Supporting information for:

Revisiting the spectroscopy of Xanthine derivatives: theobromine and theophylline

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Table S1. Relative stability and spectroscopic values of theobromine and theophylline. All values are ZPE-corrected. The ZPE from the PBE0/aug-cc-pVDZ calculation were used to correct the values of the CCSD(T) calculation.

	Theobromine			**Theophylline**	
	Keto	*C2-Enol*	*C6-Enol*	*7H*	*9H*
Relative Stability (kJ/mol)	0	69.3	65.4	0	36.3
0_0^0 transition (cm^{-1})	35319.8	-	-	35633.3	-
Adiabatic Ionization Energy (eV)					
Experimental values					
IP	8.120	-	-	8.170	-
ZEKE	8.133	-	-	8.184	-
TPEPICO	8.137	-	-	8.187	-
Computation level					
M06-2X/6-311++G(d,p)	8.217	8.169	8.078	8.266	8.235
M06-2X/aug-cc-pVDZ	8.120	8.074	7.975	8.165	8.147
PBE0/aug-cc-pVDZ	8.088	8.010	7.921	8.113	8.065
CCSD(T)/cc-pVTZ	7.961	7.928	7.832	8.009	7.989

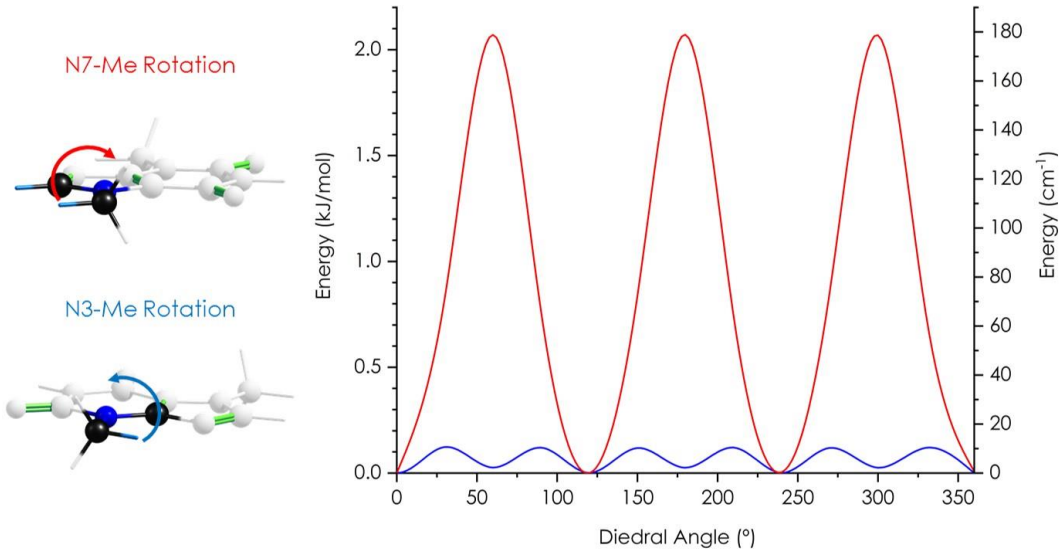


Figure S1. Rotational energy barriers of the methyl groups of theobromine (THB), computed at M06-2X/6-311++G(d,p) level. The shape of the barriers is similar to those computed by Kim's group (ref 10 in the main text).

