Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

A quantum chemical investigation of the electronic structure of thionine†

Electronic Supporting Information

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†Geometries and vibrational frequencies of the ground and excited states are provided as molden files: S0.molden, S1.molden, S2.molden, T1.molden, T2.molden, T3.molden.

Fig. 1 DFT/MRCI energies of the low-lying states of thionine along a linearly interpolated path between the S_0 and S_1 geometries. The singlet profiles are represented by solid lines and the triplet profiles by dashed lines.

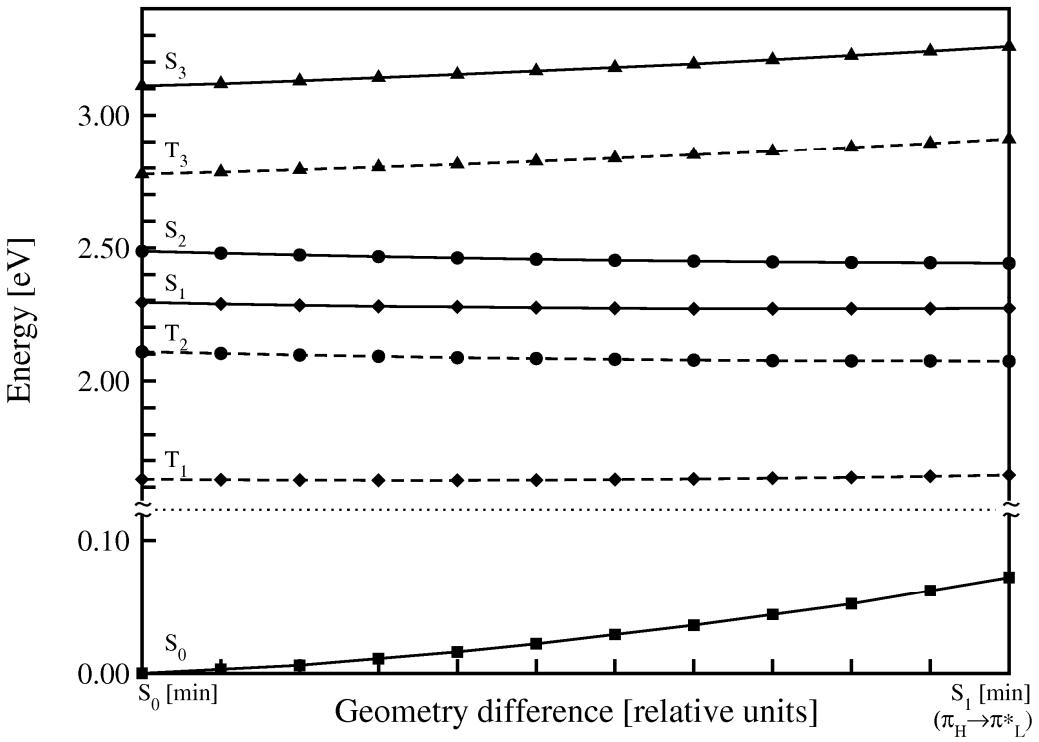

Fig. 2 Frontier BHLYP/TZVP Kohn-Sham molecular orbitals computed at the T_3 ($n\rightarrow\pi^*$) state minimum (isovalue 0.03) of thionine.

