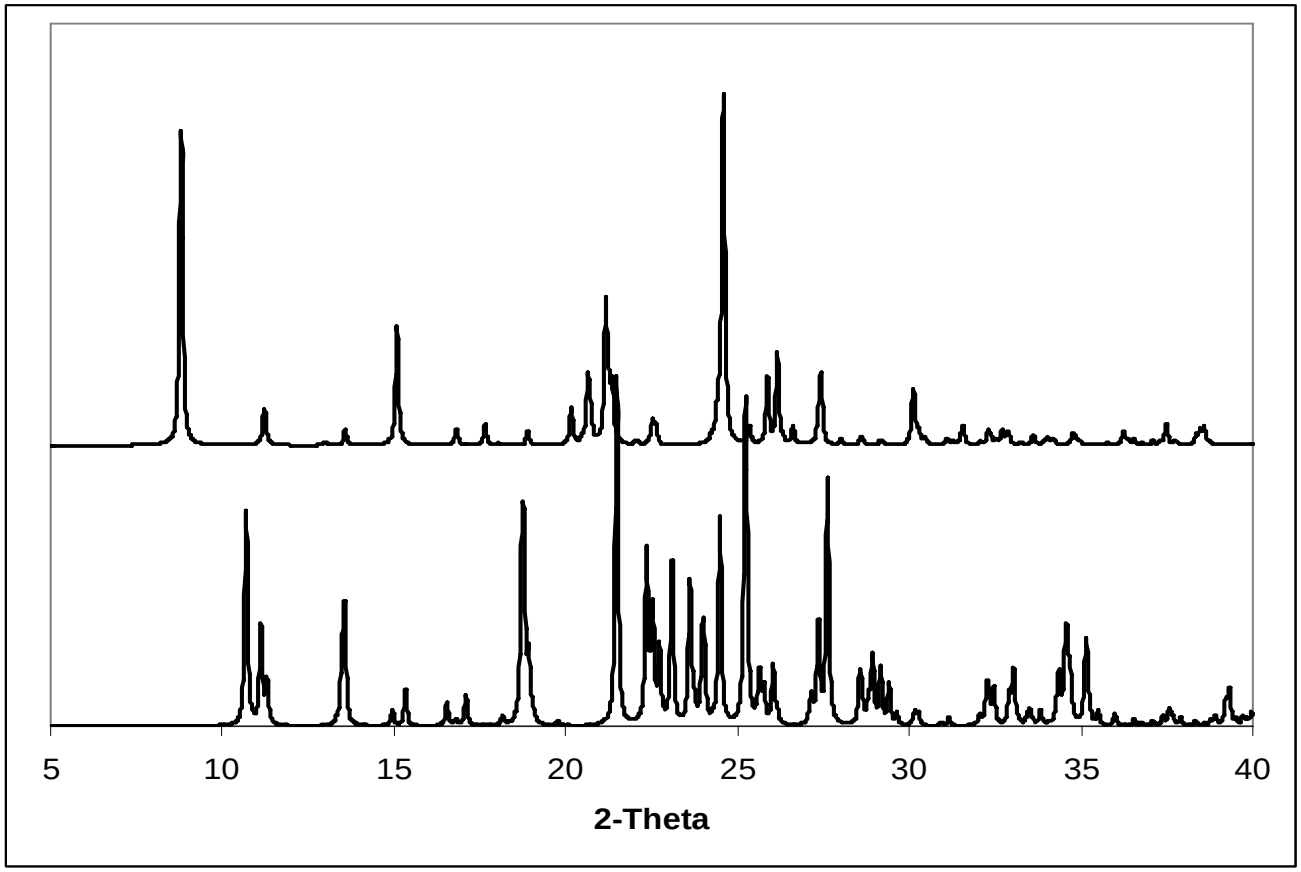
Calculated PXRDs

Comparison of the calculated and experimental PXRD patterns of form I and form II.

Experimental



Calculated



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Hydrogen bonding parameters

Table 1 H-bond parameters in the form-I-like pairs

Solvate	Pair - Intermolecular				Pair - Intramolecular				Chain	
	N-H···S		N-H···O=C		N-H···S		N-H···O=C		N-H···S	
	d(D...A)	<(DHA)	d(D...A)	<(DHA)	d(D...A)	<(DHA)	d(D...A)	<(DHA)	d(D...A)	<(DHA)
DCM	3.533(5)	134(6)	3.191(6)	148(6)	3.456(4)	131.1	2.666(5)	135.9	3.370(5)	175(6)
1,2-DCE	3.429(2)	139(2)	3.121(3)	138(2)	3.360(2)	133(2)	2.670(3)	136(2)	3.338(2)	171(2)
Form I	3.472(3)	146(3)	3.445(4)[a]	138(3)	3.419(3)	134(3)	2.670(4)	137(3)	-	-
Chain		**N-H···O=C**	2.984(4)	138(4)						
		N-H···O-C	3.282(4)	132(3)						

[a] Rather long hydrogen bond but fitting to the structure.

