The Molecular Mechanism of Photochromism in Photo-Enolizable Quinoline and Napthyridine Derivatives

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Supplementary information

Wiberg bond indices for 0B

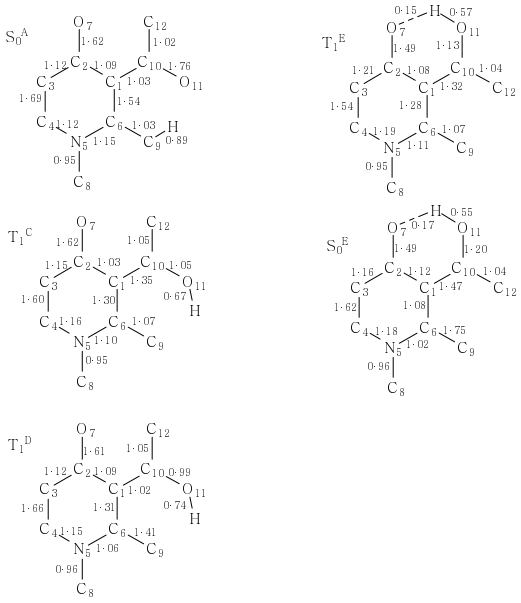

Figure S7: The Wiberg bond indices obtained at the B3LYP/6-31G* level of theory for the discriminated structures along the PES for **0B** (See Figure 6). For T_1^C, T_1^D and T_1^E, the highest Mulliken spin densities are found at $\{C_6(0.38), C_9(0.96),$ and $C_{10}(0.49)\}$, $\{C_1(0.47), C_9(0.72),$ and $C_{10}(0.84)\}$, and $\{C_6(0.35), C_9(1.05),$ and $C_{10}(0.44)\}$, respectively.

CC2 results

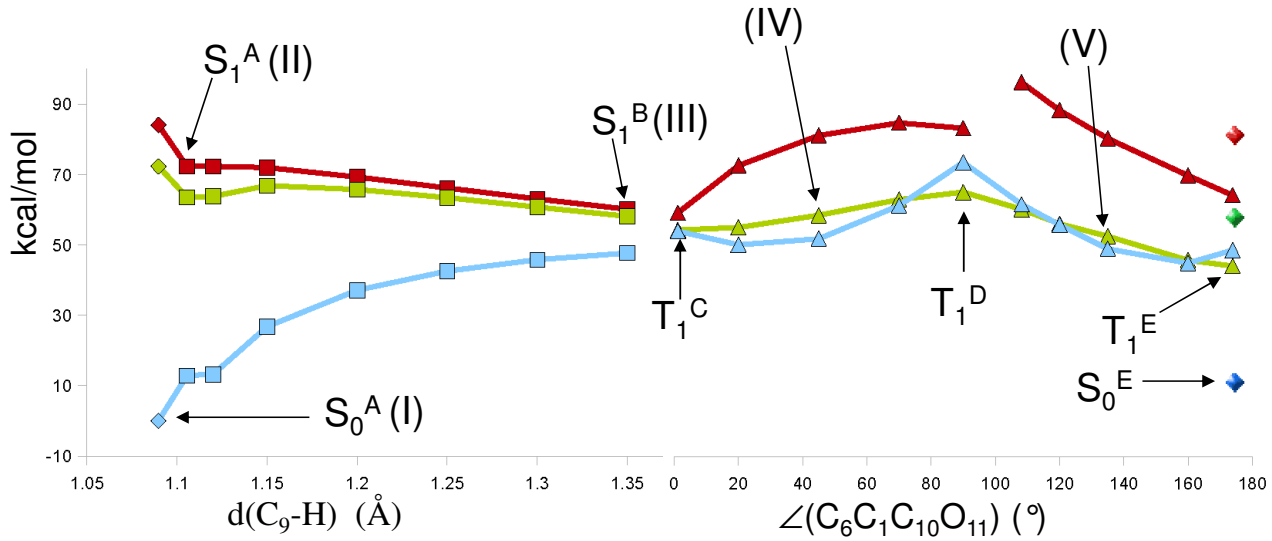

Figure S8: The potential energy surface of **0A** and the proton transfer from the methyl group at the second position of the pyridon group to the acetyl group (O_{11} in Figure 1) and the rotation of the acetyl group, which enables a proton transfer to the oxygen at the fourth position at the pyridon group (O_7 in Figure 1, B3LYP/6-31G* data). The legend is the same as the one in Figure 4. For the structure points indicated by Roman numbers, the TDDFT energetics has been checked against CC2 ones, which are given in Table S3.