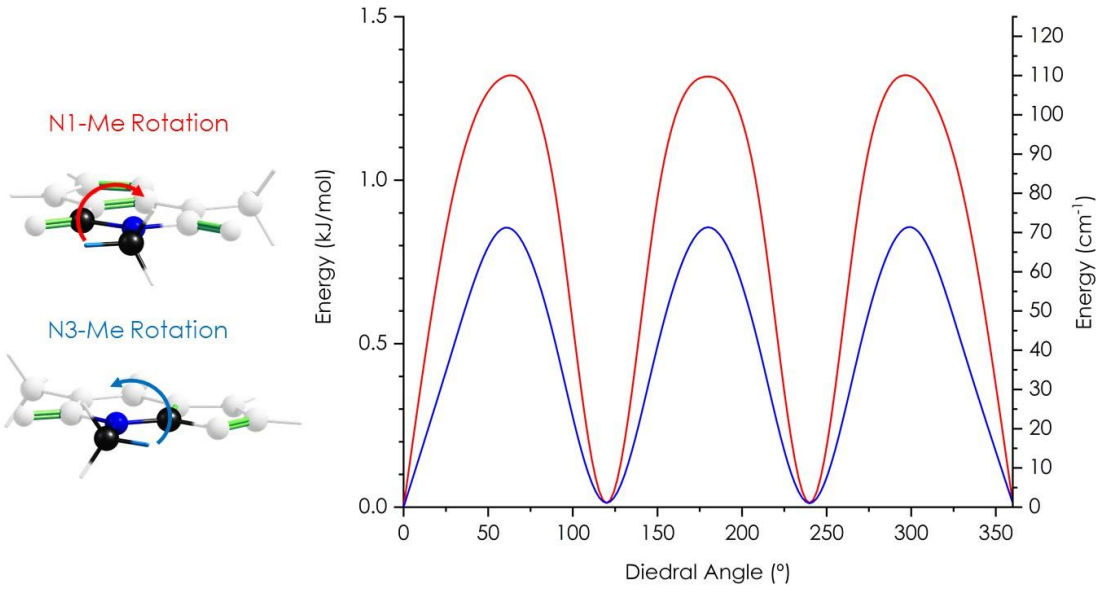
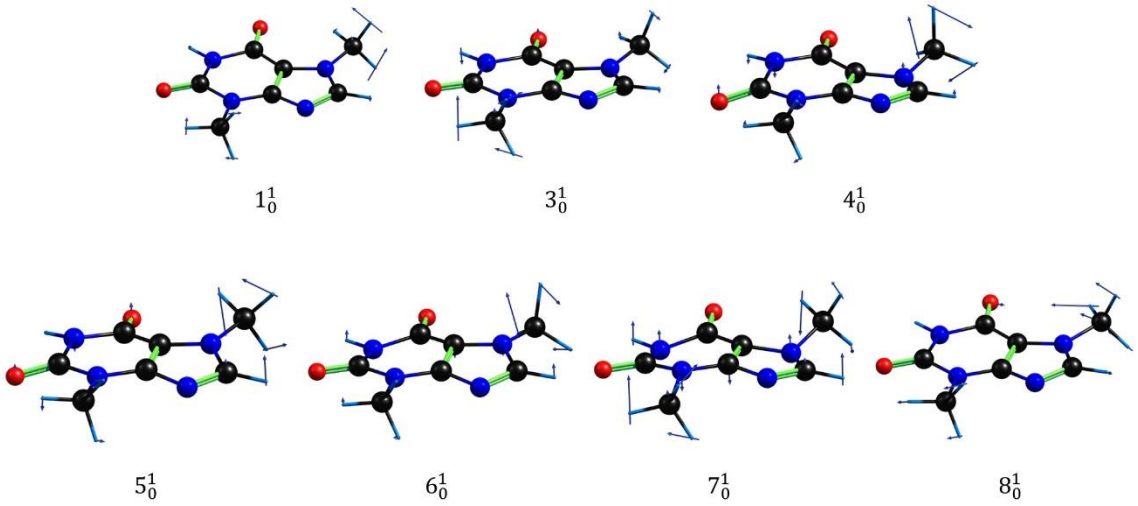


Figure S2. Rotational energy barriers of methyl groups of theophylline (THP), computed at M06-2X/6-311++G(d,p) level. The shape of the barriers is similar to those computed by Kim's group (ref 10 in the main text).

Table S2. Assignment of vibronic transitions in the theobromine REMPI spectrum (ν – stretching, β – bending, δ – deformation, γ – wagging, η – twisting, τ – torsion). A cartoon with the atom movement for each vibrational mode is also shown.

