Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

to

Computational and Experimental Study of Reversible Hydration/Dehydration Processes in Molecular Crystals of Natural Products – A Case of Catechin

Marta K. Dudek, Agata Jeziorna, Marek J. Potrzebowski

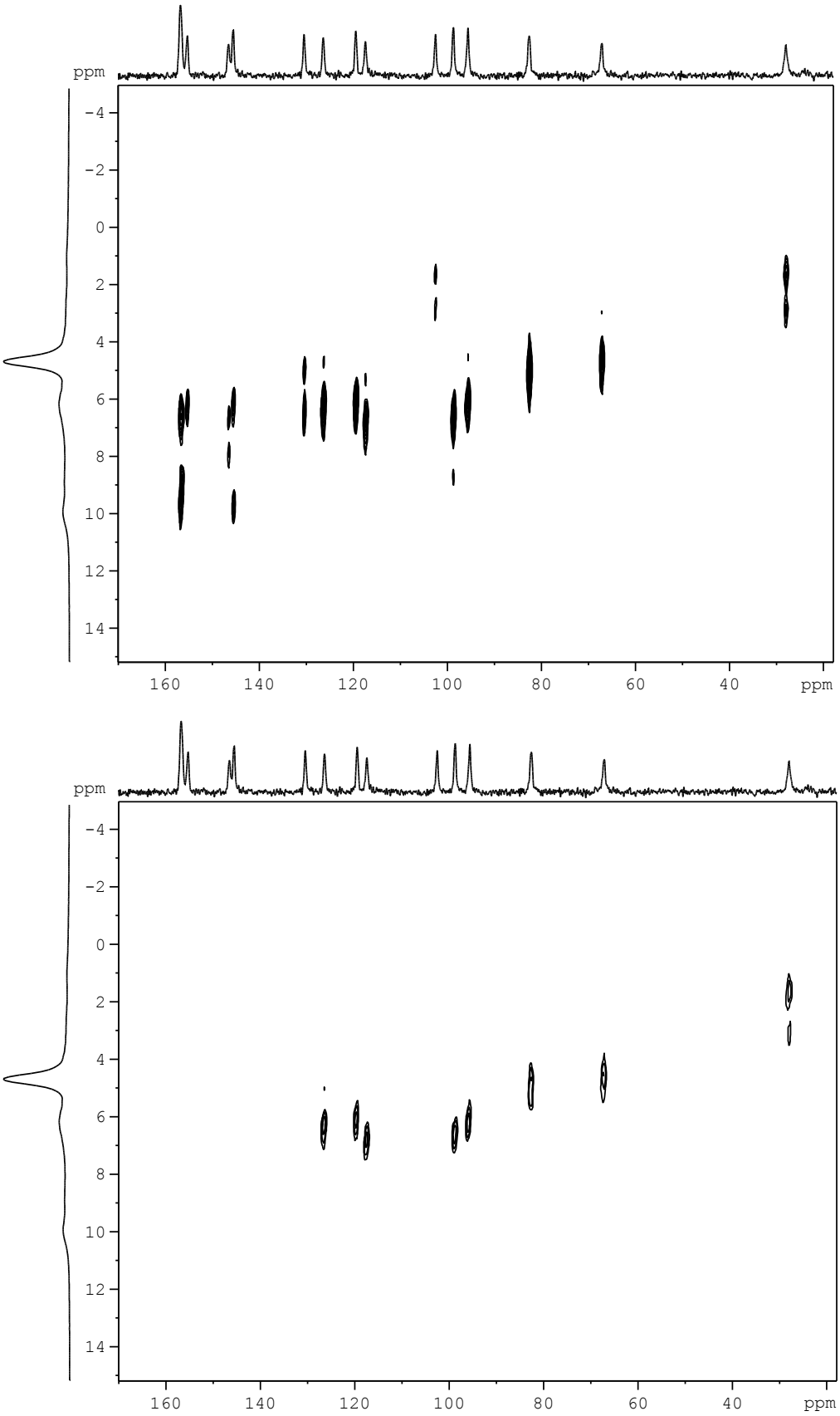


Fig. S1. ^{1}H-^{13}C FSLG HETCOR spectra (600 MHz, RO=20kHz) of (+)-catechin form I registered with 800 (upper) and 100us (lower).

