

Supplement material of

“Solvent effect on the photo-induced proton transfer in 2-(N-methyl- α -iminoethyl)-phenol”

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Section 1. Validity of restricted DFT calculations for the study of the MIEP

Position of the intramolecularly bonded hydrogen in the MIEP compound may be sensitive with respect to the assumptions made during calculation phase because of an easy internal proton transfer within the O...H...N fragment. One such assumption is the use of a restricted (closed-shell) wavefunction, which is common in studies of charge-neutral molecules. The suitability of the restricted method was tested by determining the stability of the resulting wavefunction with respect to spin and symmetry relaxation (keyword *Stable* in *Gaussian09*) for the optimized structures of enol and *cis*-keto tautomeric forms. The wavefunction generated by RDFT method was found to be stable, and energy calculations (both ground-state and electronic excitations) yielded identical values for RDFT and UDFT. Additionally, geometric parameters of enol and *cis*-keto tautomers, as well as enol-keto transition state, were optimized using UDFT (keyword *ub3lyp* in this case). The obtained results coincide with earlier RDFT calculations up to the limit of chemical accuracy. Comparison of the results is provided in Fig. S1.1.

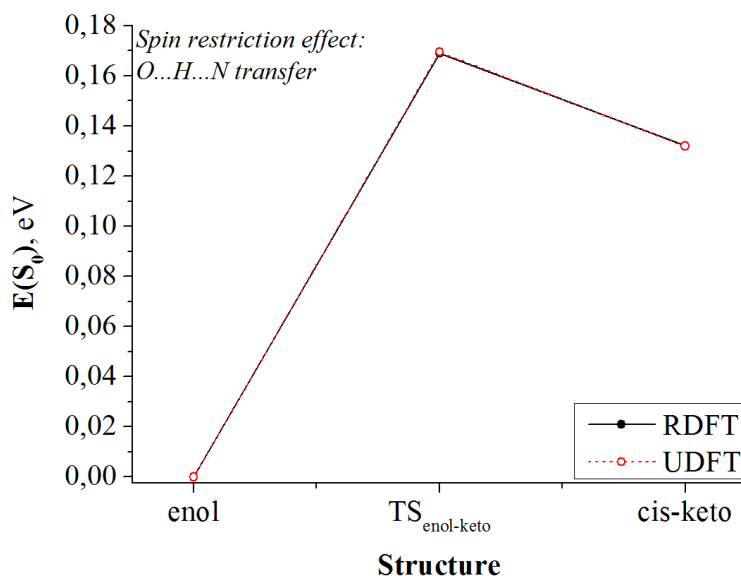


Fig. S1.1. Comparison of the RDFT and UDFT energy calculations during the internal proton transfer process in the MIEP compound

Section 2. BSSE corrections for the MIEP compound in water

To assess the importance of the basis set superposition error during the study of the MIEP, a counterpoise method (keyword *Counterpoise* in *Gaussian09*) was additionally used during the repeated calculation of the ground-state energies of the various conformations of the compound. The intramolecular BSSE was estimated by artificially dividing the compound into two fragments connected by the C₆-C₉ bond, while in the case of intermolecular interaction the MIEP and water molecules constituted the fragments. Both sets of calculations resulted in a small shift of the total energy. The change in energy value was ~0.07 eV and 0.50 eV for the intramolecular and intermolecular corrections, respectively. This change was found to be almost constant for the various conformations, which led to the cancellation of the BSSE effect on the shapes of the potential energy surfaces of MIEP. Results of BSSE calculations are shown in Fig. S2.1.

