SUPLEMENTARY MATERIAL

Table 1-supl. Optimized geometrical parameters at the B3LYP/6-311++G(3df,pd) level, bond lengths (in Å) and angles (in degrees), obtained in the thymine ring of the tautomers of the most stable conformers of D4T.

Parameters[a]	Conformer I			Conformer II			Conformer III			Conformer IV		
	T1	T3	T5	T1	T3	T5	T1	T3	T5	T1	T3	T5
Bond lengths												
N1-C2	1.3958	1.4297	1.3658	1.3924	1.4236	1.3629	1.3885	1.4209	1.3662	1.3955	1.4289	1.3661
C2-N3	1.3791	1.3729	1.2832	1.3787	1.3710	1.2834	1.3769	1.3688	1.2816	1.3789	1.3724	1.2830
N3-C4	1.3999	1.2979	1.3982	1.4005	1.2999	1.3987	1.4004	1.2989	1.3987	1.4000	1.2981	1.3980
C4-C5	1.4606	1.4295	1.4771	1.4580	1.4256	1.4751	1.4586	1.4264	1.4752	1.4608	1.4294	1.4773
C5=C6	1.3456	1.3558	1.3427	1.3464	1.3583	1.3431	1.3449	1.3559	1.3418	1.3449	1.3554	1.3419
N1-C6	1.3824	1.3610	1.3914	1.3810	1.3577	1.3900	1.3839	1.3615	1.3925	1.3806	1.3586	1.3900
N1-C7	1.4634	1.4653	1.4675	1.4668	1.4732	1.4694	1.4770	1.4792	1.4703	1.4645	1.4677	1.4679
C2=O	1.2128	1.2128	1.3448	1.2148	1.2163	1.3474	1.2164	1.2167	1.3468	1.2129	1.2133	1.3447
C4=O	1.2151	1.3417	1.2166	1.2163	1.3437	1.2178	1.2144	1.3402	1.2159	1.2149	1.3414	1.2164
C5-C_{methyl}	1.4972	1.4996	1.4954	1.4976	1.4999	1.4958	1.4969	1.4993	1.4951	1.4969	1.4993	1.4951
Bond angles												
N1-C2-N3	113.54	115.68	125.79	113.51	115.78	125.76	114.13	116.33	125.92	113.52	115.66	125.76
C2-N3-C4	128.57	120.98	120.51	128.47	120.68	120.40	128.64	121.07	120.83	128.57	120.98	120.53
N3-C4-C5	114.13	125.66	116.46	114.12	125.66	116.45	113.79	125.24	116.15	114.14	125.64	116.46
C4-C5=C6	118.08	113.64	118.59	118.26	113.88	118.77	117.95	113.48	118.43	117.98	113.55	118.49
C2-N1-C7	118.04	118.33	122.59	118.38	118.02	123.30	120.68	121.09	125.53	118.24	118.52	122.76
N3-C2=O	122.58	124.00	119.63	122.52	124.15	119.44	121.61	123.10	119.12	122.60	124.05	119.65
N3-C4=O	120.33	117.87	121.44	120.18	117.67	121.32	120.45	118.05	121.51	120.36	117.91	121.47
C4-C5-C_{methyl}	118.32	122.51	118.39	118.30	122.48	118.33	118.40	122.60	118.46	118.29	122.48	118.35
N1-C7-O11	110.40	110.34	110.43	110.15	110.07	110.21	110.98	110.93	111.05	110.31	110.19	110.57

[a]The numering of the atoms appear plotted in Figure 2.

Table 2-supl. Dipole moments (in Debye) calculated in the three tautomers of the most stable conformers of the D4T molecule.