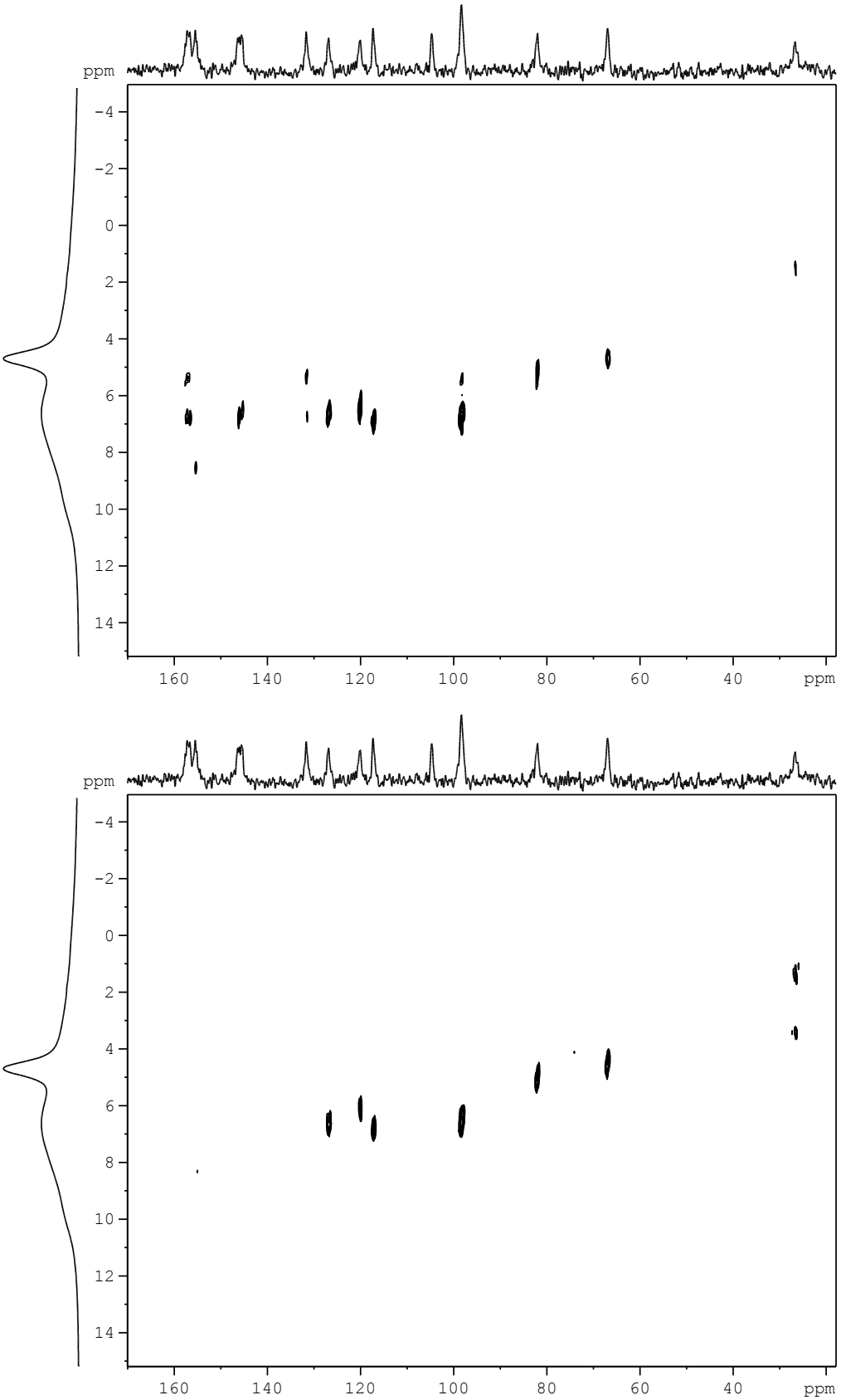


Fig. S2. ^{1}H-^{13}C FSLG HETCOR spectra (600 MHz, RO=20kHz) of (+)-catechin form II registered with 800 (upper) and 75us (lower).

