Tautomerisation of thymine acts against the Hückel 4N+2 rule. Effect of metal ion and H-bond complexations on the electronic structure of thymine.

Olga A. Stasyuk,[a*] Halina Szatyłowicz,[a*] Tadeusz M. Krygowski[b]

[a] Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw (Poland) *ostasyuk@ch.pw.edu.pl; halina@ch.pw.edu.pl*
[b] Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw (Poland) *tmkryg@chem.uw.edu.pl*

Supplementary Information

Table S1. Relative energies for thymine tautomers in comparison with previous studies.[a,b,c]

Tautomer	E_{rel} /kcal/mol	E_{rel}[a] /kcal/mol	E_{rel}[b] /kcal/mol	E_{rel}[c] /kcal/mol	HOMA
thy1	0.00	0.00	0.00	0.00	0.490
thy2	10.83	10.64	9.41	11.19	0.629
thy3	12.38	13.17	11.77	13.08	0.718
thy4	13.02	11.66	9.45	14.17	0.984
thy5	14.17	12.96	10.55	15.30	0.987
thy6	18.25	19.21	17.25	18.75	0.370
thy7	18.41	18.14	15.48	19.89	0.974
thy8	18.46	20.96	17.23	18.82	0.639
thy9	18.52	18.28	15.49	19.95	0.980
thy10	19.30	21.66	19.61	20.37	0.672
thy11	22.66	24.02	21.68	22.81	0.784
thy12	25.31	27.18	24.18	25.29	0.772
thy13	27.99	30.64	27.36	28.37	0.339

[a] - MP2/6-31G** [T.-K. Ha, H. H. Gunthard *J. Am. Chem. Soc. 1993,115,* 11939-11950].

[b] - RI-MP2/TZVPP [J. Rejnek, M. Hanus, M. Kabelac, F. Ryjacek, P. Hobza *Phys . Chem. Chem. Phys*. 2005, 7, 2006].

[c] - B3LYP/6-311++G** [J.-C. Fan, Z.-C. Shang, J. Liang, X.-H. Liu, H. Jin *J. Mol. Struct.*: THEOCHEM 939 (2010) 106–111].

Table S2. Natural atomic $2p_z$ orbital occupancies for thymine tautomers.

n	Atom	**Thy1**	**Thy2**	**Thy3**	**Thy4**	**Thy5**
1	N	1.656	1.331	1.611	1.254	1.254
2	C	0.826	0.870	0.832	0.874	0.869
3	N	1.645	1.614	1.312	1.268	1.316
4	C	0.808	0.825	0.894	0.889	0.877
5	C	1.081	1.067	1.111	1.067	1.084
6	C	0.960	0.925	0.924	0.890	0.887
8	O	1.527	1.848	1.505	1.866	1.840
10	O	1.469	1.492	1.826	1.866	1.840
	Sum total	9.971	9.973	10.016	9.974	9.968
	Sum ring	6.976	6.633	6.685	6.242	6.288

Table S3. Energies of isomeric diazines, diazoles and triazoles.

	E /hartree	E_{rel} /kcal/mol
1,2-diazine	-264.36740	22.61
1,3-diazine	-264.40343	0.00
1,4-diazine	-264.39689	4.10
1,2-diazole	-226.27345	10.55
1,3-diazole	-226.29026	0.00
1,2,3-triazole	-242.30776	6.28
1,2,4-triazole	-242.31777	0.00

Table S4. Characteristics for H-bonded complexes of thymine tautomers. Bolded values concern properties of free tautomers.

Tautomer	Interaction	d_{HB} /Å	E_{int} /kcal/mol	E_{def} /kcal/mol	E_{HB} /kcal/mol	d_{C2O8} /Å	d_{C4O10} /Å	HOMA
thy1						**1.213**	**1.217**	**0.490**
	N1H···F⁻*	1.499	-28.00	4.71	-23.29	1.230	1.238	0.726
	N3H···F⁻*	1.583	-25.20	3.02	-22.17	1.233	1.237	0.369
	O8···HF	1.589	-13.69	1.65	-12.04	1.234	1.214	0.527
	O10···HF	1.648	-10.25	0.72	-9.53	1.211	1.229	0.574
thy2						**1.343**	**1.219**	**0.629**
	N1···HF	1.571	-16.00	2.96	-13.04	1.326	1.216	0.618
	N3H···F⁻*	1.589	-23.98	2.80	-21.19	1.367	1.238	0.683
	O8···HF	1.822	-4.60	0.34	-4.26	1.359	1.216	0.595
	O8H···F⁻*	1.503	-24.26	2.64	-21.62	1.257	1.239	0.778
	O10···HF	1.499	-10.91	0.80	-10.12	1.339	1.232	0.721
thy3						**1.214**	**1.345**	**0.718**
	N1H···F⁻*	1.485	-29.69	5.40	-24.28	1.230	1.374	0.844
	N3···HF	1.600	-15.99	2.75	-13.23	1.212	1.328	0.745
	O8···HF	1.523	-17.05	2.67	-14.38	1.237	1.340	0.806
	O10···HF	1.773	-4.92	0.41	-4.50	1.212	1.363	0.734
	O10H···F⁻	1.493	-25.37	2.84	-22.53	1.235	1.264	0.455
thy4						**1.345**	**1.346**	**0.984**
	N1···HF	1.571	-15.36	2.76	-12.60	1.330	1.342	0.973
	N3···HF	1.622	-14.16	2.16	-11.99	1.341	1.332	0.980
	O8···HF	1.795	-6.36	0.28	-6.07	1.357	1.342	0.978
	O8H···F⁻*	1.462	-28.03	3.77	-24.26	1.258	1.374	0.921
	O10···HF	1.765	-5.19	0.39	-4.80	1.342	1.363	0.989
	O10H···F⁻	1.479	-26.37	3.19	-23.18	1.372	1.265	0.799
thy5						**1.346**	**1.347**	**0.987**
	N1···HF	1.677	-12.10	0.94	-11.16	1.339	1.342	0.981
	N3···HF	1.588	-12.81	2.40	-10.41	1.342	1.334	0.984
	O8···HF	1.808	-6.19	0.25	-5.94	1.358	1.344	0.981
	O8H···F⁻*	1.451	-28.75	4.15	-24.61	1.259	1.373	0.923
	O10···HF	1.768	-5.03	0.36	-4.66	1.343	1.364	0.991
	O10H···F⁻	1.468	-27.13	3.49	-23.65	1.371	1.266	0.820

* Proton transfer takes place

Table S5. Statistics of linear regressions between the H-bond energy and its length for H-bonded complexes of thymine tautomers, E_{HB}=a·$d_{N\cdots H}$ + b; *cc* – correlation coefficients.

Interaction	a	b	*cc*
O···HF	33.5	-64.9	0.967
N···HF	11.7	-30.9	0.423
O^-···HF	56.0	-106.0	0.989
N^-···HF	23.3	-58.6	0.945

Table S6. The main characteristics for metal complexes of thymine tautomers. Energy in kcal/mol. Bolded HOMA values concern aromaticity of free tautomers.

		E_{rel} (Li^+)	E_{rel} (Na^+)	E_{rel} (K^+)	HOMA (Li^+)	HOMA (Na^+)	HOMA (K^+)	E_{def} (Li^+)	E_{def} (Na^+)	E_{def} (K^+)	E_{int} (Li^+)	E_{int} (Na^+)	E_{int} (K^+)	E_{tot} (Li^+)	E_{tot} (Na^+)	E_{tot} (K^+)
thy1						**0.490**										
	M···O8	2.48	2.00	1.72	0.450	0.465	0.472	2.72	1.76	1.34	-52.35	-35.36	-26.11	-49.63	-33.60	-24.77
	M···O10	0.00	0.00	0.00	0.727	0.688	0.663	2.51	1.59	1.21	-54.59	-37.12	-27.66	-52.08	-35.53	-26.45
thy2						**0.629**										
	M···N1	29.05	26.73	25.91	0.476	0.505	0.528	1.92	1.47	1.14	-35.88	-21.22	-12.56	-33.96	-19.75	-11.42
	M···O8	42.69	36.27	–	0.434	0.472	–	4.38	3.25	–	-24.68	-13.62	–	-20.29	-10.37	–
	M···O10	7.90	8.56	8.89	0.884	0.843	0.818	2.65	1.69	1.29	-57.67	-39.49	-29.67	-55.02	-37.81	-28.38
thy3						**0.718**										
	M···N3,O8	0.83	1.54	3.62	0.841	0.829	0.823	3.25	1.83	1.27	-66.78	-48.17	-36.49	-63.53	-46.34	-35.22
	M···O10	34.47	31.34	29.55	0.704	0.720	0.728	2.70	1.94	1.45	-32.69	-18.54	-10.80	-29.99	-16.60	-9.35
thy4						**0.984**										
	M···N3,O8	16.78	15.35	16.37	0.946	0.962	0.970	2.51	1.31	0.85	-50.73	-34.42	-23.94	-48.22	-33.11	-23.08
	M···O10	33.07	30.06	28.49	0.982	0.987	0.990	2.49	1.76	1.31	-34.53	-20.29	-12.36	-32.04	-18.53	-11.05
thy5						**0.987**										
	M···N1,O8	11.31	10.01	11.45	0.942	0.953	0.959	2.36	1.21	0.76	-57.19	-40.82	-29.90	-54.83	-39.62	-29.14
	M···O10	35.27	32.27	30.71	0.981	0.986	0.989	2.48	1.74	1.28	-33.47	-19.22	-11.26	-30.99	-17.48	-9.98

Table S7 Cartesian coordinates of equilibrium geometries for free tautomers of the thymine.

thy1 *E*=-454.28959 a.u.