Level of theory	Conformer I			Conformer II			Conformer III			Conformer IV		
	T1	T3	T5	T1	T3	T5	T1	T3	T5	T1	T3	T5
Isolated state:												
B3LYP/6-31G**	4.89	4.34	7.20	6.66	6.73	8.27	5.09	5.89	6.68	4.75	4.82	6.64
B3LYP/6-311++G(3df,pd)	5.20	4.63	7.57	7.01	6.96	8.71	5.46	6.11	7.21	5.04	5.07	6.97
MP2/6-31G**	5.91	5.32	7.91	7.64	7.66	9.43	6.15	6.89	7.91	5.90	5.94	7.81
Water solution (PCM):												
B3LYP/6-31G**	6.57	6.49	10.33	8.62	9.09	11.79	7.34	8.70	9.93	6.42	7.73	9.37
B3LYP/6-311++G(2d,p)	7.23	7.15	11.34	9.40	9.73	12.84	8.40	9.60	11.29	7.35	8.90	10.29

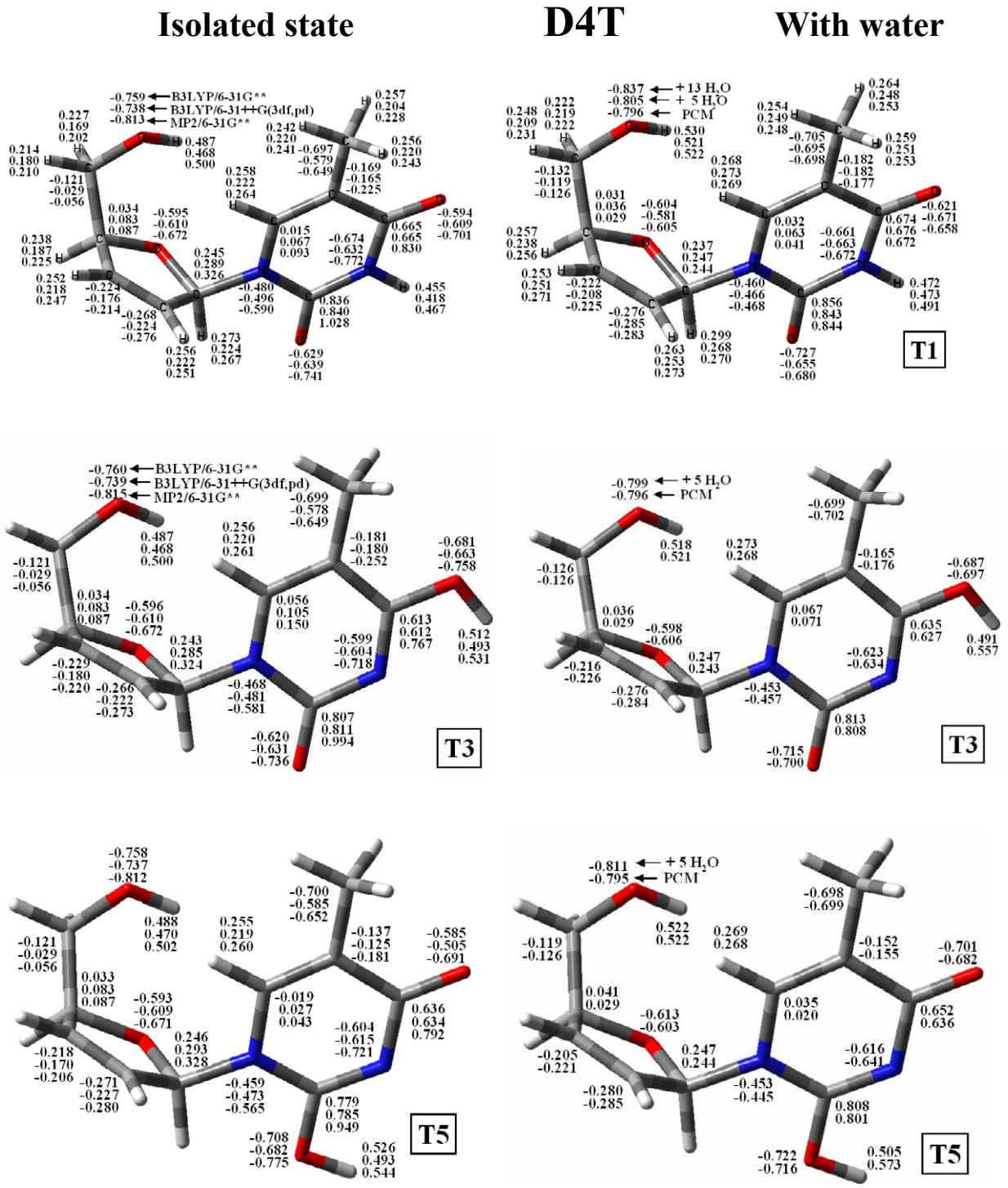
Table 3-supl. Dipole moments (in Debye) calculated in the three tautomers of the two most stable conformers of Thymidine nucleoside