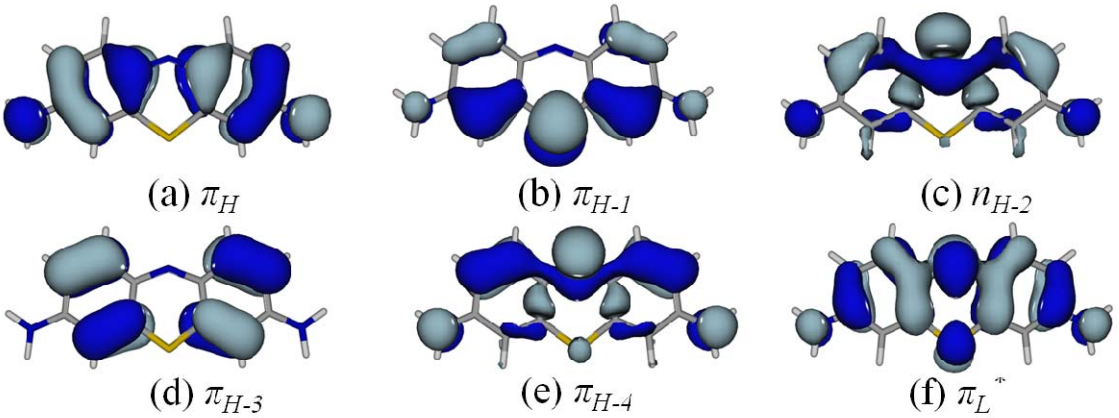

Table 1 Selected geometrical parameters of the thionine ground state calculated with the B3LYP functional and the TZVP, TZVPP and TZVP+R basis sets. Bond lengths are reported in Å and angles in degrees (°).

Parameter	TZVP	TZVPP	TZVP+R
r(C(11)-C(12))	1.358	1.357	1.358
r(C(12)-C(13))	1.429	1.428	1.429
r(C(11)-C(3))	1.430	1.428	1.430
r(N(4)-C(3))	1.330	1.329	1.331
r(C(3)-C(2))	1.438	1.437	1.437
r(C(2)-C(14))	1.380	1.380	1.380
r(C(2)-S(1))	1.751	1.738	1.750
r(C(13)-C(14))	1.408	1.406	1.408
r(C(13)-N(15))	1.345	1.344	1.346
r(N(18)-H(19))	1.007	1.005	1.007
r(N(18)-H(20))	1.007	1.005	1.007
θ(S(1)-C(6)-C(7))	118.3	118.4	118.2
θ(S(1)-C(6)-C(5))	120.6	120.6	120.7
θ(C(2)-S(1)-C(6))	103.1	103.6	103.1
θ(N(4)-C(5)-C(10))	117.2	117.3	117.2
θ(N(4)-C(5)-C(6))	125.7	125.5	125.6
θ(C(3)-N(4)-C(5))	124.3	124.3	124.3
θ(C(6)-C(7)-C(8))	120.3	120.3	120.3
θ(C(5)-C(10)-C(9))	121.8	121.8	121.8
θ(C(5)-C(6)-C(7))	121.1	121.1	121.1
θ(C(10)-C(5)-C(6))	117.2	117.2	117.2
θ(C(8)-C(9)-C(10))	120.3	120.3	120.3
θ(C(7)-C(8)-C(9))	119.4	119.4	119.3
θ(N(18)-C(8)-C(9))	119.8	119.7	119.8
θ(N(18)-C(8)-C(7))	120.9	120.9	120.9
θ(C(8)-N(18)-H(19))	121.2	121.1	121.2
θ(C(8)-N(18)-H(20))	121.7	121.6	121.7
θ(H(19)-N(18)-H(20))	117.1	117.3	117.1

Table 2 Vertical singlet and triplet excitation energies ΔE (eV) of thionine calculated using the TZVP+R and the TZVP basis sets.