Wavenumber (cm^{-1})	Transition	Calculated wavenumber. (cm^{-1})	Vibrational mode
0	0_0^0	-	-
+ 36	1_0^1	44.3	τ_{ring}, γ CH_3 (N7)
+ 86	3_0^1	82.4	γ CO6, γ CH_3 (N7), τ_{ring}
+ 109	4_0^1	114.9	τ_{ring}, γ CH_3 (N7), η CH_3 (N7)
+ 128	5_0^1	129.6	τ_{ring}, γ CH_3 (N7), η CH_3 (N7)
+ 145	$4_0^1 1_0^1$	-	Combination band
+ 158	$5_0^1 1_0^1$	-	Combination band.
+ 169	$4_0^1 1_0^2$	-	Combination band.
+ 179	$5_0^1 1_0^2$	-	Combination band.
+ 188	$4_0^1 1_0^3$	-	Combination band.
+ 192	6_0^1	185	τ_{ring}, γ CH_3 (N7), η CH_3 (N7)
+ 201	$5_0^1 1_0^3$	-	Combination band.
+ 207	7_0^1	199.6	τ_{ring}
+ 224	8_0^1	212.2	τ_{ring}, rocking CH_3

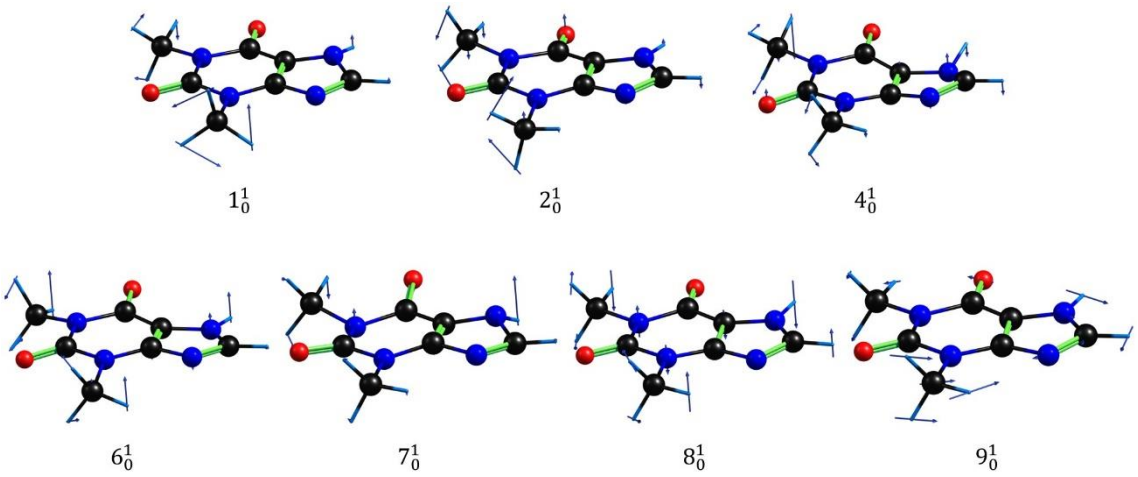


1_0^1 3_0^1 4_0^1

5_0^1 6_0^1 7_0^1 8_0^1

Table S3. Assignment of vibronic transitions of the theophylline REMPI spectrum (ν – stretching, β – bending, δ – deformation, γ – wagging, η – twisting, τ – torsion). A cartoon with the atom movement for each vibrational mode is also shown

Wavenumber (cm^{-1})	Transition	Calculated Wavenumber (cm^{-1})	Vibrational mode
0	0_0^0	-	-
+ 32	1_0^1	41.2	τ_{ring}, η CH_3 (N1 & N3)
+ 59	2_0^1	66.7	τ_{ring}, γ CH_3 (N1 & N3)
+ 96	4_0^1	102.6	τ_{ring}
+ 140	6_0^1	140.5	τ_{ring}
+ 207	7_0^1	200.8	τ_{ring}, γ N7H, γ CH_3 (N1)
+ 245	8_0^1	226.4	τ_{ring}, γ N7H, γ CH_3 (N1)
+ 287	9_0^1	278.7	Ring rocking



