Table S 6 Calculated structural parameters of caffeine monohydrates{$Caff_1$-$(H_2O)_1$}.

Parameters [a]	MP2/6-311++G(d,p)					
	Bare caffeine Conformer **(A)**	Conformer **(I)**	Conformer **(II)**	Conformer **(III)**	Conformer **(IV)**	Conformer **(V)**
Bond lengths (Å)						
N1-C2	1.4119	1.4151	1.4151	1.4055	1.4038	1.4142
C2-N3	1.3831	1.3834	1.3834	1.3771	1.3799	1.3890
N3-C4	1.3768	1.3773	1.3773	1.3789	1.3789	1.3761
C4-C5	1.3870	1.3899	1.3899	1.3875	1.3865	1.3865
C5-C6	1.4378	1.4347	1.4347	1.4347	1.4374	1.4390
C6-N1	1.4101	1.4036	1.4036	1.4036	1.4141	1.4077
C5-N7	1.3745	1.3763	1.3762	1.3745	1.3743	1.3743
N7-C8	1.3637	1.3617	1.3617	1.3639	1.3640	1.3602
C8-N9	1.3377	1.3385	1.3386	1.3372	1.3379	1.3398
N9-C4	1.3591	1.3566	1.3567	1.3584	1.3583	1.3619
N1-C10	1.4659	1.4671	1.4671	1.4667	1.4698	1.4666
C2-O11	1.2241	1.2229	1.2229	1.2317	1.2311	1.2220
N3-C12	1.4608	1.4621	1.4621	1.4671	1.4622	1.4642
C6-O13	1.2279	1.2348	1.2347	1.2268	1.2262	1.2274
N7-C14	1.4591	1.4627	1.4627	1.4597	1.4597	1.4602
C8-H1	1.0819	1.0820	1.0820	1.0820	1.0820	1.0820
Bond angles (º)						
C2-N1-C6	127.53	127.04	127.05	126.99	126.76	127.05
N1-C2-N3	116.92	116.50	116.49	117.54	117.39	116.74
C2-N3-C4	120.01	119.50	119.53	119.32	119.44	119.13
N3-C4-C5	121.09	121.47	121.47	121.28	121.10	121.50
C4-C5-C6	123.88	122.91	123.91	123.59	123.55	123.53
C5-C6-N1	110.57	111.29	110.28	110.45	110.69	110.59
N9-C4-C5	111.89	111.99	111.99	111.88	111.99	111.28
C4-C5-N7	105.32	105.18	105.18	105.30	105.26	105.63
C5-N7-C8	106.99	105.89	105.89	105.95	105.98	106.18
N7-C8-N9	113.38	113.62	113.61	113.41	113.38	113.03
C8-N9-C4	103.42	103.30	103.30	103.44	103.36	103.87
C5-C6-O13	126.04	126.46	126.47	126.46	126.33	126.02
O13-C6-N1	123.39	122.25	122.24	123.06	122.96	123.38
C6-N1-C10	118.09	117.84	117.87	117.73	117.29	117.43
C10-N1-C2	114.38	114.38	114.36	114.78	115.41	114.65
N1-C2-O11	121.06	120.96	120.96	120.28	121.44	120.85
O11-C2-N3	122.02	122.50	122.51	122.17	121.13	122.36
C2-N3-C12	118.05	118.08	118.09	119.33	118.25	118.17
C12-N3-C4	121.95	120.77	120.74	121.33	121.07	121.06
N3-C4-N9	127.03	126.52	126.52	126.84	126.90	127.21
N9-C8-H1	125.02	124.93	124.94	125.00	125.01	125.03
H1-C8-N7	121.59	121.45	121.44	121.60	121.61	121.94
C8-N7-C14	127.22	126.53	126.669	127.19	127.22	127.09
C14-N7-C5	126.79	127.51	127.55	126.81	126.77	126.72
N7-C5-C6	130.80	131.58	131.59	130.74	130.87	130.55
Dihedral angles (º)						
N3-C4-C5-N7	179.98	179.75	179.88	179.39	179.84	179.81
N9-C4-C5-C6	179.95	175.78	175.93	175.46	175.81	175.66
C=O...H-OH		-29.41	30.14	5.25	-5.26	
N1-C6-O13...OH_2		-127.46	127.45			
C5-C6-O13...OH_2		51.33	-51.30			
N1-C2-O11...OH_2				139.03	38.81	
N3-C2-O11...OH_2				-39.60	-143.81	
N7-C8-N9...OH_2						-159.42
C5-C4-N9...OH_2						158.26