Level of theory	Conformer I			Conformer II		
	T1	T3	T5	T1	T3	T5
Isolated state:						
B3LYP/6-31G**	4.27	2.98	6.50	6.80	6.55	8.29
B3LYP/6-311++G(3df,pd)	4.40	3.43	6.61	7.15	6.70	8.74
MP2/6-31G**	5.20	3.63	7.57	7.76	7.53	9.36
Water solution (PCM):						
B3LYP/6-31G**	4.27	-	-	9.14	9.57	11.57

Table 4-supl. Optimized geometrical parameters at the B3LYP/6-311++G(3df,pd) level, bond lengths (in Å) and angles (in degrees), obtained in the thymine ring of the three tautomers of the two most stable conformers of Thymidine nucleoside.

Parameters[a]	Conformer I			Conformer II		
	T1	T3	T5	T1	T3	T5
Bond lengths						
N1-C2	1.3954	1.4226	1.3653	1.3914	1.4220	1.3618
C2-N3	1.3791	1.3682	1.2831	1.3796	1.3705	1.2841
N3-C4	1.3996	1.3009	1.3974	1.3997	1.3005	1.3976
C4-C5	1.4604	1.4245	1.4771	1.4584	1.4252	1.4755
C5=C6	1.3450	1.3600	1.3419	1.3464	1.3590	1.3430
N1-C6	1.3810	1.3552	1.3904	1.3807	1.3565	1.3900
N1-C1’	1.4524	1.4691	1.4550	1.4604	1.4666	1.4625
C2=O	1.2126	1.2165	1.3447	1.2144	1.2164	1.3467
C4=O	1.2150	1.3427	1.2166	1.2164	1.3440	1.2179
C5-C_{methyl}	1.4968	1.4998	1.4950	1.4973	1.4998	1.4956
Bond angles						
N1-C2-N3	113.49	116.14	125.73	113.50	115.86	125.77
C2-N3-C4	128.62	120.64	120.59	128.50	120.60	120.41
N3-C4-C5	114.12	125.52	116.43	114.10	125.62	116.45
C4-C5=C6	117.99	113.92	118.50	118.20	113.84	118.74
C2-N1-C1’	118.49	122.57	123.24	118.50	117.38	123.40
N3-C2=O	122.63	124.74	119.61	122.54	124.39	119.49
N3-C4=O	120.39	117.79	121.51	120.27	117.70	121.42
C4-C5-C_{methyl}	118.32	122.48	118.36	118.29	122.49	118.33
N1-C1’-O4’	108.68	108.98	108.65	108.46	108.74	108.39

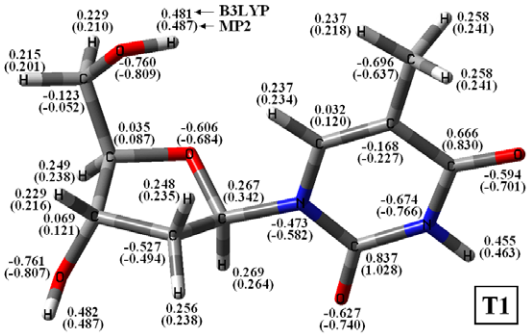
[a]The numering of the atoms appears plotted in Scheme 1.