7	1.116416	-1.240143	0.000006
6	1.676236	0.025945	0.000000
7	0.727609	1.030532	-0.000014
6	-0.669525	0.895874	-0.000007
6	-1.154324	-0.486724	0.000001
6	-0.240881	-1.475904	0.000008
1	1.774440	-2.000989	0.000016
8	2.873566	0.222815	0.000004
1	1.086878	1.974285	-0.000016
8	-1.379375	1.884152	-0.000005
6	-2.634475	-0.716614	0.000004
1	-2.865737	-1.780778	0.000010
1	-3.098239	-0.258648	0.874259
1	-3.098240	-0.258659	-0.874257
1	-0.522996	-2.519125	0.000014

thy2 *E*=-454.27233 a.u.

7	-1.128068	-1.302560	-0.000022
6	-1.530944	-0.076161	0.000000
7	-0.709301	0.996253	0.000007
6	0.699067	0.886997	-0.000015
6	1.164471	-0.489729	-0.000004
6	0.234669	-1.482830	-0.000021
8	-2.837270	0.234025	0.000006
1	-1.095249	1.929866	0.000025
8	1.384682	1.894630	0.000022
6	2.643007	-0.729638	0.000013
1	2.864270	-1.795763	0.000017
1	3.111555	-0.275008	-0.874013
1	3.111538	-0.275005	0.874046
1	0.550577	-2.518783	-0.000030
1	-3.322015	-0.602237	-0.000006

thy3 *E*=-454.26987 a.u.

7	-1.170469	-1.204351	0.000008
6	-1.670583	0.116809	-0.000019
7	-0.711014	1.104790	0.000004
6	0.551336	0.790756	0.000016
6	1.095974	-0.535636	0.000008
6	0.151250	-1.510183	0.000015
8	-2.870233	0.303982	-0.000025
8	1.446362	1.794535	-0.000011
6	2.573696	-0.798738	0.000006
1	2.772372	-1.869761	0.000001
1	3.054738	-0.363297	-0.876572
1	3.054737	-0.363306	0.876589
1	0.402159	-2.561628	0.000023
1	0.937226	2.618321	-0.000006
1	-1.869918	-1.929583	0.000013

thy4 *E*=-454.26885 a.u.

7	-1.183558	-1.267230	0.000002
6	-1.524617	0.014604	0.000001
7	-0.701303	1.058444	-0.000001
6	0.591326	0.775830	0.000014
6	1.108026	-0.529666	0.000011
6	0.133945	-1.512134	0.000006
8	-2.835910	0.312007	-0.000027
8	1.450747	1.811442	-0.000008
6	2.581443	-0.814756	0.000012
1	2.762701	-1.888661	0.000010
1	3.070187	-0.386794	-0.876387
1	3.070184	-0.386798	0.876414
1	0.421893	-2.557500	0.000009
1	-3.309845	-0.529403	-0.000032
1	0.919479	2.619788	-0.000018

thy5 *E*=-454.26701 a.u.

7	-1.141968	-1.336652	-0.000004
6	-1.530077	-0.074710	-0.000026
7	-0.742812	1.005274	-0.000019
6	0.562117	0.778644	-0.000016
6	1.123717	-0.505432	0.000003
6	0.183786	-1.523247	0.000009
8	-2.858152	0.141327	0.000009
8	1.381648	1.847607	0.000004
6	2.606361	-0.738042	0.000020
1	2.824657	-1.804980	0.000035
1	3.080166	-0.293933	-0.876558
1	3.080150	-0.293912	0.876595

thy6 *E*=-454.26051 a.u.

7	-1.078388	-1.232602	-0.000034
6	-1.503952	0.054794	0.000004
7	-0.744918	1.088725	-0.000006
6	0.649377	0.921417	-0.000152
6	1.165778	-0.467984	-0.000044
6	0.283605	-1.481881	-0.000044
8	-2.845699	0.165682	0.000040
8	1.399478	1.881072	0.000139
6	2.648069	-0.669940	0.000023
1	2.908729	-1.727844	0.000085
1	3.097178	-0.194252	-0.872412
1	3.097117	-0.194164	0.872441

1	0.514369	-2.556302	0.000022
1	-2.994047	1.096380	0.000017
1	0.824772	2.637644	0.000002

thy7 *E*=-454.26026 a.u.

7	-1.206333	-1.250670	-0.000008
6	-1.533150	0.037767	-0.000021
7	-0.707418	1.076944	-0.000013
6	0.579834	0.791085	-0.000005
6	1.083462	-0.525245	0.000005
6	0.106603	-1.504527	0.000003
8	-2.842260	0.342171	-0.000004
8	1.395765	1.867080	0.000008
6	2.554625	-0.834736	0.000018
1	2.717477	-1.911203	0.000026
1	3.059624	-0.433631	-0.883276
1	3.059610	-0.433620	0.883316
1	0.389329	-2.551617	0.000010
1	-3.321178	-0.496241	0.000003
1	2.315108	1.582320	0.000026

thy9 *E*=-454.26007 a.u.

7	-1.167074	-1.320955	-0.000005
6	-1.539606	-0.051224	-0.000020
7	-0.748319	1.022673	-0.000014
6	0.551400	0.792051	-0.000005
6	1.098779	-0.503442	0.000007
6	0.154422	-1.517309	0.000007
8	-2.864379	0.176763	-0.000006
8	1.323101	1.900674	0.000003
6	2.579901	-0.761237	0.000020
1	2.779309	-1.831525	0.000030
1	3.071153	-0.343651	-0.883407
1	3.071140	-0.343638	0.883447
1	0.478987	-2.552602	0.000016
1	-2.985042	1.134513	-0.000006
1	2.253052	1.652341	0.000020

thy11 *E*=-454.25348 a.u.

7	-1.213417	-1.340945	-0.000011
6	-1.712903	-0.058350	-0.000033
7	-0.734219	0.980046	0.000002
6	0.593182	0.765432	0.000002
6	1.085407	-0.517028	-0.000004
6	0.083182	-1.516867	-0.000002
8	-2.884725	0.252198	0.000023
8	1.327834	1.892526	0.000010
6	2.558021	-0.824557	-0.000001
1	2.711978	-1.902432	-0.000006
1	0.565947	-2.524241	-0.000026
1	-3.039706	1.112928	0.000063
1	-1.753625	-1.977759	-0.000027

thy8 *E*=-454.26018 a.u.

7	-1.091534	-1.344455	-0.000076
6	-1.539246	-0.138089	0.000006
7	-0.734200	0.959265	-0.000040
6	0.680998	0.889195	-0.000313
6	1.181708	-0.469849	-0.000079
6	0.272520	-1.483672	-0.000095
8	-2.873944	0.047079	0.000146
1	-1.104180	1.899501	0.000070
8	1.330019	1.921785	0.000185
6	2.665556	-0.675217	0.000079
1	2.910368	-1.736158	0.000212
1	3.123859	-0.210855	-0.874249
1	3.123713	-0.210671	0.874386
1	0.615827	-2.511225	-0.000039
1	-3.107263	0.980613	0.000201

thy10 *E*=-454.25882 a.u.

7	-1.191411	-1.188529	0.000035
6	-1.678547	0.141726	0.000162
7	-0.716660	1.124552	0.000010
6	0.540095	0.810138	-0.000024
6	1.071995	-0.530189	0.000019
6	0.124469	-1.501814	0.000009
8	-2.877160	0.331052	-0.000138
8	1.393898	1.857003	-0.000029
6	2.546430	-0.822187	0.000010
1	2.724384	-1.896289	0.000021
1	3.046155	-0.415554	-0.883658
1	3.046172	-0.415532	0.883660
1	0.371651	-2.554423	-0.000028
1	2.304954	1.546655	-0.000004
1	-1.897388	-1.907494	-0.000018

thy12 *E*=-454.24925 a.u.

7	1.204644	-1.351835	-0.000009
6	1.708688	-0.076775	0.000099
7	0.730101	0.969853	0.000023
6	-0.604900	0.762260	-0.000003
6	-1.095679	-0.518683	0.000013
6	-0.095618	-1.519163	-0.000013
8	2.879678	0.240370	-0.000061
8	-1.439709	1.818608	-0.000029
6	-2.567345	-0.825153	0.000010
1	-2.721466	-1.903123	0.000009

1	3.069307	-0.433848	-0.884439
1	3.069301	-0.433858	0.884445
1	0.414796	-2.553266	0.000006
1	2.265880	1.672745	0.000009
1	-1.084012	1.927381	0.000007

thy13 *E*=-454.24498 a.u.

7	-1.099545	-1.194573	-0.000934
6	-1.505539	0.112609	0.001797
7	-0.716680	1.116543	0.010740
6	0.671726	0.916523	-0.002003
6	1.163399	-0.481677	0.003810
6	0.260387	-1.474330	-0.005089
8	-2.838721	0.341269	-0.010256
8	1.443287	1.858482	-0.013056
6	2.640744	-0.714519	0.010630
1	2.880220	-1.777476	0.005882
1	3.103148	-0.241726	-0.856261
1	3.094263	-0.252791	0.888319
1	0.517029	-2.523479	-0.011147
1	-3.344210	-0.461886	0.149625
1	-1.757701	-1.946082	-0.113427
1	-3.069161	-0.416463	0.878282
1	-3.069157	-0.416463	-0.878264
1	-0.431874	-2.553554	-0.000023
1	-0.962400	2.655380	-0.000015
1	1.120216	1.901347	-0.000004

Table S8 Cartesian coordinates of equilibrium geometries for H-bonding complexes of tautomers of the thymine.

thy1 N1H···F$^-$ *E*=-554.26729 a.u.