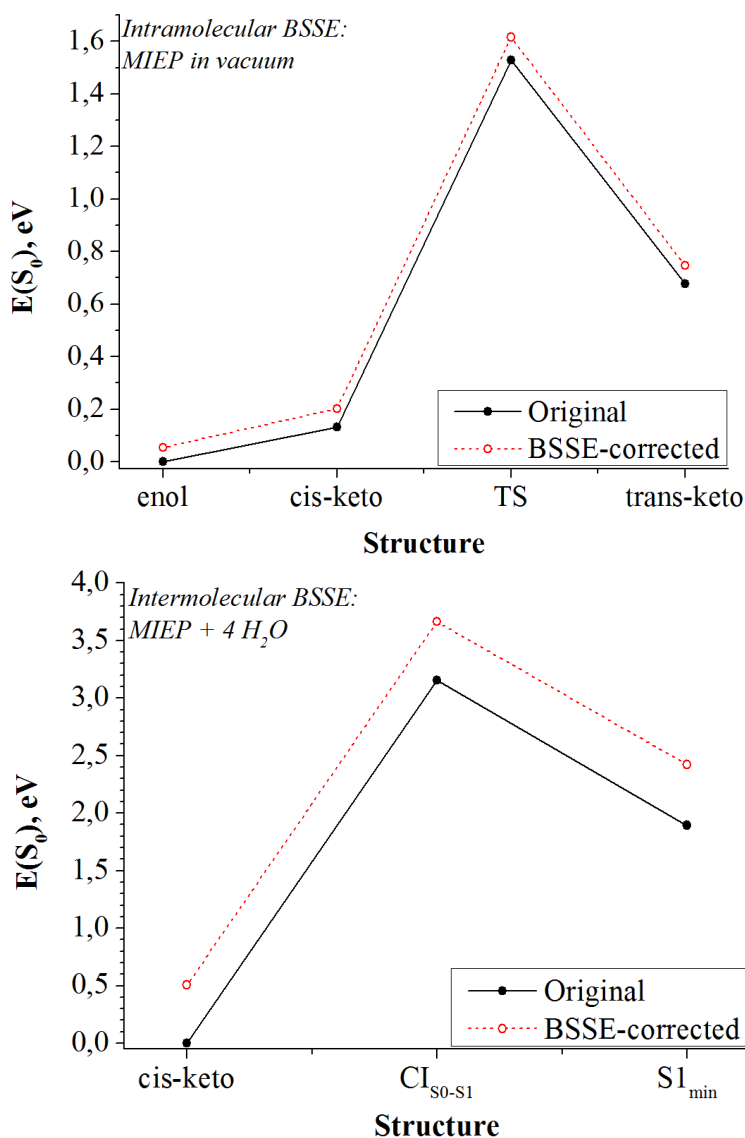


Fig. S2.1. BSSE corrections to the ground-state energy surfaces of the MIEP compound in vacuum (*top*) and as a MIEP-water cluster (*bottom*)

Section 3. Electronic excitation properties of the twisted conformations of the MIEP

Table S3.1. Electronic excitations of the twisted conformations of the MIEP molecule in the ground state S_0 . Oscillator strength of the excitation is equal to 0 except where marked. In the “Transition” column, numbers 1, 2, 3... denote occupied MOs, starting from HOMO. Numbers 1', 2', 3'... denote unoccupied MOs, starting from LUMO

Structure	CI (vacuum)		S_1 min. (vacuum)		S_1 min. (water, C-PCM)	
	E_{tr} , eV	Transition	E_{tr} , eV	Transition	E_{tr} , eV	Transition
1	0	1-1' ($\pi^- - n_N^*$)	0.120	1-1' ($\pi^- - n_N^*$)	0.847	1-1' ($\pi - n_N^*$)
2	0.997	2-1' ($n - n_N^*$)	1.001	2-1' ($n - n_N^*$)	2.012	2-1' ($n - n_N^*$)
3	2.268	3-1' ($\pi_N - n_N^*$)	2.279	3-1' ($\pi_N - n_N^*$)	2.883	3-1' ($\pi_N - n_N^*$)
4	3.879	4-1'	3.618	1-2'	4.109 ^b	1-2' ($\pi - \pi^*$)
5	3.924 ^a	1-2' ($\pi^- - \pi^*$)	3.785	4-1'	4.580	4-1'