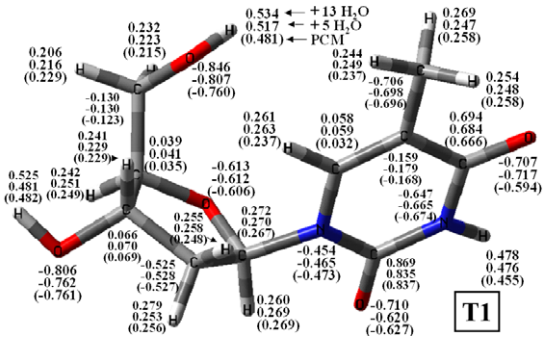
(Figure 1-supl). Optimised natural atomic charges (NBO) of conformer I of D4T in the isolated state at the B3LYP/6-31G**, B3LYP/6-311++G(3df,pd) and MP2/6-31G** levels, and under hydration at the B3LYP/6-31G** level and by using the PCM model.

Thymidine, conformer I

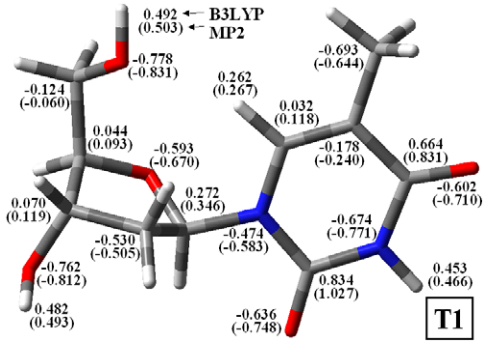
(isolated state)

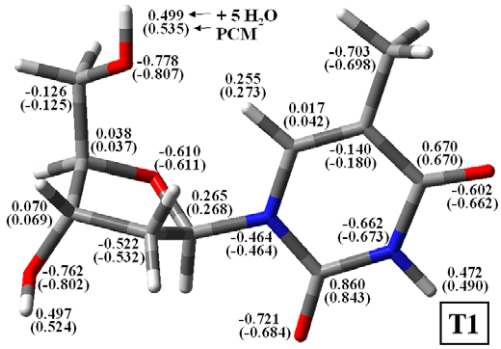


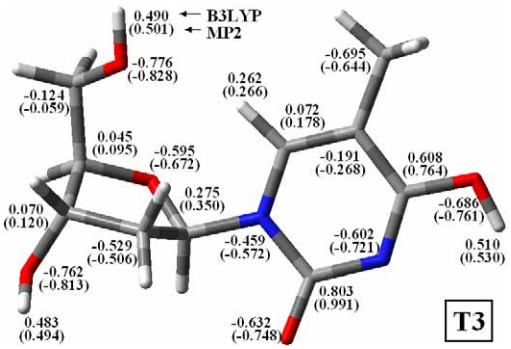
(with water)