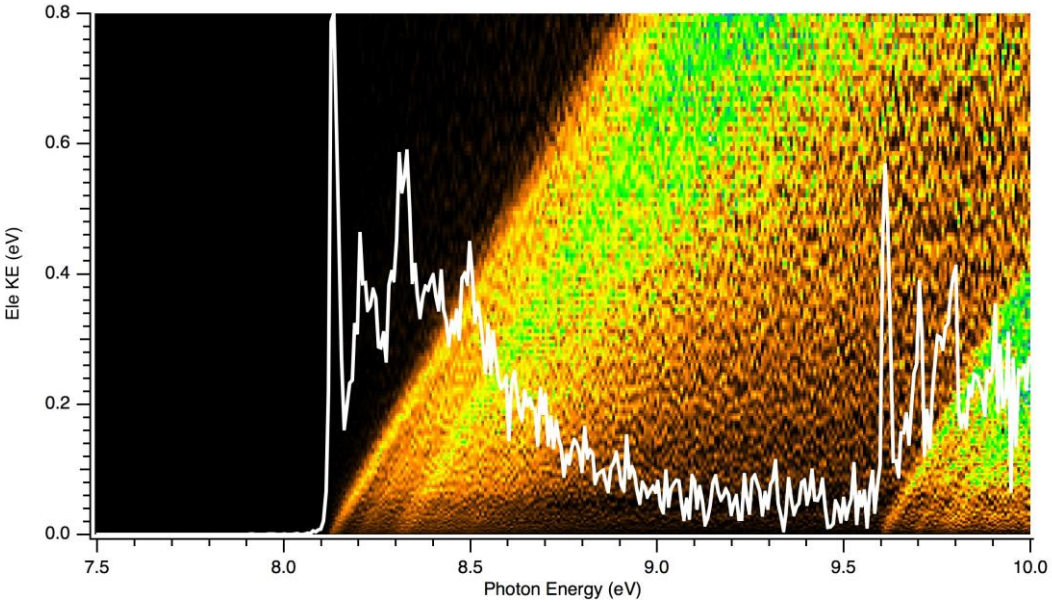


Figure S3. PES matrix of theobromine (THB)

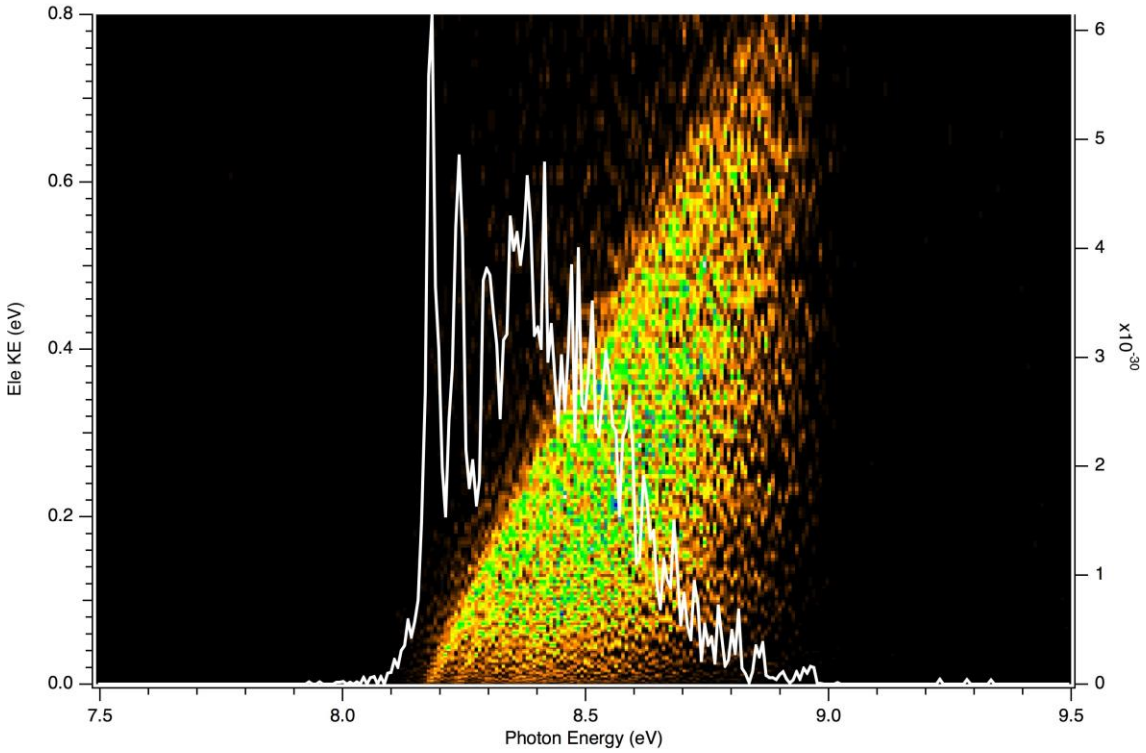
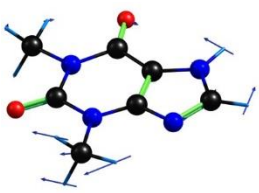