Electronic State	Electronic Structure[a]	DFT/MRCI /TZVP+R// B3LYP /TZVP+R[b]	DFT/MRCI /TZVP// B3LYP /TZVP+R[b]	DFT/MRCI /TZVP// B3LYP /TZVP[b]	TD-B3LYP/TZVP+R// B3LYP /TZVP+R[b]	TD-B3LYP/TZVP// B3LYP /TZVP[b]
S_0 (1^1A_1)	(0.93) Ground State					
S_1 (1^1B_1)	(0.80) $\pi_H \rightarrow \pi_L^*$	2.29(0.832)	2.29(0.831)	2.29(0.833)	2.74(0.612)	2.74(0.613)
S_2 (2^1A_1)	(0.82) $\pi_{H-1} \rightarrow \pi_L^*$	2.49(0.012)	2.48(0.012)	2.49(0.012)	2.72(0.010)	2.73(0.010)
S_3 (1^1B_2)	(0.79) $n_{H-4} \rightarrow \pi_L^*$	3.12(0.003)	3.11(0.003)	3.11(0.003)	3.21(0.001)	3.21(0.001)
S_4 (3^1A_1)	(0.52) $\pi_{H-2} \rightarrow \pi_L^*$ (0.21) $\pi_H \rightarrow \pi_L^* \pi_H \rightarrow \pi_L^*$	3.55(0.014)	3.56(0.014)	3.56(0.014)	4.03(0.002)[c]	4.03(0.002)[c]
⋮	⋮	⋮	⋮	⋮	⋮	⋮
S_8 (4^1A_1)	(0.64) $\pi_H \rightarrow \pi_{L+1}^*$	4.37(0.132)	4.37(0.133)	4.37(0.133)	4.53(0.088)	4.53(0.089)
S_9 (3^1B_1)	(0.50) $\pi_H \rightarrow \pi_{L+2}^*$ (0.23) $\pi_{H-1} \rightarrow \pi_{L+1}^*$	4.41(0.044)	4.42(0.058)	4.42(0.056)	4.61(0.024)	4.62(0.027)
S_{10} (4^1B_1)	(0.34) $\pi_{H-1} \rightarrow \pi_L^* \pi_H \rightarrow \pi_L^*$ (0.20) $\pi_{H-1} \rightarrow \pi_{L+1}^*$	4.57(0.532)	4.57(0.526)	4.57(0.526)	5.02(1.063)[d]	5.02(1.058)[d]
⋮	⋮	⋮	⋮	⋮	⋮	⋮
S_{12} (5^1B_1)	(0.33) $\pi_{H-5} \rightarrow \pi_L^*$ (0.14) $\pi_H \rightarrow \pi_L^* \pi_H \rightarrow \pi_{L+1}^*$ (0.12) $\pi_H \rightarrow \pi_{L+2}^*$	4.89(0.199)	4.89(0.200)	4.90(0.201)	5.48(0.008)[e]	5.50(0.010)[e]
T_1 (1^3B_1)	(0.92) $\pi_H \rightarrow \pi_L^*$	1.63	1.63	1.63	1.51	1.53
T_2 (1^3A_1)	(0.88) $\pi_{H-1} \rightarrow \pi_L^*$	2.11	2.10	2.11	2.01	2.03
T_3 (1^3B_2)	(0.81) $n_{H-4} \rightarrow \pi_L^*$	2.78	2.77	2.78	2.60	2.61
T_4 (2^3A_1)	(0.78) $\pi_{H-2} \rightarrow \pi_L^*$	3.12	3.12	3.12	3.00	3.01

[a] Dominant contributions at the DFT/MRCI/TZVP level in parentheses. [b] Oscillator strengths (length form) in parentheses. [c]The dominant contribution of these states is a combination of two single excitations: $\pi_{H-2} \rightarrow \pi_L^*$ and $\pi_H \rightarrow \pi_{L+1}^*$. [d]The dominant contribution of these states is a combination of two single excitations: $\pi_{H-1} \rightarrow \pi_{L+1}^*$ and $\pi_H \rightarrow \pi_{L+2}^*$. [e]The dominant contribution of these states is a single excitation: $\pi_{H-5} \rightarrow \pi_L^*$.

Table 3 DFT/MRCI energies (ΔE), Oscillator strengths (f(L)) and dominant contributions (DC) for each of the linearly interpolated geometries between the S_1 and the S_2 minima calculated at the DFT/MRCI/TZVP level.

Step	S_1				S_2			
	ΔE	f(L)	DC $\pi_H \rightarrow \pi_L^*$	DC $\pi_{H-1} \rightarrow \pi_L^*$	ΔE	f(L)	DC $\pi_{H-1} \rightarrow \pi_L^*$	DC $\pi_H \rightarrow \pi_L^*$
S_1	2.270	0.790	0.800	-	2.44	0.010	0.815	-
1	2.269	0.790	0.799	-	2.42	0.011	0.815	-
2	2.269	0.787	0.796	-	2.41	0.015	0.813	-
3	2.271	0.777	0.789	-	2.39	0.025	0.806	-
4	2.274	0.758	0.774	-	2.38	0.045	0.792	0.024
5	2.277	0.722	0.746	0.053	2.37	0.081	0.764	0.051
6	2.281	0.664	0.698	0.101	2.37	0.139	0.716	0.098
7	2.284	0.582	0.630	0.171	2.37	0.221	0.646	0.166
8	2.287	0.488	0.549	0.254	2.38	0.315	0.563	0.246
9	2.385	0.404	0.323	0.484	2.29	0.399	0.334	0.472
10	2.400	0.476	0.385	0.420	2.29	0.327	0.398	0.410
S_2	2.419	0.533	0.432	0.371	2.3	0.269	0.448	0.362