N	1.201194	0.216975	0.000001
C	0.897367	-1.112702	0.000016
N	-0.472645	-1.425066	0.000014
C	-1.548981	-0.542913	0.000017
C	-1.155009	0.841520	0.000005
C	0.189844	1.109151	-0.000002
H	2.577422	0.811197	-0.000017
O	1.718850	-2.028796	-0.000004
H	-0.696170	-2.408080	0.000011
O	-2.709806	-0.974035	0.000007
C	-2.212415	1.906184	-0.000002
H	-1.757545	2.898284	-0.000012
H	-2.864110	1.829454	-0.874498
H	-2.864105	1.829469	0.874499
H	0.517337	2.145658	-0.000013
F	3.432238	1.351763	-0.000033

thy1 N3H···F$^-$ *E*=-554.24674 a.u.

N	0.260388	1.874345	0.000023
C	-0.944087	1.131132	-0.000010
N	-0.833233	-0.216943	0.000021
C	0.381361	-0.861420	0.000132
C	1.623222	-0.049286	0.000036
C	1.497056	1.288620	0.000032
H	0.145845	2.871898	0.000009
O	-1.996960	1.773396	-0.000051
H	-2.161414	-1.077495	-0.000072
O	0.469159	-2.095541	-0.000082
C	2.945866	-0.752045	-0.000008
H	3.772722	-0.037628	-0.000061
H	3.044606	-1.401720	0.872147
H	3.044532	-1.401762	-0.872141
H	2.345805	1.962690	0.000016
F	-2.997810	-1.609183	-0.000026

thy1 O8···HF *E*=-554.79536 a.u.

N	0.874042	0.756952	-0.000086
C	1.023235	-0.604177	-0.000053
N	-0.153336	-1.301106	0.000023
C	-1.458757	-0.768041	0.000096
C	-1.519471	0.693820	0.000069
C	-0.357716	1.375199	-0.000021
H	1.736012	1.289945	-0.000160
O	2.123400	-1.162052	-0.000148
H	-0.078146	-2.308606	0.000022
O	-2.417089	-1.514048	0.000153
C	-2.868396	1.344469	0.000135
H	-2.779190	2.429442	0.000107
H	-3.444559	1.040636	-0.874299
H	-3.444455	1.040673	0.874650
H	-0.322156	2.454843	-0.000052
H	3.278731	-0.070717	-0.000123
F	3.716107	0.788227	-0.000122

thy1 O10···HF *E*=-554.79126 a.u.

N	2.034195	0.922365	-0.000009
C	2.147619	-0.457048	0.000026
N	0.915824	-1.091110	-0.000095
C	-0.344408	-0.501856	-0.000089
C	-0.360272	0.955487	-0.000033
C	0.832266	1.587303	-0.000001
H	2.905381	1.426493	0.000069
O	3.207677	-1.042129	0.000118
H	0.941179	-2.101212	-0.000047
O	-1.333705	-1.230378	-0.000093
C	-1.674503	1.676910	-0.000005
H	-1.520770	2.754672	-0.000097
H	-2.271313	1.412086	-0.872659
H	-2.271209	1.412223	0.872764
H	0.905554	2.665289	0.000027
H	-2.955703	-0.936726	0.000074
F	-3.886582	-0.759592	0.000111

thy2 N1···HF *E*=-554.78009 a.u.

N	0.986891	0.679611	0.000097
C	0.961416	-0.625199	0.000138
N	-0.186807	-1.329412	0.000161
C	-1.472639	-0.736274	-0.000011
C	-1.436468	0.718307	0.000084
C	-0.225391	1.330154	0.000143
O	2.070691	-1.352045	0.000217
H	-0.148605	-2.339378	0.000032
O	-2.461843	-1.443174	-0.000407
C	-2.741891	1.452051	0.000050
H	-2.583569	2.529019	-0.000027
H	-3.336902	1.185148	-0.874230
H	-3.336906	1.185263	0.874362
H	-0.155261	2.409754	0.000192
H	2.843019	-0.746942	0.000243
H	2.496403	1.116593	0.000096
F	3.471144	0.970741	-0.000376

thy2 N3H···F$^-$ *E*=-554.24196 a.u.

N	0.156726	1.933941	0.000015
C	-0.829997	1.048194	0.000006
N	-0.768393	-0.270220	-0.000018
C	0.488680	-0.869516	-0.000054
C	1.636402	0.032523	-0.000005
C	1.395697	1.373500	0.000013
O	-2.090708	1.577456	0.000021
H	-2.091452	-1.151116	-0.000009
O	0.616233	-2.101064	-0.000008
C	3.014443	-0.557473	0.000011
H	3.776186	0.225664	0.000044
H	3.171240	-1.196814	0.872439
H	3.171275	-1.196777	-0.872438
H	2.224478	2.077637	0.000035
H	-1.946692	2.531283	0.000034
F	-2.939880	-1.656714	-0.000002

thy2 O8···HF *E*=-554.76544 a.u.

N	0.031899	-1.810484	-0.000040
C	-0.829647	-0.855536	-0.000015
N	-0.536606	0.459256	-0.000018
C	0.797646	0.934327	-0.000083
C	1.787882	-0.132388	-0.000025
C	1.352046	-1.419363	-0.000039
O	-2.158308	-1.139193	0.000016
H	-1.277531	1.152498	0.000018
O	1.014721	2.131270	0.000053

thy2 O8H···F$^-$ *E*=-554.26412 a.u.

N	-0.724615	-1.068388	-0.000055
C	-0.990074	0.246382	-0.000081
N	0.081144	1.138964	-0.000020
C	1.436051	0.813976	-0.000010
C	1.676367	-0.602240	-0.000006
C	0.573609	-1.425417	-0.000025
O	-2.140479	0.753266	-0.000011
H	-0.148809	2.120824	0.000019
O	2.292240	1.709987	0.000081

C	3.233283	0.259039	0.000022
H	3.875372	-0.620135	0.000051
H	3.470371	0.867300	-0.873881
H	3.470314	0.867316	0.873928
H	2.063315	-2.235454	-0.000028
H	-2.240780	-2.102742	0.000012
H	-3.325893	0.259740	0.000053
F	-3.488976	1.179665	0.000060

thy2 O10···HF *E*=-554.77495 a.u.

N	-2.059304	0.990957	-0.000085
C	-2.045113	-0.300423	-0.000023
N	-0.915600	-1.043746	0.000025
C	0.365620	-0.480125	0.000069
C	0.374083	0.963888	-0.000001
C	-0.832917	1.600710	-0.000090
O	-3.173437	-1.021415	0.000002
H	-0.972228	-2.053083	0.000039
O	1.334503	-1.240890	0.000135
C	1.687624	1.685790	0.000130
H	1.531252	2.762985	-0.001039
H	2.285003	1.422003	0.873240
H	2.286235	1.420202	-0.871557
H	-0.867675	2.682894	-0.000192
H	-3.910485	-0.395709	-0.000057
H	2.946445	-0.962075	-0.000118
F	3.882386	-0.803144	-0.000167

thy3 N3···HF *E*=-554.77796 a.u.

N	0.425694	1.950425	-0.000066
C	-0.866331	1.392889	-0.000041
N	-0.897372	0.013481	-0.000051
C	0.210010	-0.696820	0.000172
C	1.530987	-0.143144	-0.000009
C	1.565263	1.213664	-0.000111
O	-1.844666	2.107852	0.000376
O	0.121198	-2.021835	0.000396
C	2.752705	-1.014193	-0.000016
H	3.656347	-0.406606	-0.000157
H	2.776448	-1.662316	0.876442
H	2.776323	-1.662515	-0.876330
H	2.493171	1.767959	-0.000215
H	-0.825330	-2.284127	-0.000116
H	0.458175	2.957580	-0.000116
H	-2.161381	-0.967631	-0.000035
F	-2.582230	-1.854688	-0.000534

C	3.089773	-1.105768	0.000019
H	3.107643	-2.197336	0.000016
H	3.644813	-0.755146	-0.874356
H	3.644780	-0.755152	0.874418
H	0.741978	-2.501535	-0.000042
H	-3.428227	-0.021334	0.000031
F	-4.331815	-0.405776	0.000055

thy3 N1H···F⁻ *E*=-554.23836 a.u.

N	1.211212	0.188235	0.000002
C	0.849570	-1.162679	-0.000011
N	-0.511487	-1.476897	-0.000010
C	-1.389678	-0.514244	0.000000
C	-1.102287	0.861672	0.000004
C	0.260244	1.113681	0.000006
O	1.704225	-2.047275	-0.000002
O	-2.710888	-0.890976	-0.000013
C	-2.153606	1.934223	0.000009
H	-1.683741	2.919757	0.000012
H	-2.805247	1.877555	-0.876721
H	-2.805244	1.877549	0.876741
H	0.613572	2.142750	0.000012
H	-2.674692	-1.857754	-0.000020
H	2.592309	0.735216	0.000003
F	3.459201	1.270628	0.000010

thy3 O8···HF *E*=-554.77949 a.u.

N	0.903915	0.743881	0.000037
C	1.002188	-0.647554	-0.000063
N	-0.164674	-1.346567	-0.000083
C	-1.302038	-0.703542	0.000011
C	-1.461471	0.716482	0.000112
C	-0.283987	1.395637	0.000123
O	2.117534	-1.182986	-0.000179
O	-2.427810	-1.431067	-0.000029
C	-2.809738	1.374526	0.000194
H	-2.707306	2.458575	0.000260
H	-3.390783	1.086634	-0.876485
H	-3.390731	1.086522	0.876871
H	-0.235241	2.475088	0.000195
H	-2.163091	-2.362854	-0.000111
H	1.786747	1.247254	0.000048
H	3.222823	-0.134963	-0.000161
F	3.701708	0.717964	-0.000099

thy3 O10···HF *E*=-554.76354 a.u.

