Electronic Supplementary Material (ESI) for RSC Advances.

Table S 1 Calculated total electronic energies (A.U), relative energies (kJ/mol) in parenthesis and dipole moment (Debye) of two lowest energy theophylline tautomers **.**

Theophylline Tautomers	**MP2/ 6-311++G(d,p) values**	**DFT/6-311++G(d,p) values**				
		M06	M06-2X	X3LYP	B3LYP	Wb97X-D
Tautomer (N7)H	-639.519435 (0.0) 4.276	-640.841284 (0.0) 3.592	-640.998360 (0.0) 3.590	-640.976490 (0.0) 3.593	-641.243702 (0.0) 3.580	641.032214 (0.0) 3.630
	-639.412059* 4.275 -639.489422** 3.351	-640.747949* 3.539	-	-	-640.800924 3.500	-640.947727* 3.581
Tautomer (N9)H	-639.503759 (41.12) 7.908	-640.825667 (40.96) 7.157	-640.982887 (40.59) 7.224	-640.960394 (42.22) 7.289	-641.227628 (42.16) 7.278	641.016183 (42.05) 7.320

*Corresponding values employing the basis seaug-cc-pvdz, ** Corresponding value at CC2/ aug-cc-pvdz level.

Table S 2 Calculated structural parameters of neutral theophylline

Structural parameters	Experimental values[a]	Calculated values at MP2/6-311++G(d,p) level	
		Tph Tautomer N(7) H	Tph Tautomer N(9)H
Bond lengths (Å)			
N1-C2	1.413	1.4125	1.3940
C2-N3	1.360	1.3843	1.3956
N3-C4	1.384	1.3759	1.3695
C4-C5	1.349	1.3827	1.3844
C5-C6	1.430	1.4371	1.4493
C6-N1	1.418	1.4090	1.4314
C5-N7	1.388	1.3710	1.3795
N7-C8	1.327	1.3645	1.3171
C8-N9	1.316	1.3340	1.3867
N9-C4	1.350	1.3537	1.3686
N1-C10	1.488	1.4661	1.4666
C2-O11	1.221	1.2237	1.2243
N3-C12	1.469	1.4610	1.4585
C6-O13	1.213	1.2266	1.2175
N7-H15/N9-H15	0.90	1.0119	1.0098
C8-H14	1.02	1.0808	1.0812
Bond angles (º)			
C2-N1-C6	126.6	127.45	128.01
N1-C2-N3	117.4	116.99	116.75
C2-N3-C4	119.7	119.89	118.49
N3-C4-C5	121.4	121.04	124.90
C4-C5-C6	124.8	124.19	120.48
C5-C6-N1	110.1	110.43	111.36
N9-C4-C5	111.3	111.84	105.89
C4-C5-N7	105.4	104.99	110.84
C5-N7-C8	105.7	106.78	104.52
N7-C8-N9	113.4	112.61	112.63
C8-N9-C4	104.2	103.78	106.12
C5-C6-O13	127.9	125.72	126.92
O13-C6-N1	122.0	123.85	121.72
C6-N1-C10	116.3	118.11	117.77
C10-N1-C2	117.1	114.44	114.22
N1-C2-O11	120.2	121.05	122.69
O11-C2-N3	122.4	121.96	120.56
C2-N3-C12	120.1	118.03	116.98
C12-N3-C4	120.2	122.08	124.53
N3-C4-N9	127.3	127.12	129.20
N9-C8-H14	125.0	125.04	121.33
H14-C8-N7	121.0	122.35	126.04
C8-N7-H15/C8-N9H15	126.0	127.72	126.07
H15-N7-C5/H15-N9-C4	128.0	125.50	127.81
N7-C5-C6	129.8	130.82	128.68
Dihedral angles (º)		Dihedral angles (º)	
N3-C4-C5-N7	-	-179.9976	179.99
N9-C4-C5-C6	-	179.9954	179.99

[a] Experimental values are taken from ref. 8

Table S 3 Rotational constants (GHz) and zero-point vibrational energy (kJ mol^{-1}) of the two most stable tautomers of theophylline

Rotational Constants/ZPVE	Calculated values at MP2/6-311++G(d,p) level	
	N(7)H	N(9)H
A (GHz)	4.94816	4.94582
B (GHz)	3.70273	3.65641
C (GHz)	2.13147	2.12201
ZPVE*	420.43444	418.1864

*values obtained at B3LYP/6-311++G(2d,2p) level using MP2/6-311++G(d,p) level optimized geometries.