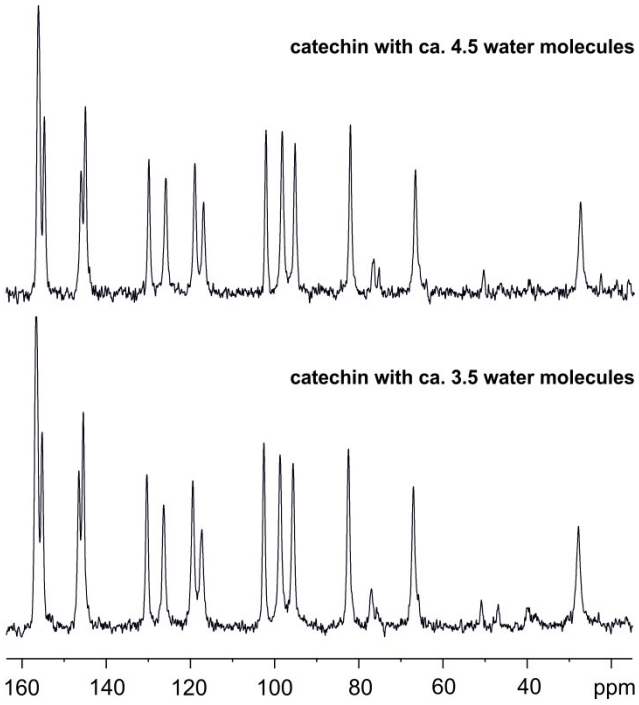


Fig. S3. ^{13}C CPMAS spectra of form I with different water content, corresponding to that included in Table 2

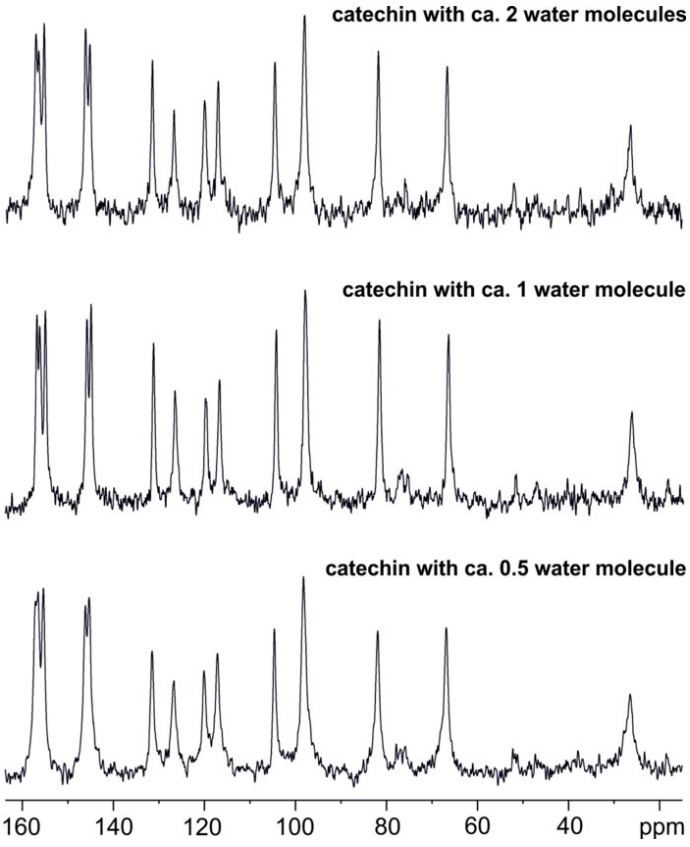


Fig. S3. ^{13}C CPMAS spectra of form I with different water content, corresponding to that included in Table 2

Calculations of (+)-catechin CSTs for structures with variable C3-C2-C11-C12 dihedral angle.

The CSTs for isolated molecule of (+)-catechin were calculated in order to determine the influence of the C3-C2-C11-C12 dihedral angle value changes on the respective NMR parameters. Crystal structure of 4.5-hydrate was used as a starting geometry and optimized at B3LYP/6-31G(d,p) level of theory using Gaussian09 software [S1]. Then, the relaxed scan procedure was performed with a step of 10° for changes in the C3-C2-C11-C12 dihedral angle value. For each resulting structure the NMR parameters were calculated at PBE0/6-31G(d,p) level of theory.