N	2.023849	0.862116	-0.247265
C	2.086322	-0.540840	-0.091015
N	0.875650	-1.146362	0.177513
C	-0.200980	-0.432077	0.273453
C	-0.308033	0.986240	0.134642
C	0.883540	1.584224	-0.134324
O	3.148388	-1.114467	-0.196454
O	-1.351415	-1.109117	0.547933
C	-1.600865	1.735746	0.283758
H	-1.431059	2.806450	0.180934
H	-2.333471	1.437780	-0.466699
H	-2.051830	1.559195	1.260999
H	0.975184	2.653047	-0.266552
H	-1.103096	-2.043293	0.628442
H	2.903798	1.312135	-0.445324
H	-2.936160	-0.891595	-0.216484
F	-3.761728	-0.783898	-0.644218

thy3 O10H···F$^-$ *E*=-554.24708 a.u.

N	2.175069	-0.063405	0.000010
C	1.374008	-1.235836	-0.000015
N	0.034315	-1.069857	-0.000045
C	-0.526555	0.153419	-0.000077
C	0.307603	1.371369	-0.000011
C	1.642314	1.193823	0.000011
O	1.975210	-2.314959	0.000010
O	-1.779043	0.321035	-0.000012
C	-0.343157	2.721042	0.000015
H	0.404021	3.518641	0.000060
H	-0.987796	2.846753	-0.872222
H	-0.987843	2.846701	0.872225
H	2.347178	2.016889	0.000039
H	-2.842761	-0.727300	0.000029
H	3.167940	-0.216829	0.000033
F	-3.651227	-1.291504	0.000062

thy4 N1···HF *E*=-554.77583 a.u.

N	-1.023645	0.627666	-0.002052
C	-0.915488	-0.704202	-0.001098
N	0.230154	-1.377801	0.000085
C	1.339281	-0.659431	0.000857
C	1.370847	0.748744	-0.000108
C	0.121992	1.329711	-0.001430
O	-2.026299	-1.436506	-0.001434
O	2.505578	-1.322337	0.001336
C	2.654106	1.526071	0.000210
H	2.453510	2.596208	-0.000679
H	3.258578	1.292434	0.877432
H	3.259779	1.291199	-0.875849
H	0.016215	2.407363	-0.002216
H	-2.802694	-0.845401	-0.000747
H	2.299683	-2.267953	0.001426
H	-2.539410	1.039423	-0.000520
F	-3.516654	0.929230	0.002790

thy4 N3···HF *E*=-554.77487 a.u.

N	0.242199	-2.032801	0.000410
C	-0.832127	-1.266410	-0.000211
N	-0.850294	0.067435	-0.000872
C	0.330648	0.689345	-0.000448
C	1.550817	-0.008569	0.000085
C	1.417983	-1.383405	0.000496
O	-2.038856	-1.850219	-0.000322
O	0.347553	2.021178	-0.000825
C	2.871477	0.703363	0.000281
H	3.691357	-0.013063	0.000711
H	2.976476	1.343824	-0.876188
H	2.975944	1.344294	0.876471
H	2.302063	-2.010408	0.000912
H	-1.890717	-2.804767	0.000036
H	-0.569135	2.362297	-0.000814
H	-2.047975	1.161793	-0.000303
F	-2.409301	2.066664	0.001152

thy4 O8···HF *E*=-554.76466 a.u.

N	0.005783	-1.742552	0.000021
C	-0.781455	-0.684075	0.000040
N	-0.425926	0.591811	0.000017
C	0.878193	0.823087	0.000003
C	1.848887	-0.193626	0.000009
C	1.321312	-1.471479	0.000006
O	-2.120331	-0.905913	-0.000011
O	1.282051	2.103112	0.000010
C	3.320270	0.100489	0.000014

thy4 O8H···F$^-$ *E*=-554.23788 a.u.

N	-0.779919	-1.017477	-0.000018
C	-0.981365	0.342771	-0.000032
N	0.088950	1.215967	-0.000015
C	1.299167	0.717132	0.000000
C	1.610970	-0.645941	0.000008
C	0.470437	-1.447266	-0.000002
O	-2.144764	0.822421	-0.000027
O	2.331279	1.623867	0.000015
C	3.013521	-1.182805	0.000026

H	3.894792	-0.824460	0.000018
H	3.608512	0.682067	-0.876533
H	3.608509	0.682071	0.876559
H	1.981808	-2.330571	0.000011
H	-2.260286	-1.861581	-0.000025
H	0.489117	2.657754	0.000014
H	-3.430531	0.320305	-0.000051
F	-4.196436	0.856182	-0.000076

thy4 O10···HF *E*=-554.76300 a.u.

N	2.055384	0.925362	-0.255712
C	1.983680	-0.387763	-0.084769
N	0.885894	-1.092073	0.178664
C	-0.231006	-0.398768	0.276233
C	-0.322513	0.989671	0.127842
C	0.898453	1.588288	-0.144361
O	3.116956	-1.099269	-0.182059
O	-1.356786	-1.116012	0.552196
C	-1.608630	1.753589	0.258828
H	-1.425875	2.821252	0.148690
H	-2.336971	1.456213	-0.496424
H	-2.071750	1.588973	1.232663
H	0.951873	2.662548	-0.278921
H	3.825832	-0.472210	-0.374853
H	-1.085681	-2.042588	0.632012
H	-2.937705	-0.917493	-0.206450
F	-3.767771	-0.830842	-0.631234

thy5 N1···HF *E*=-554.77137 a.u.

N	1.164414	0.246510	0.000020
C	0.768538	-1.016670	0.000034
N	-0.494430	-1.441482	0.000013
C	-1.433704	-0.506927	0.000021
C	-1.159441	0.870673	0.000014
C	0.188222	1.169464	0.000008
O	1.737655	-1.940173	-0.000033
O	-2.714213	-0.908881	-0.000024
C	-2.243752	1.907868	0.000004
H	-1.814717	2.908290	-0.000004
H	-2.885077	1.810997	-0.876815
H	-2.885080	1.811012	0.876821
H	0.521441	2.200082	-0.000001
H	1.318051	-2.809220	-0.000060
H	-2.719527	-1.875802	-0.000038
H	2.736308	0.832134	-0.000002
F	3.570222	1.303698	-0.000017

H	2.996685	-2.274802	0.000029
H	3.582316	-0.859862	-0.876699
H	3.582295	-0.859857	0.876764
H	0.599051	-2.530272	0.000004
H	-3.367703	0.021307	-0.000034
H	1.885172	2.482273	0.000008
F	-4.267726	-0.404652	0.000028

thy4 O10H···F$^-$ *E*=-554.24492 a.u.

N	2.230449	-0.020023	-0.000059
C	1.366046	-1.033308	-0.000160
N	0.052186	-1.014333	-0.000051
C	-0.553560	0.209209	0.000042
C	0.281949	1.391834	0.000019
C	1.635335	1.196366	0.000001
O	1.939151	-2.280014	0.000084
O	-1.812858	0.324706	0.000039
C	-0.353591	2.750096	0.000048
H	0.404533	3.536862	0.000038
H	-0.996889	2.886975	-0.872515
H	-0.996841	2.886953	0.872650
H	2.309994	2.049188	0.000023
H	2.887556	-2.104932	0.000130
H	-2.798243	-0.778282	-0.000001
F	-3.561774	-1.408776	-0.000026

thy5 N3···HF *E*=-554.77052 a.u.

N	0.281236	-2.040782	-0.000005
C	-0.802411	-1.295262	-0.000044
N	-0.835296	0.045728	-0.000022
C	0.336712	0.689003	-0.000002
C	1.561506	0.007560	0.000010
C	1.442317	-1.371206	0.000024
O	-1.975713	-1.946113	0.000008
O	0.334783	2.023349	0.000006
C	2.875161	0.732578	0.000017
H	3.701102	0.023282	0.000030
H	2.974610	1.373829	-0.876524
H	2.974591	1.373838	0.876554
H	2.336396	-1.984542	0.000026
H	-2.696253	-1.305469	0.000021
H	-0.581283	2.358848	-0.000008
H	-2.010946	1.113321	-0.000014
F	-2.463563	1.979815	-0.000006

thy5 O8···HF *E*=-554.76264 a.u.

N	0.692185	-1.041262	-0.157917
C	0.830488	0.265238	-0.133043
N	-0.128470	1.184079	-0.042764
C	-1.368292	0.719393	0.028819
C	-1.680952	-0.648342	0.012873
C	-0.574954	-1.475262	-0.083780
O	2.103482	0.730453	-0.210518
O	-2.367742	1.613016	0.121672
C	-3.092866	-1.149837	0.095747
H	-3.113763	-2.237923	0.064374
H	-3.575744	-0.825254	1.018322
H	-3.697343	-0.772522	-0.730008
H	-0.706423	-2.551005	-0.102725
H	2.078373	1.693997	-0.161050
H	-1.973946	2.495875	0.119962
H	3.652611	-0.153793	0.086464
F	4.535974	-0.407110	0.255166

thy5 O10···HF *E*=-554.76094 a.u.