Table S 7 Calculated NBO Charges of caffeine monohydrates at MP2/6-311++G(d,p) level.

Atom No.	NBO Charge				
	Conformer I	Conformer II	Conformer III	Conformer IV	Conformer V
O11	-0.727	-	-0.778	-0.778	-0.725
O13	-0.773	-	-0.721	-0.716	-0.721
N1	-0.619	-	-0.619	-0.619	-0.624
N3	-0.577	-	-0.572	-0.574	-0.579
N7	-0.442	-	-0.443	-0.442	-0.435
N9	-0.612	-	-0.606	-0.607	-0.657
C2	1.016	-	1.031	1.032	1.018
C4	0.485	-	0.478	0.473	0.488
C5	-0.088	-	-0.083	-0.080	-0.080
C6	0.836	-	0.821	0.821	0.821

Parameters	Calculated values at MP2/6-311++G(d,p) level					
	Conformer (A) of bare caffeine	Conformer **(I)**	Conformer **(II)**	Conformer **(III)**	Conformer **(IV)**	Conformer **(V)**
A (GHz)	1.0618291	0.8001420	0.8000160	0.9585128	0.9874298	0.7257027
B (GHz)	0.7037817	0.5296876	0.5296528	0.4430883	0.4321887	0.5518783
C (GHz)	0.4266568	0.3348015	0.3348300	0.3119960	0.3121389	03178640
ZPVE*	117.87432	133.09525	133.09877	132.92729	132.90136	133.70439

Table S8 Rotational constants (GHz) and zero-point vibrational energy (kcal mol^{-1}) of the most stable conformers of caffeine monohydrate.
*values obtained at B3LYP/6-311++G(d,p) level using MP2/6-311++G(d,p) level optimized geometries.

Table S 9 Selected ground state vibrational stretching frequencies (cm^{-1}) and IR intensity with tentative vibrational assignments of the most stable conformers of caffeine monohydrate

Assignment	Calculated values at B3LYP/6-311++G(d,p) level				
	Conformer **(I)**	Conformer **(II)**	Conformer **(III)**	Conformer **(IV)**	Conformer **(V)**
(OH)2 Str.()	3916(92)	3916 (92)	3918(93)	3919(97)	3911 (85)
(OH)2 Str.()	3712(480)	3713 (478)	3718(524)	3730 (526)	3650 (742)
NH str.	3226 (2)	3226 (2)	3225 (2)	3225 (2)	3228 (4)
CH_3 str. (+) at N_1	3050 (24)	3050 (24)	3051 (25)	3056 (11)	3051 (24)
CH_3 str. (+) at N_3	3039 (32)	3039 (32)	3048 (20)	3040 (31)	3034 (29)
CH_3 str. (+) at N_7	3049 (22)	3049 (22)	3049 (24)	3050 (26)	3048 (27)
$(C=O)_2$ sym. str.	1727 (486)	1727 (486)	1724 (471)	1725 (513)	1733 (441)
$(C=O)_2$ asym. str.	1675 (977)	1675 (978)	1674 (957)	1675 (881)	1690 (889)
C=C str.	1600 (104)	1600 (104)	1601 (65)	1604 (56)	1606 (99)
(C=N + C=C) str.	1577 (91)	1577 (91)	1579 (126)	1580 (135)	1579 (153)

Abbreviations used: (+), in phase; (-), out of phase.