Table 2 H-bond parameters in form II, the one- and two-armed chains and the MeCN solvate mono hydrate

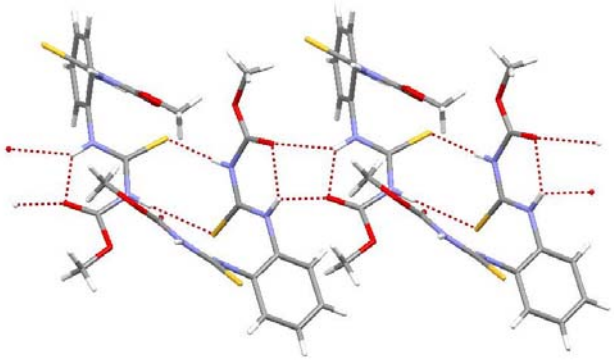
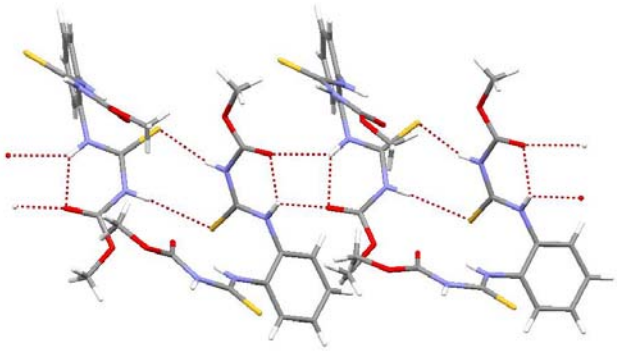
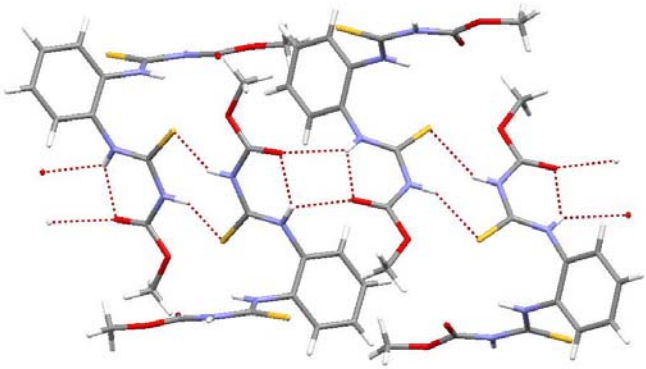
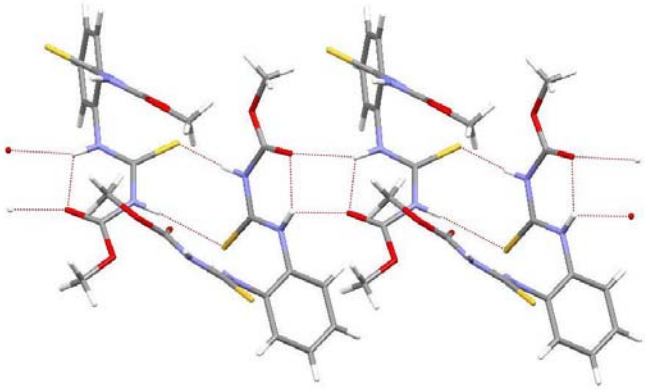
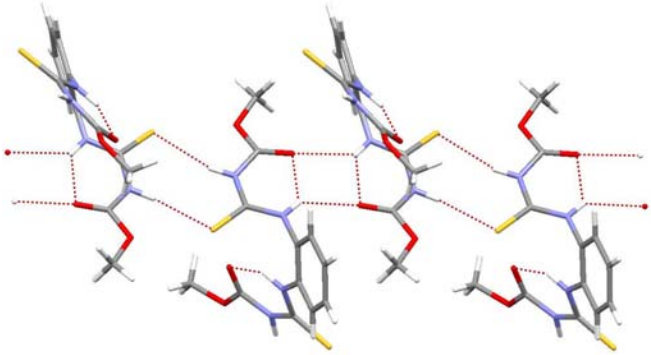
Solvate	N-H···S homosynthon				N-H···O=C homosynthon			
	d(D...A)	<(DHA)	d(D...A)	<(DHA)	d(D...A)	<(DHA)	d(D...A)	<(DHA)
Form II	3.371(2)	174(2)	3.247(2)	157(2)	3.082(3)	129(2)	3.086(3)	121(2)
Methanol	3.414(7)	178.0	3.325(6)	177.7	3.012(9)	136.0	3.022(8)	138.1
Ethanol	3.36(2)	177.1	3.29(2)	177.4	2.97(2)	139.0	2.95(2)	136.9
Cyclohexanone	3.306(3)	169.4	3.516(3)	171.6	3.061(3)	137.0	2.984(3)	136.1
	3.316(3)	163.0	3.365(3)	168.9	2.978(3)	137.0	2.921(3)	134.4
DMSO	3.322(5)	145.1	-	-	3.036(6)	135.0	-	-
THF	3.380(3)	159(3)	3.287(3)	171(4)	2.956(4)	135(3)	2.964(4)	131(3)
Chloroform	3.326(3)	164(3)	3.279(3)	168(4)	2.990(4)	138(3)	2.986(4)	134(3)
Dioxane	3.299(4)	171(4)	-	-	3.060(4)	140(3)	-	-
Pyridine	3.312(2)	162(2)	-	-	3.382(2)	144(2)	-	-
MeCN/H_2O	3.293(4)	159(5)	3.464(4)	166(5)	3.235(5)	136(4)	3.165(6)	137(4)
	3.283(4)	164(4)	3.334(4)	172(5)	3.034(5)	132(4)	3.048(5)	139(4)