N	2.058366	0.967055	-0.268008
C	2.001837	-0.341525	-0.096457
N	0.907349	-1.060274	0.174030
C	-0.221474	-0.383229	0.277248
C	-0.324275	1.001130	0.126500
C	0.893014	1.610120	-0.151696
O	3.161322	-1.009383	-0.205662
O	-1.338870	-1.112215	0.560021
C	-1.616114	1.755036	0.260307
H	-1.441143	2.823786	0.148720
H	-2.343994	1.452366	-0.493398
H	-2.075765	1.588400	1.235446
H	0.931542	2.685274	-0.287150
H	2.975574	-1.945223	-0.062217
H	-1.063509	-2.036466	0.642723
H	-2.923970	-0.934210	-0.201918
F	-3.755143	-0.873089	-0.628294

thy5 O8H···F$^-$ *E*=-554.23848 a.u.

N	0.075892	-1.763551	-0.000099
C	0.947317	-0.697098	-0.000401
N	0.477745	0.598555	-0.000176
C	-0.816102	0.795753	-0.000029
C	-1.784212	-0.213156	0.000009
C	-1.217473	-1.486855	0.000021
O	2.187927	-0.913873	0.000005
O	-1.231844	2.103965	-0.000028
C	-3.263447	0.045785	0.000097
H	-3.809266	-0.900314	0.000137
H	-3.586002	0.614699	0.876864
H	-3.586113	0.614689	-0.876634
H	-1.886082	-2.348715	0.000098
H	3.172885	0.151122	0.000248
H	-0.406683	2.609758	-0.000095
F	3.931182	0.802935	0.000368

thy5 O10H···F$^-$ *E*=-554.24759 a.u.

N	-2.241886	-0.165439	-0.000046
C	-1.310807	-1.104053	-0.000119
N	0.007309	-0.983483	-0.000031
C	0.530521	0.275173	0.000031
C	-0.391657	1.388231	0.000004
C	-1.727576	1.087712	-0.000006
O	-1.775593	-2.393614	0.000092
O	1.781066	0.473851	0.000026
C	0.136903	2.791878	0.000014
H	-0.680412	3.516607	0.000001
H	0.767251	2.979017	0.872798
H	0.767284	2.979023	-0.872746
H	-2.460890	1.890913	0.000004
H	-0.972808	-2.929960	0.000138
H	2.785622	-0.597132	0.000003
F	3.551989	-1.230174	-0.000016

Table S9 Cartesian coordinates of equilibrium geometries for complexes of thymine tautomers with cations.

thy1 O8···Li$^+$ *E*= -461.65456 a.u.

N	-0.857997	-1.301345	-0.000009
C	-1.442436	-0.084750	0.000000
N	-0.597256	0.965103	0.000006
C	0.832681	0.911072	0.000002
C	1.384246	-0.446715	-0.000002
C	0.523929	-1.479105	-0.000009
H	-1.468814	-2.102363	-0.000015
O	-2.691435	0.051352	-0.000001
H	-0.994307	1.894922	0.000012
O	1.456647	1.941031	0.000014
C	2.872515	-0.596258	-0.000001
H	3.164225	-1.643912	-0.000005
H	3.303813	-0.108967	-0.874533
H	3.303811	-0.108974	0.874537
H	0.844100	-2.509856	-0.000015
Li	-4.371124	0.389437	0.000001

thy1 O8···Na$^+$ *E*= -616.43254 a.u.

N	0.277374	-1.371634	0.000003
C	0.934482	-0.184665	0.000004
N	0.132931	0.907443	-0.000011
C	-1.293001	0.926630	-0.000032
C	-1.915710	-0.399430	-0.000005
C	-1.109781	-1.474879	0.000002
H	0.844713	-2.203218	0.000011
O	2.180143	-0.112226	0.000007
H	0.576764	1.815139	-0.000009
O	-1.866924	1.987739	-0.000002
C	-3.410262	-0.473163	0.000006
H	-3.753439	-1.505267	0.000022
H	-3.817580	0.034250	0.874547
H	-3.817589	0.034226	-0.874545
H	-1.485797	-2.486784	0.000010
Na	4.258243	0.199084	0.000012

thy1 O8···K$^+$ *E*= -1054.09070 a.u.

N	0.241402	-1.402591	-0.000010
C	-0.450708	-0.231117	0.000001
N	0.329523	0.880957	0.000004
C	1.751820	0.935405	-0.000006
C	2.408213	-0.374019	-0.000004
C	1.629194	-1.469457	-0.000011
H	-0.305001	-2.247763	-0.000016
O	-1.693611	-0.188873	0.000001

thy1 O10···Li$^+$ *E*= -461.65852 a.u.

N	-1.490607	1.085850	0.000001
C	-1.770853	-0.274204	-0.000004
N	-0.604615	-1.050202	0.000005
C	0.684798	-0.597517	0.000028
C	0.886071	0.823668	0.000012
C	-0.231460	1.599018	0.000006
H	-2.297680	1.692624	-0.000004
O	-2.875737	-0.743756	-0.000014
H	-0.760853	-2.049456	-0.000005
O	1.617843	-1.440187	-0.000008
C	2.275915	1.389713	0.000006
H	2.248476	2.477015	-0.000004
H	2.833915	1.071612	0.881539
H	2.833916	1.071594	-0.881519
H	-0.171605	2.678025	0.000002
Li	2.992239	-2.454492	-0.000056

thy1 O10···Na$^+$ *E*= -616.43573 a.u.

N	-2.238297	0.539404	0.000005
C	-1.955934	-0.818794	0.000001
N	-0.581537	-1.072068	0.000010
C	0.435911	-0.149010	0.000033
C	0.048074	1.240116	0.000017
C	-1.281969	1.510276	0.000011
H	-3.218940	0.777161	0.000001
O	-2.788143	-1.687144	-0.000007
H	-0.332448	-2.051641	0.000002
O	1.617988	-0.551233	0.000001
C	1.100173	2.309635	0.000013
H	0.646060	3.298200	0.000002
H	1.739075	2.236893	0.881146
H	1.739085	2.236877	-0.881112
H	-1.654351	2.524706	0.000007
Na	3.645824	-1.085442	-0.000051

thy1 O10···K$^+$ *E*= -1054.09344 a.u.

N	-2.726073	0.297181	0.000013
C	-2.256627	-1.007435	0.000017
N	-0.862035	-1.067383	0.000070
C	0.022759	-0.011213	0.000140
C	-0.560478	1.311955	0.000065
C	-1.913457	1.393781	0.000028
H	-3.729931	0.395457	-0.000020
O	-2.961649	-1.983320	-0.000012

H	-0.137213	1.776712	0.000012
O	2.301470	2.010696	0.000018
C	3.904458	-0.410463	0.000001
H	4.272996	-1.433903	0.000000
H	4.299677	0.106461	-0.874522
H	4.299672	0.106458	0.874527
H	2.032217	-2.471039	-0.000016
K	-4.146292	0.133570	0.000002

thy2 N1···Li$^+$ *E*= -461.61222 a.u.

N	1.206938	1.024863	-0.000020
C	1.448646	-0.266293	-0.000003
N	0.481428	-1.188718	0.000005
C	-0.915636	-0.896105	-0.000013
C	-1.197994	0.539154	-0.000002
C	-0.148764	1.386101	-0.000015
O	2.674327	-0.782790	0.000005
H	0.737225	-2.169157	0.000023
O	-1.715119	-1.795698	0.000037
C	-2.630056	0.967840	0.000013
H	-2.721270	2.051889	0.000016
H	-3.145881	0.569185	-0.873877
H	-3.145864	0.569181	0.873910
H	-0.337665	2.455802	-0.000020
H	3.357472	-0.104043	0.000009
Li	2.142193	2.672614	-0.000056

thy2 O10···Li$^+$ *E*= -461.64593 a.u.

N	1.489376	1.165509	-0.000036
C	1.656245	-0.119744	-0.000025
N	0.623289	-1.001969	0.000076
C	-0.693228	-0.595108	0.000239
C	-0.910627	0.807944	0.000057
C	0.210089	1.608740	-0.000011
O	2.850664	-0.692465	-0.000109
H	0.820682	-1.994746	0.000044
O	-1.587885	-1.484782	0.000015
C	-2.307984	1.352880	-0.000014
H	-2.295162	2.440310	-0.000140
H	-2.861868	1.026385	-0.881724
H	-2.861872	1.026588	0.881768
H	0.099455	2.685894	-0.000095
H	3.528117	0.000082	-0.000171
Li	-3.015737	-2.413196	-0.000229
H	-0.478722	-2.002195	0.000058
O	1.245966	-0.242395	0.000062
C	0.333442	2.516343	0.000049
H	-0.252134	3.433155	-0.000003
H	0.977504	2.530353	0.880342
H	0.977563	2.530290	-0.880202
H	-2.425151	2.345546	-0.000003
K	3.685224	-0.592424	-0.000156

thy2 O8···Li$^+$ *E*= -461.59049 a.u.

N	0.854615	-1.404772	-0.045097
C	1.322569	-0.230634	-0.133514
N	0.623189	0.917761	-0.131725
C	-0.812532	0.908488	-0.034866
C	-1.372681	-0.438306	0.056486
C	-0.529616	-1.500594	0.027310
O	2.721151	-0.065724	-0.198106
H	1.032155	1.807748	-0.382696
O	-1.405490	1.958834	-0.055370
C	-2.860992	-0.556280	0.145830
H	-3.169354	-1.597978	0.191975
H	-3.234675	-0.036352	1.028589
H	-3.334261	-0.084651	-0.715985
H	-0.907529	-2.512082	0.069806
H	3.050076	-0.915015	-0.538323
Li	3.737727	0.835494	1.081571

thy2 N1···Na$^+$ *E*= -616.39313 a.u.

