Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Material for:

A Theoretical Study of the Photodynamics of salicylidene-2-anthrylamine in Acetonitrile Solution

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List of contents:

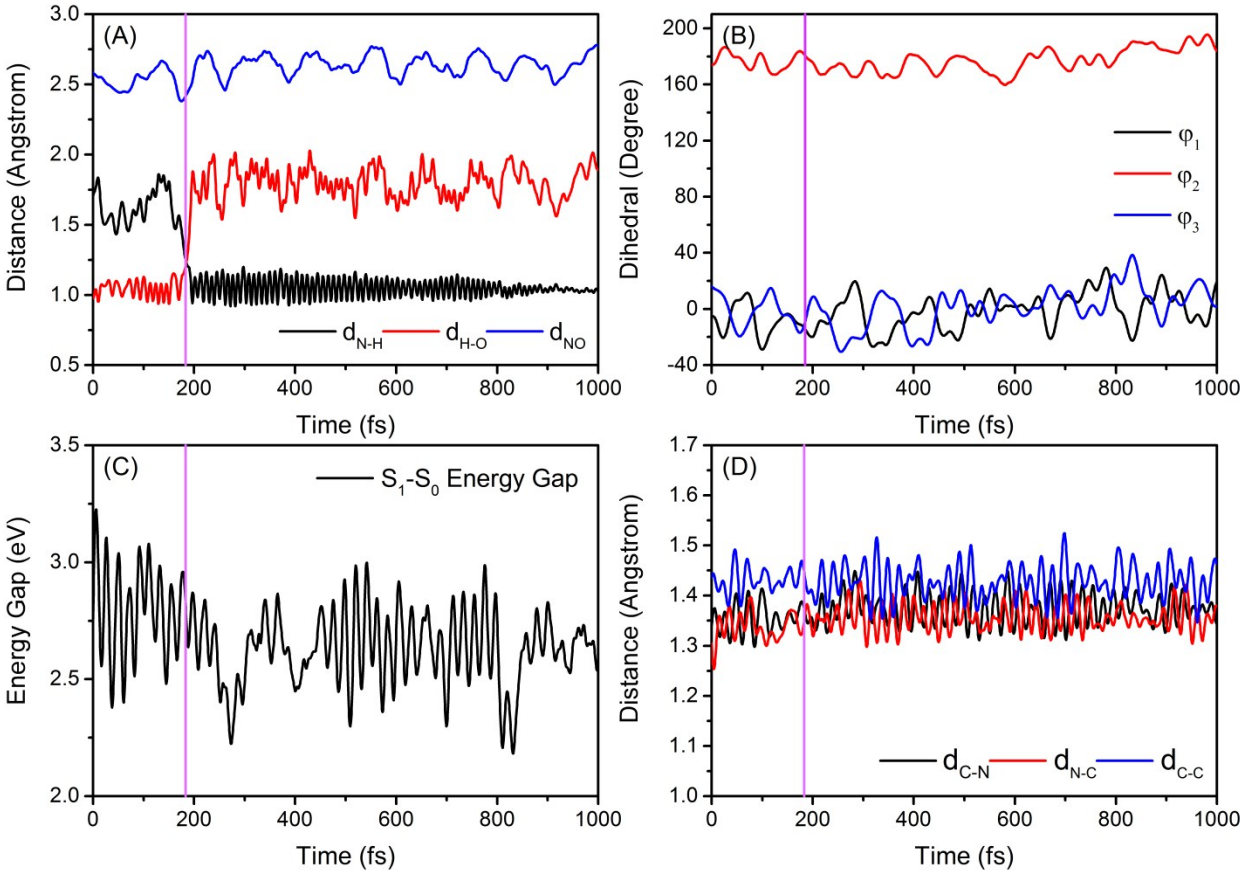

Fig. S1. Different properties vs. simulation time of a typical trajectory for (IA)S_1 in acetonitrile solution. a) N–H, O–H and NO distances, b) φ_1, φ_1 and φ_3 dihedral angles, c) S_1/S_0 energy gap and d) C_1–N, N–C_3 and C_3–C_4 distances. The vertical lines indicate the ESIPT event.