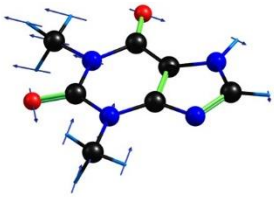
Figure S4. PES matrix of theophylline (THP)

Table S4. Assignment of the vibrational transitions in the photoelectron spectra of theophylline (THP) (ν – stretching, β – bending, δ – deformation, γ – wagging, η – twisting, τ – torsion). A cartoon with the atom movement for each vibrational mode is also shown.

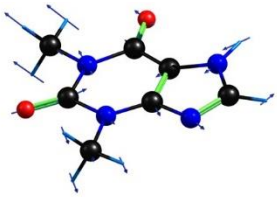
Photon Energy (cm^{-1})	Transition	Calculated wavenumber. (cm^{-1})	Vibrational mode
0.0	0_0^0	-	-
209.7	8_0^1	284.1	τ_{ring}, β CH_3
298.4	12_0^1	399.9	τ_{ring}, β C=O
443.6	14_0^1	479.1	δ_{ring}
685.6	10_0^2	-	τ_{ring}, γ CH
871.1	14_0^2	-	
911.4	26_0^1	987.0	δ_{ring}, νN_3C_2, νN_1CH_3, νN_3CH_3
1290.5	34_0^1	1333.5	δ_{ring}, β CH, β NH
1363.1	38_0^1	1433.5	δ_{ring}, β CH_3, β NH
1524.4	44_0^1	1497.8	νC_4C_5, β CH_3
1540.5	45_0^1	1508.7	νC_8N_9, δ_{ring}
1645.4	47_0^1	1687.9	νN_3C_4, νN_7C_5, β NH
1798.6	49_0^1	1830.4	νC=O, β CH_3
2129.3	$14_0^1 47_0^1$	-	Combination band.
2726.2	$14_0^2 47_0^1$	-	Combination band.