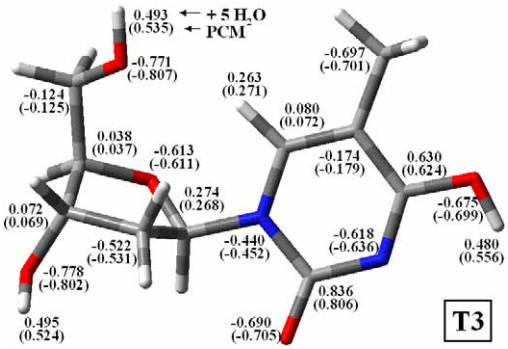


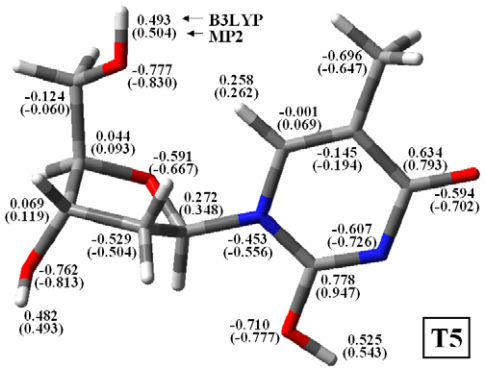
conformer II

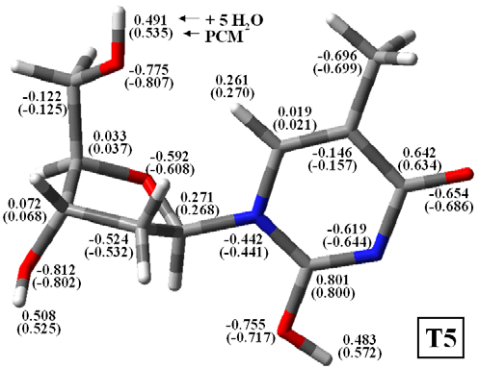






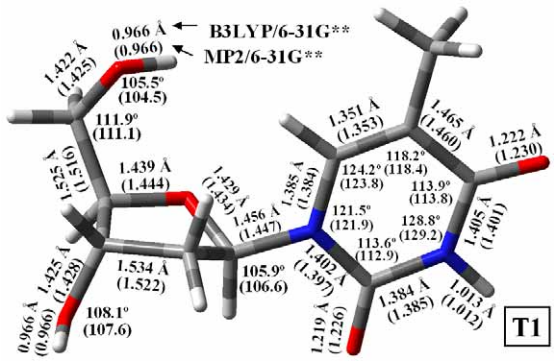




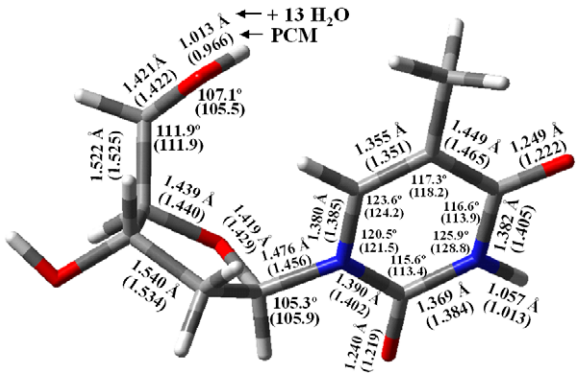


(Figure 2-supl). Optimised natural atomic charges (NBO) of conformers I and II of Thy in the isolated state at the B3LYP/6-31G**, B3LYP/6-311++G(3df,pd) and MP2/6-31G** levels, and under hydration at the B3LYP/6-31G** level and by using the PCM model.

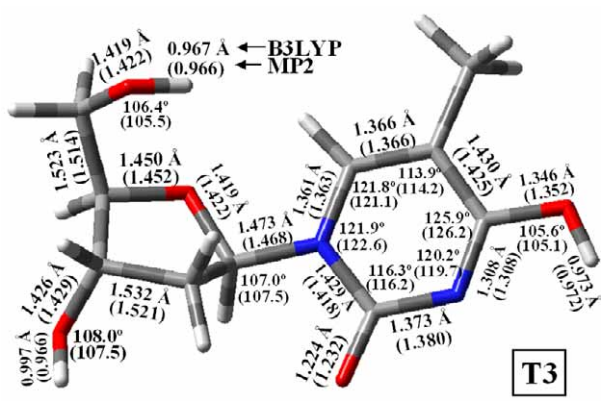
Thymidine, conformer I



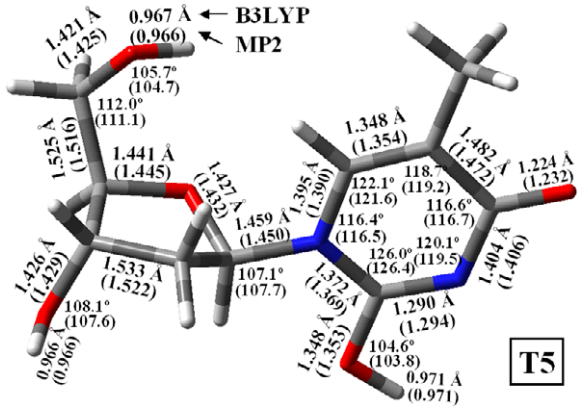
(Isolated state)



(With water)



(Isolated state)