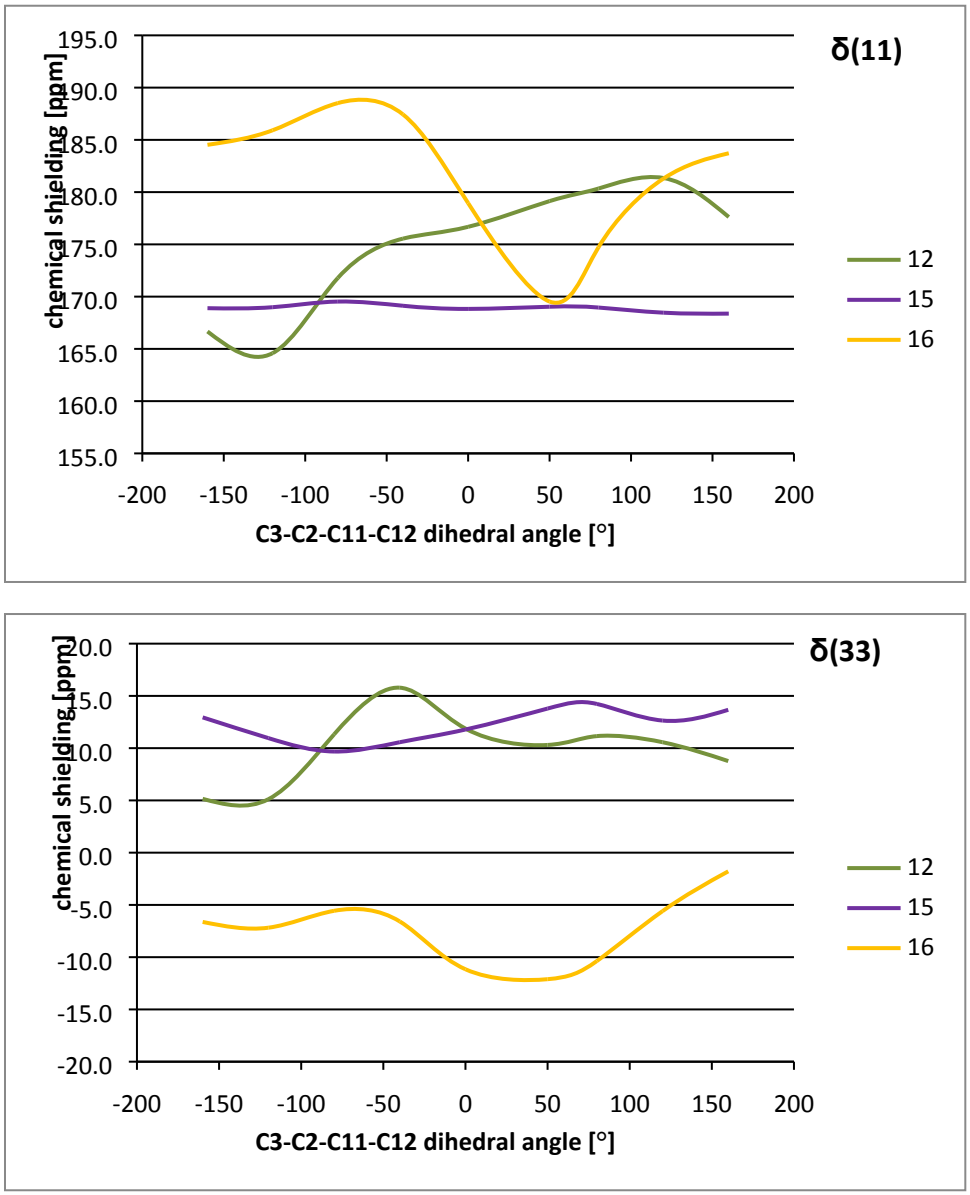


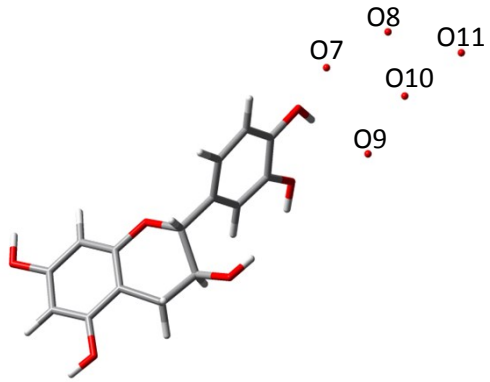
Fig. S3. The δ_{11} and δ_{33} components of chemical shielding tensor dependence on the C3-C2-C11-C12 dihedral angle for carbons C-12, C-15 and C-16 calculated at the following levels of theory: geometry optimization – B3LYP/6-31G(d,p); NMR calculations – PBE0/6-31G(d,p)

Table S1. Hydrogen bonding network for the predicted structures of partially dehydrated (+)-catechin