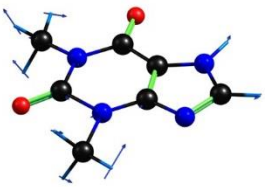
8_0^1



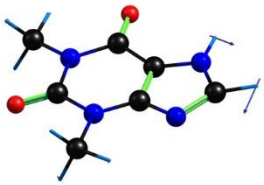
12_0^1



14_0^1

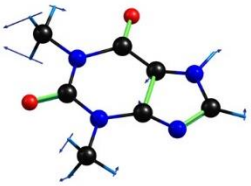


26_0^1

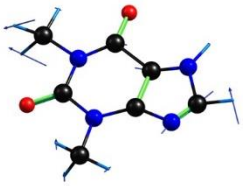


34_0^1

38_0^1

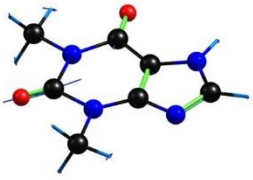


44_0^1



45_0^1

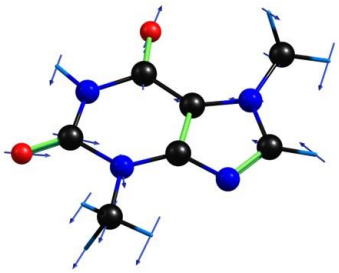
47_0^1



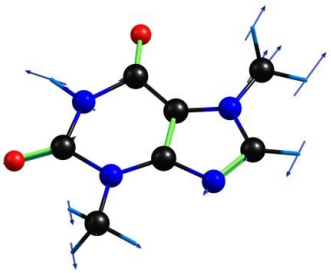
49_0^1

Table S5. Assignment of the vibrational transitions in the photoelectron spectra of theobromine (THB) (ν – stretching, β – bending, δ – deformation, γ – wagging, η – twisting, τ – torsion). A cartoon with the atom movement for each vibrational mode is also shown.

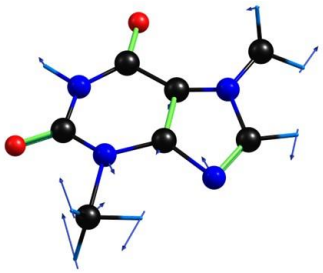
Photon Energy (cm^{-1})	**Transition**	**Calculated wavenumber. (cm^{-1})**	**Vibrational mode**
0.0	0_0^0	-	-
403.3	14_0^1	428.5	δ_{ring}
637.2	18_0^1	671.0	δ_{ring}
879.2	10_0^2	-	τ_{ring}, γ CH
1080.8	26_0^1	1041.1	δ_{ring}, νN_3C_2, νN_9C_4, β CH_3
1234.0	18_0^2	-	δ_{ring}
1484.1	37_0^1	1431.1	δ_{ring}, β NH, β CH_3, νC_2O_1, νC_6O_2
1839.0	46_0^1	1629.0	νN_3C_4, νN_7C_5, β NH
2040.6	49_0^1	1846.7	νC_2O_6, β NH
2234.2	$18_0^n 37_0^1$	-	Comb.
2887.5	37_0^2	-	δ_{ring}, β NH, β CH_3, νC_2O_1, νC_6O_2



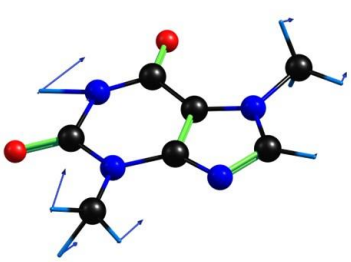
14_0^1



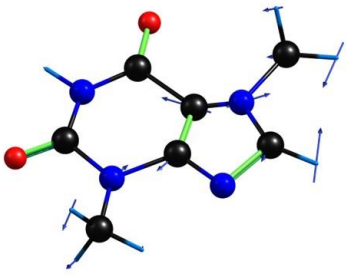
18_0^1



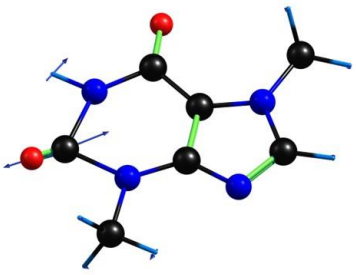
26_0^1



37_0^1



46_0^1



49_0^1

Table S6. Structure of the neutral theobromine (KETO) in Cartesian coordinates (Å), computed at PBE0/aug-cc-pVDZ level.