N	-1.173567	-0.165395	0.100524
C	-0.780543	1.081469	0.047250
N	0.505799	1.449878	-0.026222
C	1.599438	0.539183	-0.051633
C	1.177800	-0.857725	0.036883
C	-0.146207	-1.113829	0.107289
O	-1.626707	2.113149	0.053185
H	0.736125	2.435669	-0.056077
O	2.728130	0.955523	-0.130384
C	2.242663	-1.907395	0.046792
H	1.816219	-2.906128	0.115597
H	2.850021	-1.843318	-0.856426
H	2.920276	-1.754827	0.887252
H	-0.473382	-2.145957	0.183260
H	-2.525533	1.825001	0.243389
Na	-3.092696	-1.418311	-0.139908

thy2 O8···Na$^+$ *E*= -616.37794 a.u.

N	0.268361	-1.562900	-0.127294
C	0.840241	-0.463234	-0.412726
N	0.258611	0.752362	-0.434299
C	-1.135421	0.919747	-0.140818
C	-1.809714	-0.336292	0.174090
C	-1.090086	-1.486518	0.145298
O	2.206158	-0.448128	-0.682256
H	0.715885	1.556808	-0.841613
O	-1.616263	2.027251	-0.190581
C	-3.272664	-0.273754	0.481342
H	-3.671618	-1.263809	0.689488
H	-3.458145	0.370705	1.341249
H	-3.821642	0.159528	-0.355347
H	-1.560060	-2.437894	0.351400
H	2.415468	-1.352022	-0.967084
Na	3.616182	0.531616	0.837511

thy2 N1···K$^+$ *E*= -1054.05215 a.u.

N	-0.775031	0.253851	0.244140
C	-0.082855	1.350859	0.101370
N	1.247527	1.379250	-0.074411
C	2.067066	0.218901	-0.117252
C	1.312871	-1.016877	0.081523
C	-0.025493	-0.919797	0.249785
O	-0.644703	2.563982	0.108701
H	1.717479	2.271267	-0.166289
O	3.256927	0.325073	-0.292107
C	2.076355	-2.302799	0.095874
H	1.417045	-3.154714	0.250817
H	2.615585	-2.438533	-0.842016
H	2.828029	-2.292049	0.885687
H	-0.595024	-1.828982	0.417045
H	-1.559521	2.503741	0.404199
K	-3.300869	-0.715084	-0.165163

thy3 N3,O8···Li$^+$ *E*= -461.65720 a.u.

N	-0.878874	-1.445736	-0.000065
C	-1.513944	-0.234345	-0.000329
N	-0.749858	0.898658	-0.000053
C	0.568896	0.794597	0.000014
C	1.275585	-0.447573	-0.000050
C	0.481680	-1.550684	-0.000018
O	-2.756281	-0.139438	0.000348
O	1.307338	1.891907	0.000064
C	2.775120	-0.500413	-0.000007
H	3.122010	-1.531054	-0.000011
H	3.183992	0.000028	-0.877498

thy2 O10···Na$^+$ *E*= -616.42210 a.u.

N	2.249277	0.680109	-0.000030
C	1.937234	-0.576352	-0.000019
N	0.656504	-1.026866	-0.000003
C	-0.434409	-0.174130	-0.000001
C	-0.117596	1.217532	-0.000010
C	1.213161	1.557330	-0.000025
O	2.846761	-1.543307	-0.000018
H	0.482634	-2.023342	0.000008
O	-1.582759	-0.674686	0.000022
C	-1.222206	2.231747	-0.000003
H	-0.817181	3.241178	-0.000012
H	-1.857387	2.127459	-0.881430
H	-1.857370	2.127466	0.881436
H	1.500749	2.601299	-0.000034
H	3.725849	-1.136977	-0.000028
Na	-3.626081	-1.118418	0.000055

thy2 O10···K$^+$ *E*= -1054.07927 a.u.

N	2.754696	0.443317	-0.000015
C	2.272063	-0.757034	0.000012
N	0.942221	-1.029094	0.000135
C	-0.026945	-0.035085	0.000306
C	0.484063	1.301687	0.000108
C	1.846869	1.455640	0.000018
O	3.042043	-1.840661	-0.000074
H	0.634390	-1.992289	0.000117
O	-1.230276	-0.368734	0.000123
C	-0.471051	2.457548	0.000043
H	0.067960	3.402339	-0.000096
H	-1.115543	2.439182	-0.880594
H	-1.115420	2.439373	0.880775
H	2.275247	2.450083	-0.000078
H	3.967385	-1.555622	-0.000151
K	-3.669293	-0.628632	-0.000217

thy3 O10···Li$^+$ *E*= -461.60359 a.u.

N	1.443074	1.123983	0.000009
C	1.805066	-0.255924	-0.000003
N	0.718951	-1.127801	-0.000004
C	-0.467953	-0.652232	0.000002
C	-0.876413	0.707168	0.000008
C	0.179035	1.577700	0.000017
O	2.958376	-0.582415	-0.000012
O	-1.499397	-1.598951	-0.000013
C	-2.318683	1.126268	0.000006
H	-2.421501	2.209300	0.000015
H	-2.851663	0.797468	-0.906235

H	3.183938	0.000002	0.877523
H	0.879618	-2.554495	0.000084
H	0.750661	2.682725	0.000077
H	-1.464778	-2.269358	0.000075
Li	-2.728932	1.704150	-0.000127

thy3 N3,O8···Na$^+$ *E*= -616.43327 a.u.

N	-0.067160	-1.744975	-0.000003
C	-1.024817	-0.755414	-0.000035
N	-0.592790	0.543800	-0.000007
C	0.703655	0.795327	0.000002
C	1.728956	-0.199369	-0.000001
C	1.267945	-1.477326	0.000004
O	-2.230389	-1.042220	0.000030
O	1.115121	2.057467	0.000012
C	3.184942	0.163441	0.000007
H	3.802704	-0.731819	0.000010
H	3.441260	0.756993	-0.877324
H	3.441250	0.756992	0.877341
H	1.925274	-2.334206	0.000018
H	0.356825	2.656773	0.000013
H	-0.405500	-2.696642	0.000011
Na	-3.107645	0.974382	-0.000018

thy3 N3,O8···K$^+$ *E*= -1054.08768 a.u.

N	-0.551325	1.792734	0.000005
C	0.514189	0.911838	-0.000004
N	0.222290	-0.423702	0.000007
C	-1.038104	-0.808492	0.000008
C	-2.168834	0.064703	0.000004
C	-1.849329	1.384999	0.000005
O	1.673676	1.344205	0.000008
O	-1.306590	-2.111946	0.000012
C	-3.575880	-0.456313	0.000006
H	-4.288996	0.365180	0.000005
H	-3.765433	-1.074862	-0.877095
H	-3.765432	-1.074859	0.877110
H	-2.595270	2.166064	0.000008
H	-0.478247	-2.610200	0.000015
H	-0.317479	2.774808	0.000006
K	3.330798	-0.556202	-0.000021

thy4 N3,O8···Li$^+$ *E*= -461.63178 a.u.

N	-0.901376	-1.505811	-0.000001
C	-1.381527	-0.305087	-0.000008
N	-0.732757	0.867862	-0.000008
C	0.603696	0.775791	0.000001
C	1.273755	-0.463848	0.000009
C	0.449741	-1.572259	0.000008
H	-2.851668	0.797452	0.906237
H	0.047228	2.650989	0.000022
H	-1.061888	-2.467521	-0.000017
H	2.222135	1.768007	0.000009
Li	-3.271656	-1.098639	-0.000017

thy3 O10···Na$^+$ *E*= -616.38579 a.u.

N	-2.042515	0.929539	-0.000025
C	-2.150452	-0.489655	-0.000037
N	-0.929211	-1.151101	-0.000019
C	0.165382	-0.479718	-0.000040
C	0.319105	0.934027	-0.000038
C	-0.876145	1.597929	-0.000058
O	-3.229020	-1.018231	0.000080
O	1.324658	-1.246184	0.000014
C	1.648538	1.632668	-0.000009
H	1.522077	2.713491	-0.000018
H	2.234969	1.406209	0.899624
H	2.235009	1.406194	-0.899613
H	-0.936620	2.677523	-0.000045
H	1.000396	-2.163445	0.000019
H	-2.922509	1.425856	0.000011
Na	3.478644	-0.633734	0.000062

thy3 O10···K$^+$ *E*= -1054.04635 a.u.

N	-2.572464	0.786123	-0.000015
C	-2.531524	-0.634432	0.000002
N	-1.250629	-1.166278	-0.000028
C	-0.225795	-0.386907	-0.000067
C	-0.222673	1.036279	-0.000043
C	-1.479512	1.571531	-0.000055
O	-3.551358	-1.272605	0.000045
O	0.999555	-1.029386	-0.000013
C	1.025026	1.870985	-0.000009
H	0.781169	2.931552	-0.000023
H	1.633175	1.694680	0.893289
H	1.633222	1.694666	-0.893272
H	-1.651327	2.638970	-0.000044
H	0.756540	-1.971365	-0.000013
H	-3.498738	1.188493	0.000010
K	3.585731	-0.412880	0.000059

thy4 O10···Li$^+$ *E*= -461.60582 a.u.

N	1.449364	1.190985	0.000013
C	1.673626	-0.122607	0.000034
N	0.730553	-1.073321	0.000004
C	-0.497349	-0.636378	-0.000003
C	-0.896467	0.694217	0.000007
C	0.179929	1.581299	0.000009

O	-2.742720	-0.103075	-0.000015
O	1.336626	1.883625	0.000002
C	2.771305	-0.545180	0.000018
H	3.096906	-1.582606	0.000022
H	3.190803	-0.052131	-0.877037
H	3.190793	-0.052126	0.877075
H	0.872331	-2.568351	0.000013
H	-3.207943	-0.951265	-0.000014
H	0.784339	2.675236	-0.000004
Li	-2.513785	1.805330	-0.000020

thy4 N3,O8···Na$^+$ *E*= -616.41128 a.u.