^a $f_{osc} = 0.057$

^b $f_{osc} = 0.135$

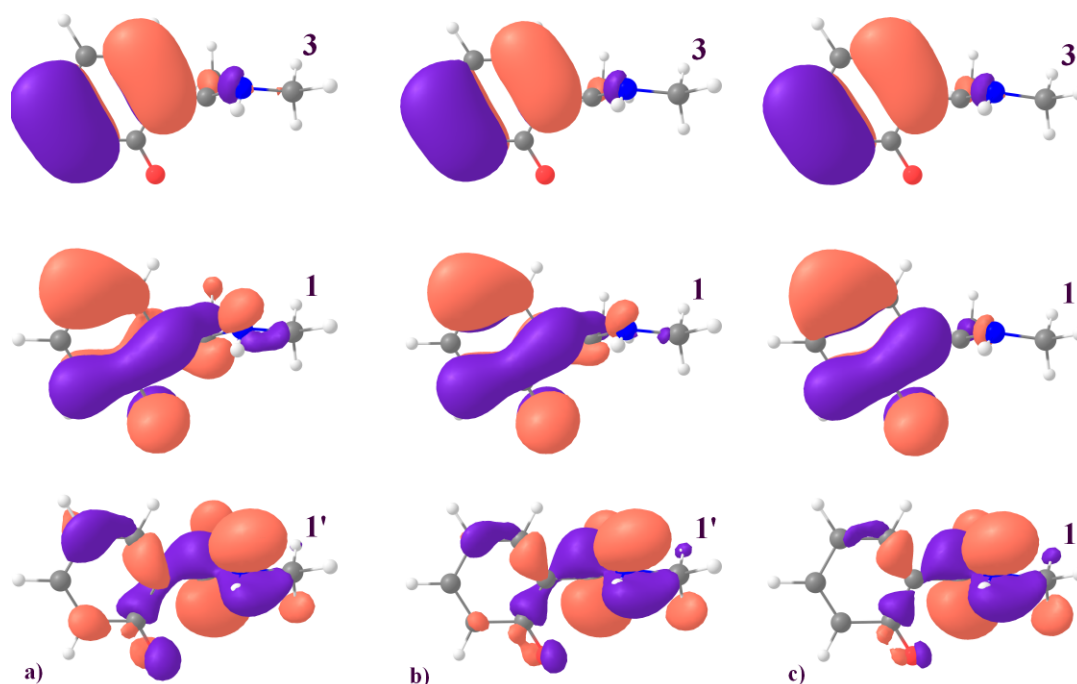


Fig. S3.1. Selected molecular orbitals of the twisted MIEP conformations: a) S_0 - S_1 conical intersection (vacuum), b) global minimum of S_1 (vacuum), c) global minimum of S_1 (water, C-PCM)

Section 4. *Electronic excitation properties of the MIEP-water cluster*

Table S4.1. Electronic excitations of the conformations of the MIEP-water cluster. In the “Transition” column, numbers 1, 2, 3... denote occupied MOs, starting from HOMO. Numbers 1', 2', 3'... denote unoccupied MOs, starting from LUMO

<i>Structure</i>	<i>Enol</i>			<i>Cis-keto</i>		
State no.	E_{tr}, eV	f_{osc}	Transition	E_{tr}, eV	f_{osc}	Transition
1	4.129	0.097	1-1' (π - π^*)	3.329	0.125	1-1' (π - π^*)
2	4.417	0	3-1' (n - π^*)	3.762	0	2-1' (n - π^*)
3	5.042	0.183	2-1' (π_N - π^*)	4.665	0.216	3-1' (π_N - π^*)
4	5.266	0	4-1' (H ₂ O)	4.808	0	4-1' (H ₂ O)
5	5.743	0.180	1-2' (π - π_O^*)	5.136	0	5-1' (H ₂ O)
<i>Structure</i>	<i>Conical</i>			<i>S₁ min.</i>		
State no.	E_{tr}, eV	f_{osc}	Transition	E_{tr}, eV	f_{osc}	Transition
1	0	0	1-1' (π - n_N^*)	0.405	0	1-1' (π - n_N^*)
2	1.476	0	2-1' (n - n_N^*)	1.938	0	2-1' (n - n_N^*)
3	1.992	0	3-1' (π_N - n_N^*)	2.290	0	3-1' (π_N - n_N^*)
4	2.852	0	4-1' (H ₂ O)	3.537	0	4-1' (H ₂ O)
5	3.476	0	5-1' (H ₂ O)	3.912	0	5-1' (H ₂ O)