Atom	X coord.	Y coord.	Z coord.
C	-1.942301	0.620915	0.00028
O	-3.131431	0.875182	0.000955
N	-1.462018	-0.668252	0.000036
N	-0.984551	1.626179	-0.000064
H	-1.366904	2.560503	0.000162
C	0.406141	1.531248	-0.001091
O	1.119153	2.520354	-0.001029
C	1.800809	-1.769945	-0.000817
C	0.800139	0.156386	-0.000439
C	-0.108257	-0.881844	-0.000181
N	2.036957	-0.44639	-0.000764
N	0.511593	-2.08297	-0.000576
C	3.319437	0.220454	0.002216
H	3.410221	0.862538	-0.876652
H	3.419953	0.838258	0.897478
H	4.102014	-0.540574	-0.012345
C	-2.415487	-1.760185	0.000303
H	-3.051002	-1.701459	-0.886858
H	-1.850429	-2.692048	-0.000152
H	-3.050149	-1.701821	0.888104
H	2.607758	-2.491837	-0.001198
H	2.607758	-2.491837	-0.001198

Table S7. Structure of the ionic theobromine (KETO) in Cartesian coordinates (Å), computed at PBE0/aug-cc-pVDZ level.

Atom	X coord.	Y coord.	Z coord.
C	-1.919432	0.677008	-0.000019
O	-3.096373	0.894169	0.000272
N	-1.446873	-0.671086	-0.000011
N	-0.95918	1.67083	-0.000529
H	-1.334685	2.61265	-0.000229
C	0.422364	1.551102	-0.000098
O	1.183354	2.485065	0.000215
C	1.750528	-1.807172	-0.000139
C	0.806417	0.145903	-0.000154
C	-0.141602	-0.912032	-0.000097
N	2.003765	-0.445838	-0.000168
N	0.479068	-2.116817	-0.000077
C	3.313561	0.196243	0.000315
H	3.410782	0.823373	-0.887943
H	3.414358	0.815112	0.894007
H	4.073207	-0.585817	-0.004798
C	-2.447278	-1.733463	0.00019
H	-1.922412	-2.687591	0.00069
H	-3.07331	-1.626035	0.888837
H	-3.073007	-1.626738	-0.888757
H	2.564424	-2.523995	-0.000187

Table S8. Structure of the neutral theophylline (7H) in Cartesian coordinates (Å), computed at PBE0/aug-cc-pVDZ level.

Atom	X coord.	Y coord.	Z coord.
C	1.319217	0.805488	-0.000026
O	2.321177	1.497483	0.000027
N	0.061464	1.368109	-0.000024
N	1.406723	-0.587066	-0.000017
C	0.338993	-1.494305	-0.000029
O	0.49581	-2.704854	0.000013
C	-3.007155	-0.197862	0.000001
C	-0.913975	-0.811171	-0.00002
C	-1.036877	0.556471	-0.000013
N	-2.204472	-1.280357	0.000018
N	-2.33763	0.943273	0.000008
C	-0.044019	2.813632	0.000008
H	-1.104031	3.067097	0
H	0.444362	3.224419	0.887185
H	0.444385	3.224456	-0.887138
H	-4.08612	-0.277225	0.00001
C	2.759042	-1.120089	0.000015
H	3.295503	-0.772661	-0.886104
H	3.295475	-0.772629	0.886138
H	2.677779	-2.206109	0.000032
H	-2.477209	-2.249087	0.000038

Table S9. Structure of the ionic theophylline (7H) in Cartesian coordinates (Å), computed at PBE0/aug-cc-pVDZ level.

Atom	X coord.	Y coord.	Z coord.
C	1.29286	0.832738	-0.000043
O	2.215744	1.598119	0.000023
N	-0.03729	1.36855	-0.000015
N	1.452554	-0.543796	-0.000019
C	0.432698	-1.486155	-0.000022
O	0.589371	-2.682793	0.000014
C	-2.990762	-0.310637	-0.000004
C	-0.877443	-0.85242	-0.000011
C	-1.076686	0.549011	-0.000009
N	-2.108196	-1.373574	0.000013
N	-2.39914	0.856006	0.000009
C	-0.175135	2.82111	0.000011
H	-1.238744	3.055936	0.000016
H	0.318907	3.220627	0.888436
H	0.318907	3.220655	-0.888401
H	-4.063813	-0.464021	0.000008
C	2.841831	-1.013906	0.000017
H	3.350285	-0.640606	-0.890669
H	3.350257	-0.640566	0.890703
H	2.816481	-2.102344	0.000041
H	-2.332894	-2.361036	0.000027