N	-0.077555	-1.829654	0.000000
C	-0.891153	-0.814619	-0.000007
N	-0.597945	0.491039	-0.000005
C	0.710055	0.774806	0.000004
C	1.708735	-0.215863	0.000012
C	1.233199	-1.512809	0.000011
O	-2.240021	-1.056116	-0.000012
O	1.097174	2.050623	0.000007
C	3.167363	0.133886	0.000021
H	3.775542	-0.767707	0.000027
H	3.429705	0.725854	-0.876966
H	3.429693	0.725857	0.877010
H	1.921536	-2.348045	0.000015
H	-2.376601	-2.014175	-0.000010
H	0.334907	2.641776	0.000002
Na	-2.928426	1.114388	-0.000023

thy4 N3,O8···K$^+$ *E*= -1054.06735 a.u.

N	-0.613032	1.903441	0.000005
C	0.361584	1.034449	-0.000004
N	0.283505	-0.298639	-0.000001
C	-0.960646	-0.787685	0.000008
C	-2.110216	0.021140	0.000016
C	-1.852717	1.378737	0.000016
O	1.642189	1.515247	-0.000008
O	-1.130926	-2.113390	0.000010
C	-3.491595	-0.563522	0.000024
H	-4.239958	0.225779	0.000029
H	-3.653837	-1.190675	-0.876813
H	-3.653826	-1.190675	0.876864
H	-2.668550	2.090331	0.000020
H	1.582556	2.481404	-0.000006
H	-0.276000	-2.559424	0.000004
K	3.128828	-0.673891	-0.000026

O	2.922047	-0.559830	-0.000037
O	-1.486533	-1.620283	-0.000009
C	-2.339058	1.115506	0.000008
H	-2.437949	2.199062	0.000013
H	-2.872699	0.788501	-0.906721
H	-2.872701	0.788492	0.906733
H	0.005879	2.651439	0.000009
H	3.517335	0.203392	-0.000060
H	-1.028740	-2.477142	-0.000012
Li	-3.259578	-1.109569	-0.000014

thy4 O10···Na$^+$ *E*= -616.38783 a.u.

N	2.051738	1.008699	-0.000004
C	2.044506	-0.322602	-0.000021
N	0.954417	-1.095003	-0.000016
C	-0.191349	-0.462540	-0.000005
C	-0.350131	0.920202	0.000005
C	0.864235	1.605349	0.000003
O	3.202722	-0.968583	-0.000005
O	-1.309047	-1.282999	-0.000003
C	-1.682078	1.615599	0.000017
H	-1.555380	2.696465	0.000024
H	-2.267984	1.389711	-0.900342
H	-2.267974	1.389698	0.900380
H	0.873566	2.689578	0.000016
H	3.915974	-0.314832	0.000007
H	-0.955168	-2.187882	-0.000011
Na	-3.458783	-0.652909	0.000012

thy4 O10···K$^+$ *E*= -1054.04803 a.u.

N	2.583670	0.871936	0.000000
C	2.442410	-0.450775	-0.000008
N	1.282678	-1.111482	-0.000009
C	0.200163	-0.370518	-0.000003
C	0.183304	1.022701	0.000006
C	1.458966	1.582417	0.000011
O	3.533614	-1.209112	-0.000018
O	-0.986742	-1.076784	-0.000008
C	-1.069933	1.850011	0.000008
H	-0.830002	2.911460	0.000012
H	-1.676785	1.671631	-0.894097
H	-1.676783	1.671626	0.894114
H	1.575384	2.660378	0.000010
H	4.305100	-0.625664	-0.000017
H	-0.708438	-2.007631	-0.000015
K	-3.564071	-0.427412	0.000009

thy5 N1,O8···Li$^+$ *E*= -461.64049 a.u.

N	-1.170172	-1.081104	0.000006
C	-1.356465	0.228971	0.000001
N	-0.462328	1.184670	-0.000008
C	0.808821	0.773997	-0.000009
C	1.181095	-0.591455	0.000004
C	0.127323	-1.475990	0.000008
O	-2.690540	0.543525	-0.000010
O	1.766013	1.686927	-0.000002
C	2.619547	-1.013564	0.000011
H	2.704234	-2.097844	0.000020
H	3.139030	-0.626074	-0.876489
H	3.139027	-0.626060	0.876506
H	0.302171	-2.542955	0.000015
H	-2.824840	1.500723	-0.000021
H	1.377135	2.574063	-0.000004
Li	-3.098319	-1.427393	-0.000003

thy5 O10···Li$^+$ *E*= -461.60232 a.u.

N	1.424328	1.247188	-0.000001
C	1.684103	-0.056187	-0.000011
N	0.764231	-1.036452	-0.000011
C	-0.480083	-0.636618	-0.000003
C	-0.910085	0.680839	0.000004
C	0.146296	1.596400	0.000001
O	2.962811	-0.398682	-0.000006
O	-1.444580	-1.645105	-0.000001
C	-2.361976	1.069635	0.000015
H	-2.483314	2.150888	0.000022
H	-2.889179	0.732809	-0.907156
H	-2.889169	0.732799	0.907188
H	-0.059567	2.661301	0.000014
H	3.043584	-1.361552	-0.000008
H	-0.973241	-2.493441	-0.000007
Li	-3.228136	-1.157359	0.000015

thy5 N1,O8···Na$^+$ *E*= -616.41978 a.u.

N	-0.975026	-0.718977	0.000003
C	-0.889885	0.600000	-0.000002
N	0.193616	1.346357	-0.000006
C	1.350143	0.685089	-0.000001
C	1.432497	-0.725469	0.000006
C	0.214947	-1.367397	0.000007
O	-2.105612	1.224112	-0.000012
O	2.477463	1.383867	-0.000005
C	2.750416	-1.440169	0.000011
H	2.605270	-2.518224	0.000016
H	3.340603	-1.171595	-0.876340
H	3.340601	-1.171587	0.876361
H	0.168311	-2.448149	0.000012
H	-1.974853	2.181926	-0.000018
H	2.273592	2.330398	-0.000010
Na	-3.309743	-0.815508	0.000001

thy5 O10···Na$^+$ *E*= -616.38431 a.u.

N	2.041904	1.059039	0.000001
C	2.061750	-0.268347	0.000002
N	0.983366	-1.066015	-0.000003
C	-0.180243	-0.459347	0.000002
C	-0.361794	0.917355	0.000007
C	0.842995	1.625168	0.000006
O	3.260559	-0.837712	-0.000024
O	-1.283467	-1.299820	0.000000
C	-1.703999	1.592926	0.000011
H	-1.591472	2.675371	0.000014
H	-2.286813	1.360973	-0.901063
H	-2.286810	1.360967	0.901084
H	0.827950	2.709763	0.000005
H	3.160485	-1.798382	-0.000034
H	-0.921522	-2.200396	-0.000004
Na	-3.440699	-0.673249	0.000004

thy5 N1,O8···K$^+$ *E*= -1054.07519 a.u.

N	-0.638608	-0.544678	0.000014
C	-0.416585	0.757541	0.000030
N	0.744951	1.384342	0.000013
C	1.825077	0.607941	0.000018
C	1.759621	-0.801866	0.000011
C	0.479161	-1.308991	0.000006
O	-1.545053	1.523943	-0.000034
O	3.021014	1.187618	-0.000017
C	2.994420	-1.652682	0.000003
H	2.735203	-2.709319	-0.000001
H	3.610067	-1.449014	-0.876314

thy5 O10···K$^+$ *E*= -1054.04450 a.u.

N	2.578120	0.921335	-0.000007
C	2.463712	-0.400003	-0.000016
N	1.312714	-1.086659	-0.000001
C	0.210190	-0.369677	0.000009
C	0.170604	1.019975	0.000012
C	1.439022	1.602775	0.000021
O	3.601138	-1.088918	-0.000025
O	-0.964613	-1.096683	0.000003
C	-1.094753	1.828682	0.000007
H	-0.868920	2.893200	0.000010
H	-1.698884	1.643540	-0.894796

H	3.610074	-1.449022	0.876317
H	0.321991	-2.379874	-0.000001
H	-1.281072	2.453922	-0.000057
H	2.911635	2.149356	-0.000028
K	-3.384745	-0.515676	-0.000005

H	-1.698888	1.643537	0.894807
H	1.531541	2.683487	-0.000003
H	3.400304	-2.033371	-0.000023
H	-0.678618	-2.024105	-0.000001
K	-3.549854	-0.434459	0.000003