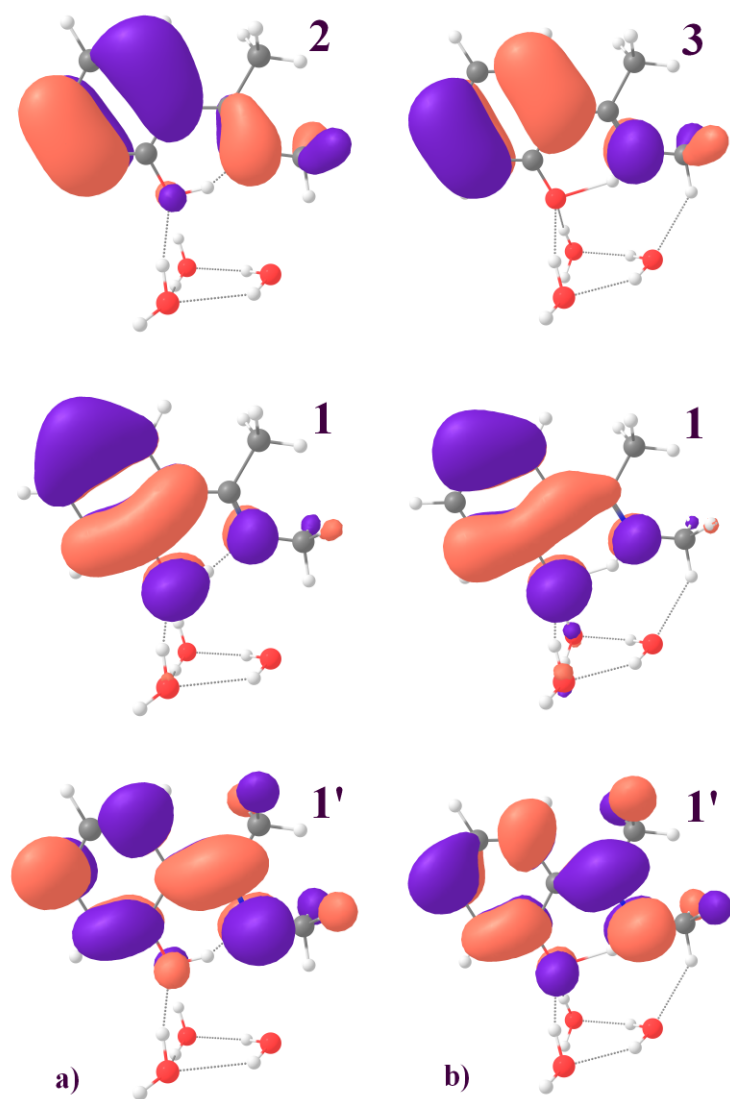


Fig. S4.1. Selected molecular orbitals of the MIEP-water cluster tautomers: a) enol, b) *cis*-keto

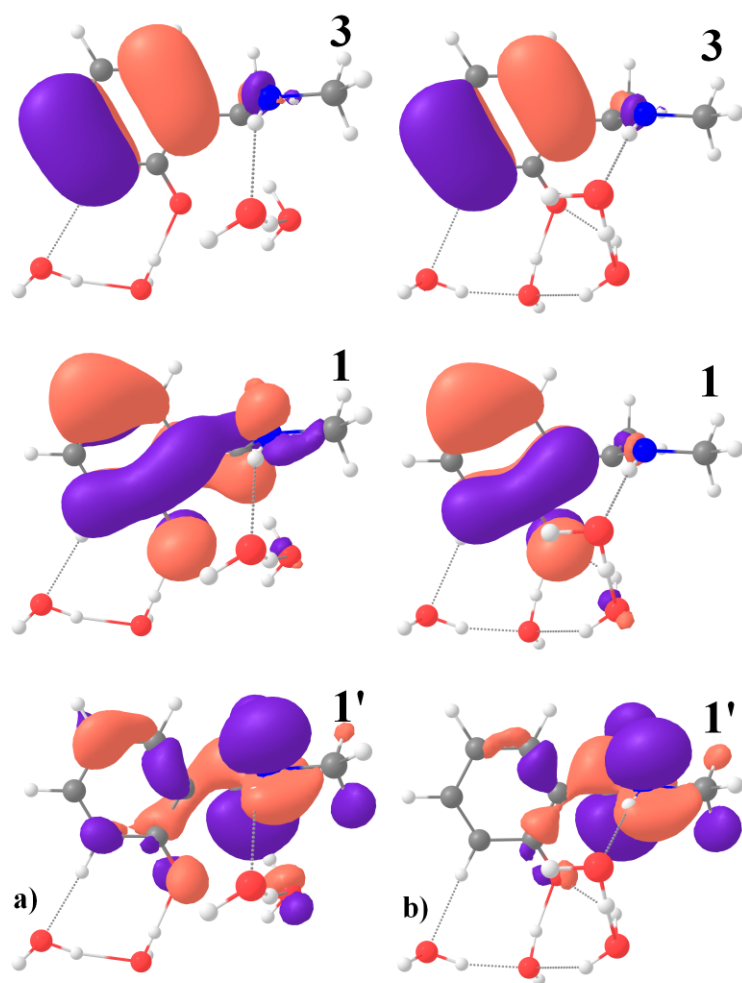


Fig. S4.2. Selected molecular orbitals of the twisted MIEP-water cluster conformations: a) S_0 - S_1 conical intersection, b) global minimum of S_1