	4.5-hydrate	1-hydrates								1.5-hydrates			
		(2)	(3)	(4)	(5)	(21)	(22)	(23)	(24)	(6)	(7)	(8)	(9)
O1…OH14					1.817								1.887
O1…H_2O		1.793								1.775			
OH3…OH3	2.962	3.178	2.296	3.001							2.294	1.996	
OH3…OH5/7						1.815	1.817	2.502					
OH3…OH13	1.866	1.906		1.874		2.132	2.134			1.837			
OH3…H_2O						1.855	1.857	2.228					
OH5…OH7	1.758	1.865	1.646	1.804	1.661					1.794	1.715	1.708	1.557
OH5…OH13/14			1.807			1.649	1.654	1.747					
OH5…H_2O	1.938			1.801	1.813	1.859	1.866	2.957				1.604	1.585
	2.133			1.860								1.970	
	2.950												
OH7…H_2O	1.738		1.818		1.917					2.057	1.730	1.861	1.878
													1.960
OH13…H_2O	1.935		1.847	2.002	2.062	1.852	1.860						
OH14…H_2O	1.806	1.540	1.941		2.295					1.544	1.793		
		1.793								1.927	2.924		

	2-hydrates						2.5-hydrates					
	(10)	(11)	(12)	(13)	(14)	(25)	(15)	(16)	(17)	(18)	(19)	(20)
O1…OH3						1.970						
O1…OH14				1.960								
O1…H_2O		1.775							1.744			
OH3…OH3		2.978			3.227					3.003		
OH3…OH5/7								2.937				
OH3…OH13	1.919	1.795	1.846		1.846	1.887	1.910	1.811	1.789	1.811		1.842
OH3…H_2O						1.918						
OH5…OH7	1.752	1.797	1.703	1.671	1.715		1.767	1.776	1.705	1.739	1.642	1.724
OH5…H_2O		1.862	1.668	1.765	1.797	1.648	1.735	1.819	1.729	1.819	1.682	1.786
		1.865	1.935		2.060			1.870		1.837		1.933
OH7…H_2O	1.848		1.932	1.802	1.948	1.625		2.114	1.876	1.870	1.642	2.008
OH13…H_2O	1.870	1.915				1.831	1.943	1.954		1.954	2.064	1.830
OH14…H_2O	1.661	1.635	1.945	1.900	2.195		1.561	1.631	1.639	1.916	1.855	1.897
		1.837						1.852	1.886		1.649	

Estimation of the energy share of each of water molecules.



Manual modification of the crystal structure of 4.5-hydrate of (+)-catechin involved removal of particular water molecules in all possible combinations so that 0.5, 1, 1.5, 2 or 2.5 water molecules per catechin remain. For each of the partially dehydrated, as well as for fully dehydrated crystals, energy optimization was performed. The water energy share was estimated by subtraction of the energy of fully dehydrated crystals from the energies of 0.5-hydrate (O11) and particular 1-hydrates (O7, O8, O9, O10). Then, the energy share of each water molecule was subtracted accordingly from the energies of the higher hydrates, so that the energies of differently hydrated crystals can be compared. The results are gathered in Table S2 below.

Hydrate		Retained water molecule(s)	Energy (kcal/mol)	Energy share of each water (kcal/mol)
0.5- and 1-hydrates	(1)	O11	-252016	-10893
	(2)	O7	-262928	-21805
	(3)	O8	-262929	-21807
	(4)	O9	-262920	-21798
	(5)	O10	-262929	-21806
anhydrous			**-241122**	
Hydrate		Retained water molecule(s)	Energy (kcal/mol)	Energy without water energy share (kcal/mol)
1.5-hydrates	(6)	O7, O11	-273820	-241121
	(7)	O8, O11	-273826	-241125
	(8)	O9, O11	-273829	-241137
	(9)	O10, O11	-273823	-241123
2-hydrates	(10)	O7, O8	-284723	-241111
	(11)	O7, O9	-284738	-241135
	(12)	O8, O9	-284728	-241123
	(13)	O8, O10	-284729	-241129
	(14)	O9, O10	-284720	-241116
2.5-hydrates	(15)	O7, O8, O11	-295621	-241116
	(16)	O7, O9, O11	-295631	-241134
	(17)	O7, O10, O11	-295630	-241125
	(18)	O8, O9, O11	-295630	-241132
	(19)	O8, O10, O11	-295630	-241123
	(20)	O9, O10, O11	-295631	-241133