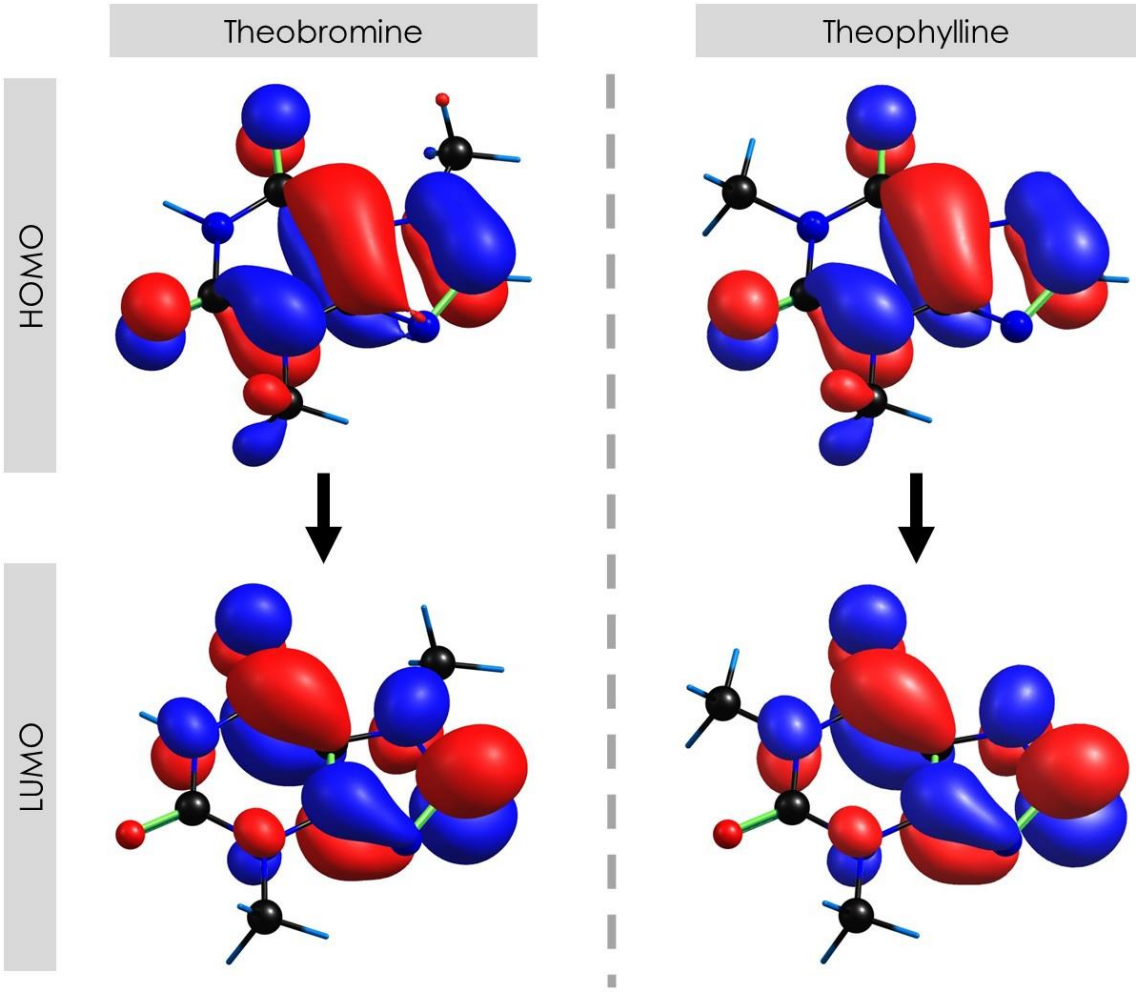


Figure S5. Representation of the molecular orbitals of theobromine (THB) and theophylline (THP) involved in the $S_0 \rightarrow S_1$ electronic transition ($\pi \rightarrow \pi^*$)