Table S 4 Calculated structural parameters of theophylline monohydrates $\{Tph_1\text{-}(H_2O)_1\}$

Structural parameters	M06-2X/6-311++G(d,p)					
	Bare Theophylline **(N7H)**	Conformer **(I)**	Conformer **(II)**	Conformer **(III)**	Conformer **(IV)**	Conformer **(V)**
Bond lengths (Å)						
N1-C2	1.4042	1.4073	1.3985	1.3956	1.4105	1.4058
C2-N3	1.3832	1.3795	1.3750	1.3779	1.3846	1.3860
N3-C4	1.3722	1.3721	1.3737	1.3735	1.3704	1.3701
C4-C5	1.3704	1.3754	1.3707	1.3697	1.3708	1.3701
C5-C6	1.4343	1.4299	1.4327	1.4342	1.4294	1.4354
C6-N1	1.4062	1.3980	1.4097	1.4098	1.3936	1.4027
C5-N7	1.3761	1.3783	1.3757	1.3755	1.3766	1.3761
N7-C8	1.3513	1.3447	1.3514	1.3513	1.3514	1.3471
C8-N9	1.3208	1.3258	1.3204	1.3208	1.3205	1.3230
N9-C4	1.3579	1.3526	1.3570	1.3569	1.3575	1.3615
N1-C10	1.4637	1.4645	1.4643	1.4677	1.4682	1.4640
C2-O11	1.2119	1.2115	1.2202	1.2200	1.2097	1.2102
N3-C12	1.4591	1.4594	1.4638	1.4599	1.4600	1.4627
C6-O13	1.2139	1.2258	1.2130	1.2123	1.2226	1.2137
N7-H15	1.0089	1.0235	1.0089	1.0089	1.0087	1.0092
C8-H14	1.0790	1.0790	1.0791	1.0790	1.0791	1.0788
Bond angles (º)						
C2-N1-C6	126.82	126.70	126.60	126.39	126.42	126.78
N1-C2-N3	117.35	117.15	117.99	118.06	116.84	117.53
C2-N3-C4	119.64	119.75	119.30	119.45	120.11	119.33
N3-C4-C5	121.30	121.54	121.39	121.17	121.25	121.44
C4-C5-C6	123.95	123.10	123.91	123.93	123.23	124.03
C5-C6-N1	110.93	111.76	110.80	110.99	112.15	110.87
N9-C4-C5	111.62	111.69	111.62	111.72	111.62	110.96
C4-C5-N7	104.97	104.98	104.98	104.93	104.99	105.30
C5-N7-C8	106.42	106.11	106.38	106.41	106.32	106.62
N7-C8-N9	112.92	113.46	112.94	112.92	113.01	112.58
C8-N9-C4	104.07	103.76	104.09	104.01	104.05	104.53
C5-C6-O13	125.77	126.34	126.03	125.79	125.36	125.51
O13-C6-N1	123.30	121.90	123.11	123.22	122.49	123.62
C6-N1-C10	118.29	118.66	118.17	118.12	116.02	118.32
C10-N1-C2	114.89	114.64	115.23	115.49	117.56	114.90
N1-C2-O11	121.14	120.94	120.27	121.42	122.16	120.92
O11-C2-N3	121.51	121.92	121.74	120.52	121.00	121.55
C2-N3-C12	118.10	118.12	118.74	118.39	117.84	117.61
C12-N3-C4	122.26	122.12	121.96	122.16	122.05	123.05
N3-C4-N9	127.08	126.77	126.99	127.11	127.13	127.60
N9-C8-H14	124.74	124.33	124.74	124.72	124.71	124.70
H14-C8-N7	122.34	122.21	122.32	122.36	122.28	122.72
C8-N7-H15	127.99	129.36	128.02	128.05	127.94	127.95
H15-N7-C5	125.59	124.53	125.60	125.53	125.73	125.43
N7-C5-C6	131.08	131.92	131.11	131.14	131.77	130.66
Dihedral angles (º)						
N3-C4-C5-N7	180.00	-179.83	-180.00	180.00	179.99	-179.59
N9-C4-C5-C6	-179.99	179.79	-179.99	180.00	-179.96	-179.60
C=O...H-OH	-	1.02	-0.11	-		
N1-C6-O13...OH_2	-	-178.57	-	-	1.63	
C5-C6-O13...OH_2	-	1.43	-	-	-178.39	
N1-C2-O11...OH_2	-	-	-179.69	0.00		
N3-C2-O11...OH_2	-	-	0.31	180.00		
N7-C8-N9...OH_2	-	-	-	-		175.46
C5-C4-N9...OH_2	-	-	-	-		-175.57
Dipole moment (Debye)	3.5899	2.7406	3.4280	5.1321	5.6913	4.3656

Table S 5 Natural atomic charges of Theophylline monomer and dimer's at the M06/6-311++G(d,p) level 0f theory

S.No	Atom	Monomer	Dimer Form IV	Dimer Form II	Dimer Form M
1.	O_{13}	-0.630	-0.706	-0.674(H-bonded)	-0.708
2.	O_{11}	-0.636	-0.634	-0.637	-0.628
3.	N_1	-0.537	-0.530	-0.539	-0.528
4.	N_7	-0.530	-0.541	-0.556(H-bonded)	-0.535
5.	C_5	-0.037	-0.043	-0.040	-0.044
6.	C_6	0.679	0.698	-0.690(H-bonded)	0.699
7.	N_3	-0.496	-0.492	-0.498	-0.490
8.	N_9	-0.531	-0.540	-0.599(H-bonded)	-0.594