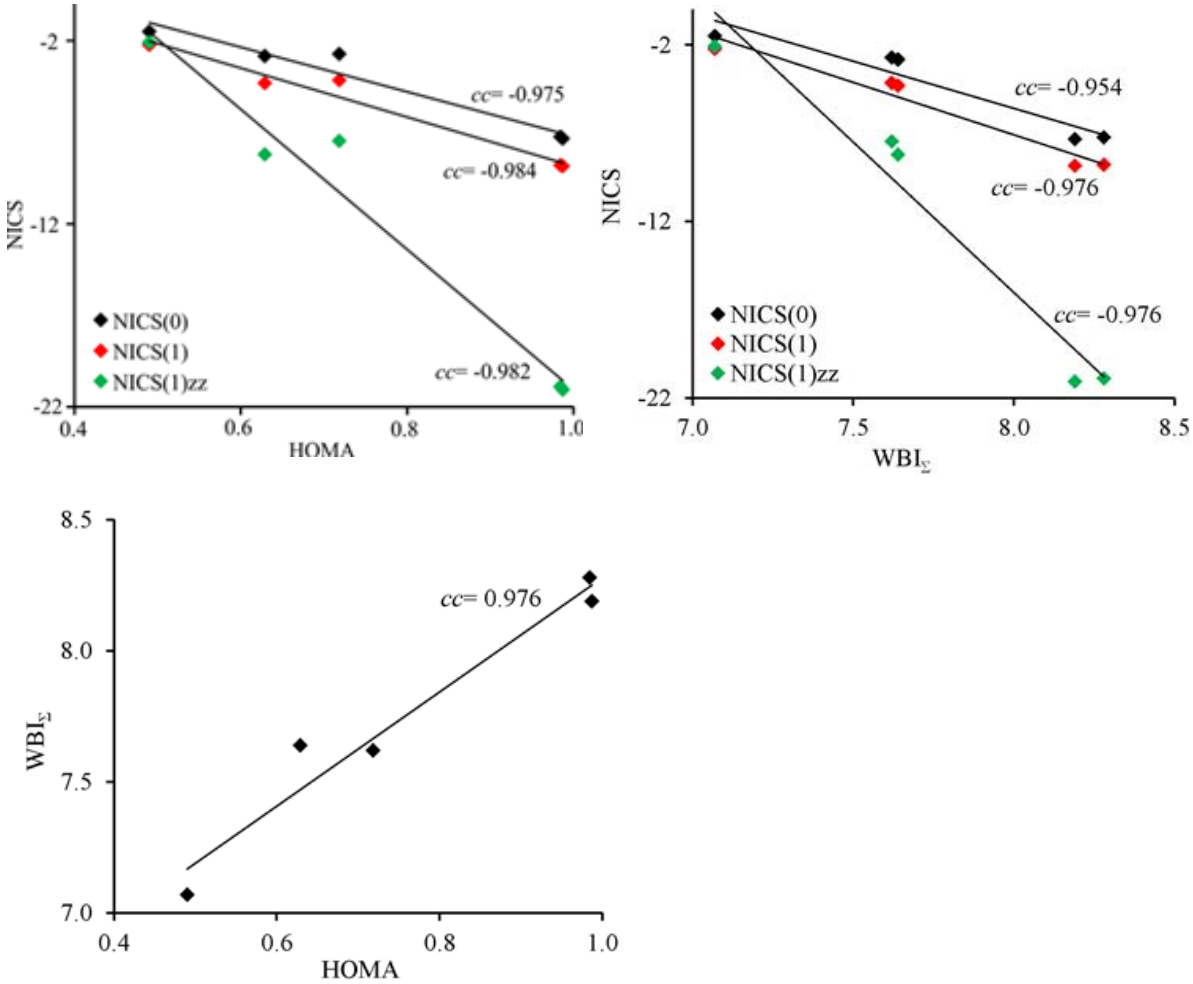

Figure S1. Correlations between aromaticity indices: NICS's, HOMA and WBI_{Σ}.

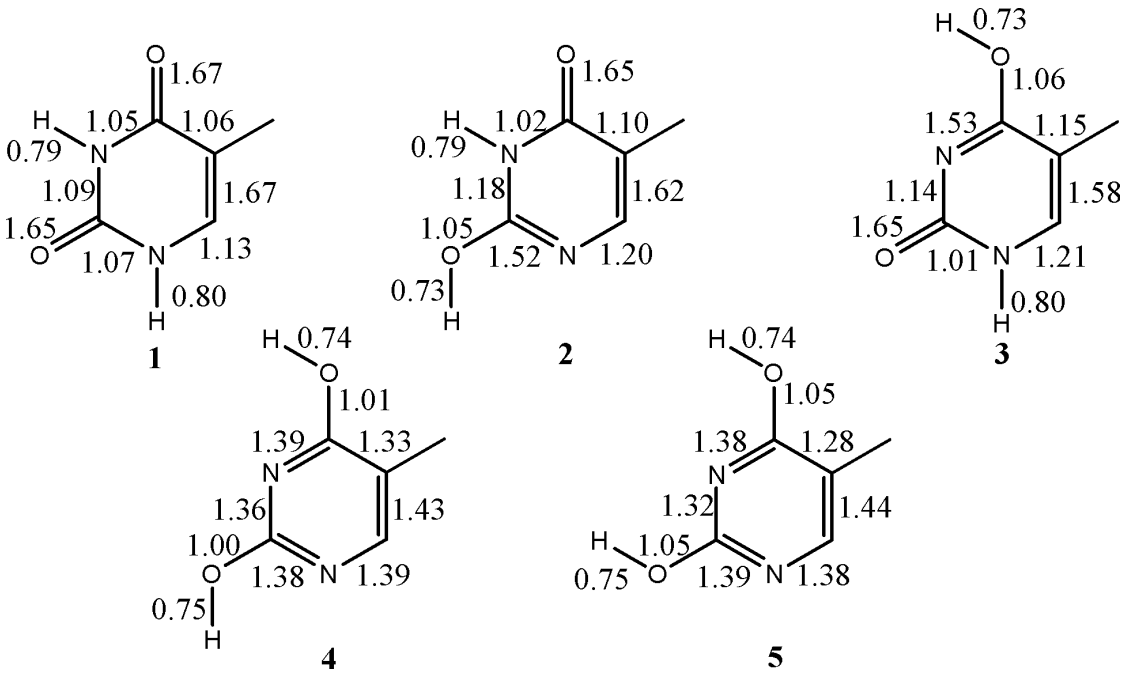

Figure S2. Wiberg bond indices for the most stable thymine tautomers.

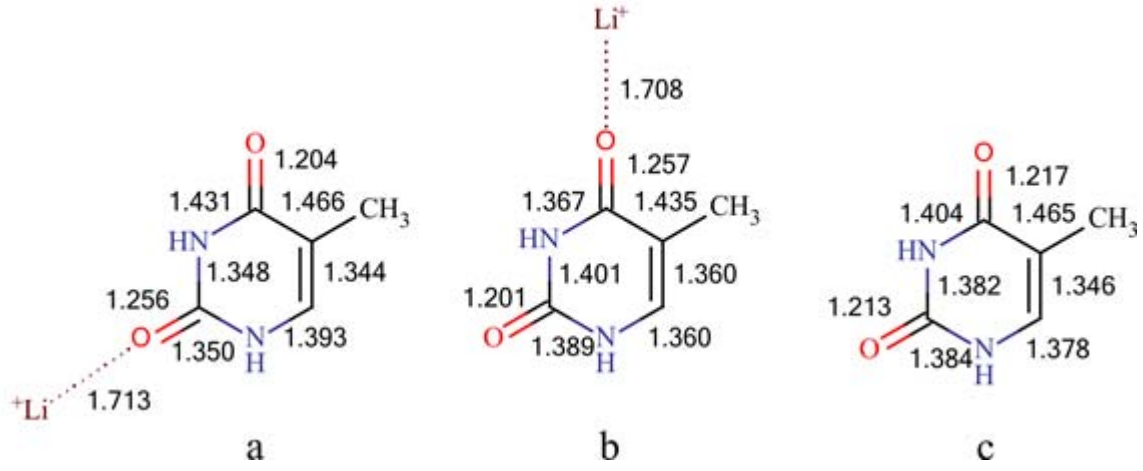

Figure S3. Structural parameters of thy1(c) and its complexes with Li^+ (a,b).

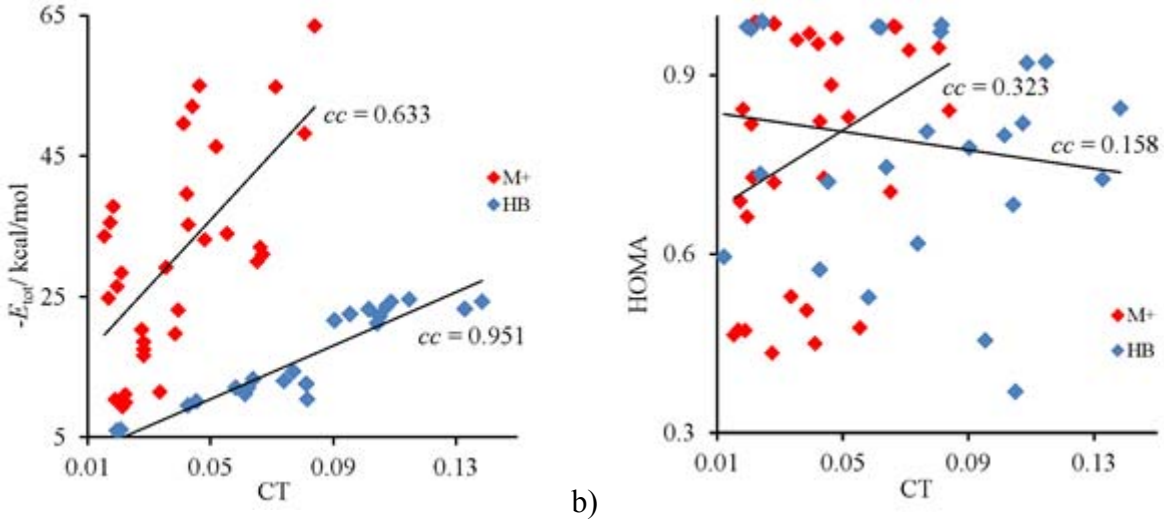

Figure S4. Relationships total energy of interactions, E_{tot} (a) and aromaticity index HOMA (b) against the amount of charge transfer, CT, for the studied complexes of thymine