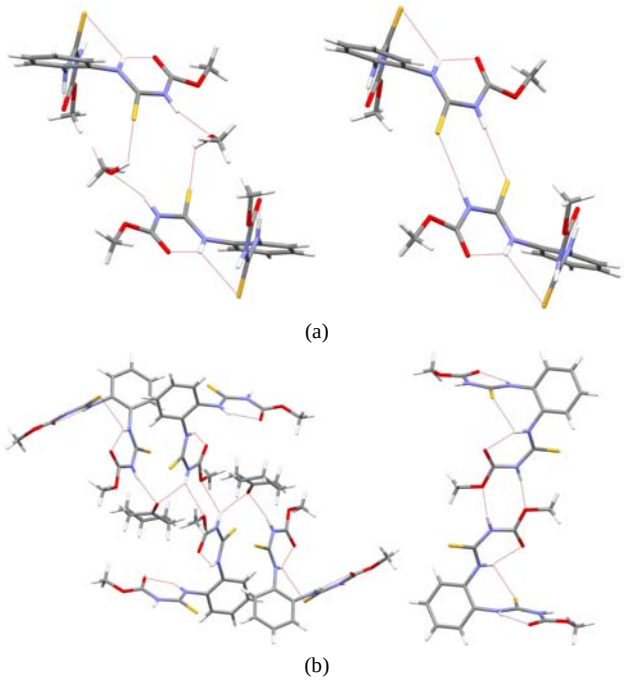
Table 3 Hydrogen bonding parameters in the aromatic structures

Solvate	N-H···S		N-H···O-C		N-H···O=C	
	d(D...A)	<(DHA)	d(D...A)	<(DHA)	d(D...A)	<(DHA)
1.2-dichlorobenzene	3.553(2)	138(2)	-	-	2.920(3)	173(3)
-Homosynthon	3.346(2)	161(3)	-	-	2.920(3)	130(2)
Benzene	3.342(2)	167(2)	3.263(2)	164(2)	-	-

Solvates

One-armed chains of TM molecules connected by N-H•••S and N-H•••O=C hydrogen bonds in other than the MeOH solvate.

EtOH solvate	Cyclohexanone solvate
	
DMSO solvate	THF solvate
	
Chloroform solvate	
	



(a)

(b)

Fig. Connecting arrangements between the one-armed chains in the (a) methanol and (b) cyclohexanone solvates.

Conformations

Table 4 Relevant torsion angles of the molecules with markedly differing conformations

	Form I	**Form II**	**1,2-DCB**	**Benzene**
C3-N2-C4-C5	-105.4(4)	-69.1(3)	114.8(3)	-83.2(39
C10-N3-C9-C8	-39.4(6)	-56.2(3)	61.9(4)	-25.4(4)
C3-N2-C4-C9	79.6(5)	112.3(2)	67.5(3)	98.1(2)
C10-N3-C9-C4	141.5(4)	126.3(2)	-119.6(3)	158.0(2)