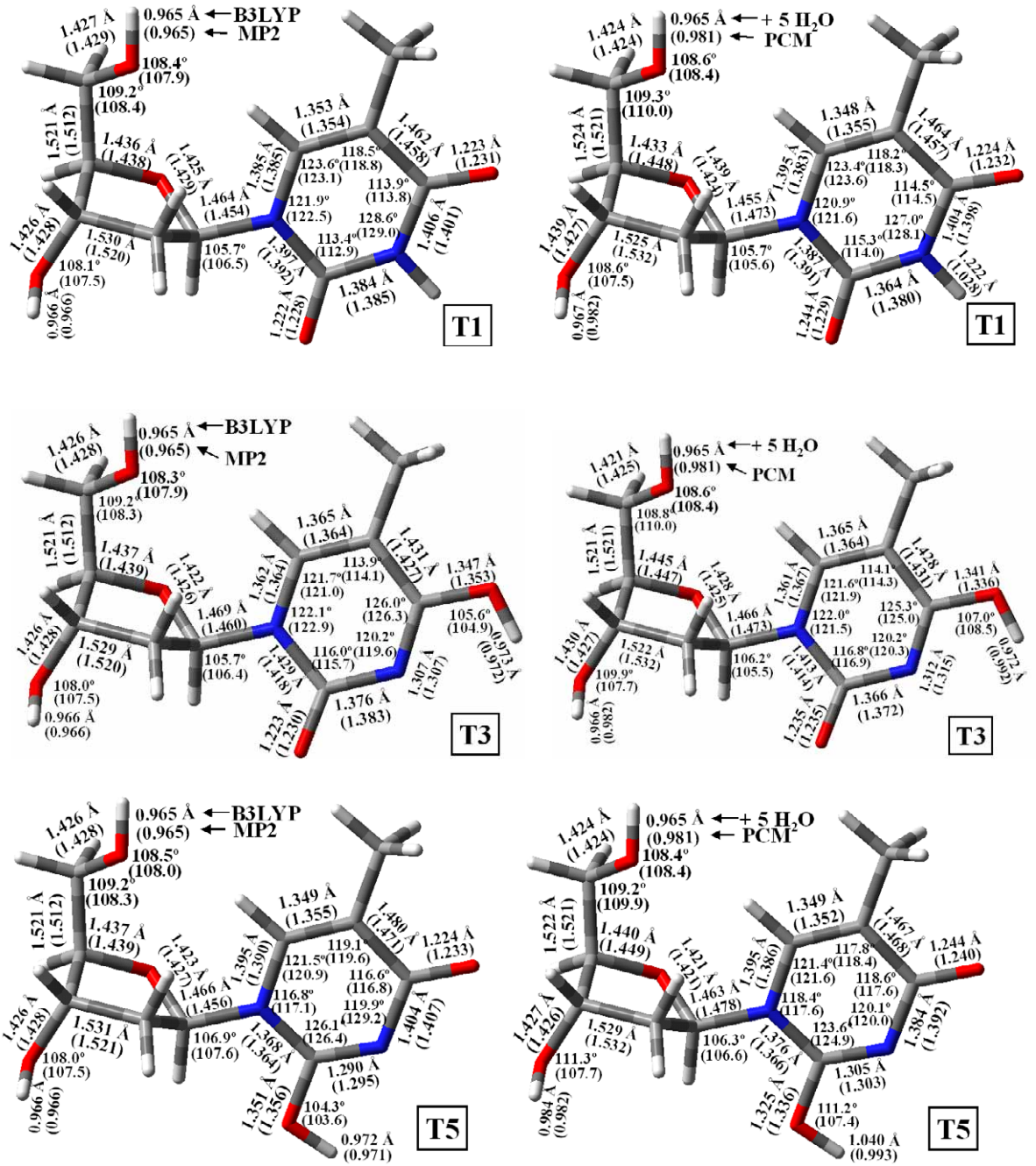


(Isolated state)

(Figure 3-supl). Some selected optimised bond lengths and angles of conformers I and II of Thy in the isolated state at the B3LYP/6-31G** and MP2/6-31G** (in parentheses) levels, and in water solution at the B3LYP/6-31G** level with explicit water molecules and with the PCM method (in parentheses).

Thymidine, conformer II

(isolated state) **(with water)**



(Figure 3-supl continued).