Table S3: Calculation of relative CC2 energies for structures related to the PES of **0A** . They are indicated by Roman characters in Figure S8. By reason of comparison, the TDDFT data are indicated, too.[a]

	CC2/DZP			TDDFT/B3LYP/6-31G*		
	S_0	T_1	S_1	S_0	T_1	S_1
I	0.0[b]	82.7[c]	89.5[c]	0.0[b]	72.3[c]	84.0[c]
II	25.6[c]	67.8[c]	71.8[b]	12.9[c]	63.5[c]	72.2[b]
III	48.9[c]	66.9[c]	67.9[b]	47.6[c]	58.1[c]	60.0[b]
IV	57.2[c]	64.6[b]	77.6[c]	52.2[c]	58.8[b]	81.6[c]
V	54.3[c]	56.0[b]	73.5[c]	49.3[c]	52.8[b]	80.8[c]

[a] Results given in kcal mol^{-1}.
[b] Optimization.
[c] Single point results.

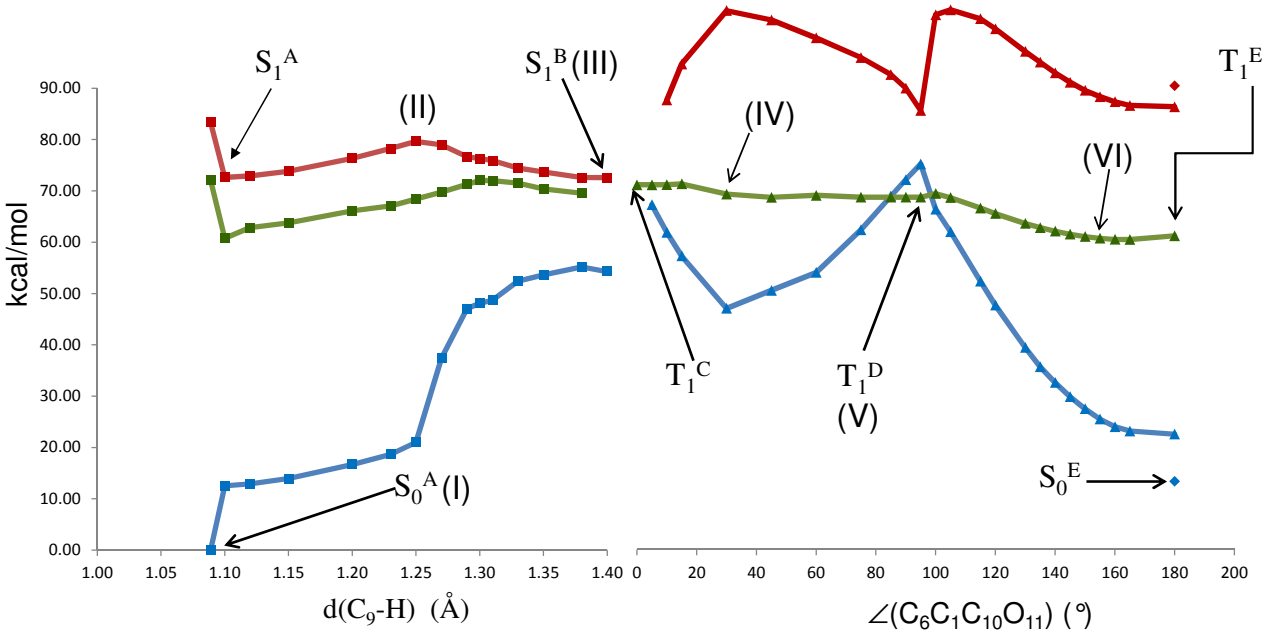

Figure S9: The potential energy surface of **0B** and the proton transfer from the methyl group at the second position of the pyridon group to the acetyl group (O_{11} in Figure 1) and the rotation of the acetyl group, which enables a proton transfer to the oxygen at the fourth position at the pyridon group (O_7 in Figure 1, B3LYP/6-31G* data). The legend is the same as the one in Figure 6. For the structure points indicated by Roman numbers, the TDDFT energetics has been checked against CC2 ones, which are given in Table S4.

Table S4: Calculation of relative CC2 energies for structures related to the PES of **0B** . They are indicated by Roman characters in Figure S9. By reason of comparison, the TDDFT data are indicated, too.[a]

	CC2/DZP			TDDFT/B3LYP/DZP		
	S_0	T_1	S_1	S_0	T_1	S_1
I	0.0[b]	82.3[c]	89.3[c]	0.0[b]	72.1[c]	83.3[c]
II	32.0[c]	75.1[c]	79.0[b]	21.0[c]	68.4[c]	79.6[b]
III	57.6[c]	77.1[c]	79.0[b]	55.2[c]	69.5[c]	72.6[b]
IV	57.4[c]	76.6[b]	112.2[c]	47.2[c]	69.6[b]	105.6[c]
V	77.3[c]	76.7[b]	102.4[c]	75.5[c]	69.0[b]	85.6[c]
VI	30.4[c]	70.5[b]	94.9[c]	27.6[c]	61.3[b]	89.9[c]

[a] Results given in kcal mol^{-1}.
[b] Optimization.
[c] Single point results.