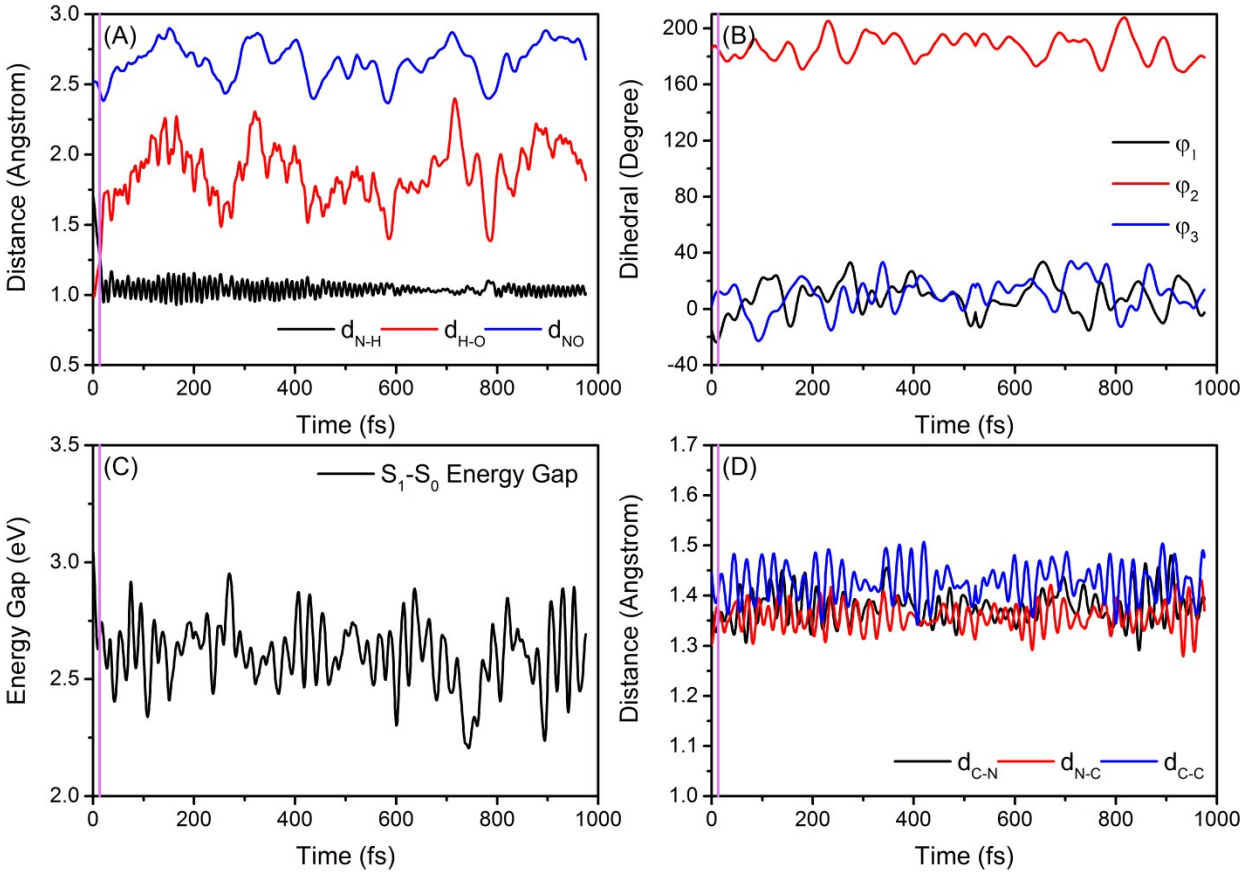

Fig. S2. Different properties vs. simulation time of a typical trajectory for (IA)S_1 in acetonitrile solution. a) N–H, O–H and NO distances, b) φ_1, φ_1 and φ_3 dihedral angles, c) S_1/S_0 energy gap and d) C_1–N, N–C_3 and C_3–C_4 distances. The vertical lines indicate the ESIPT event.

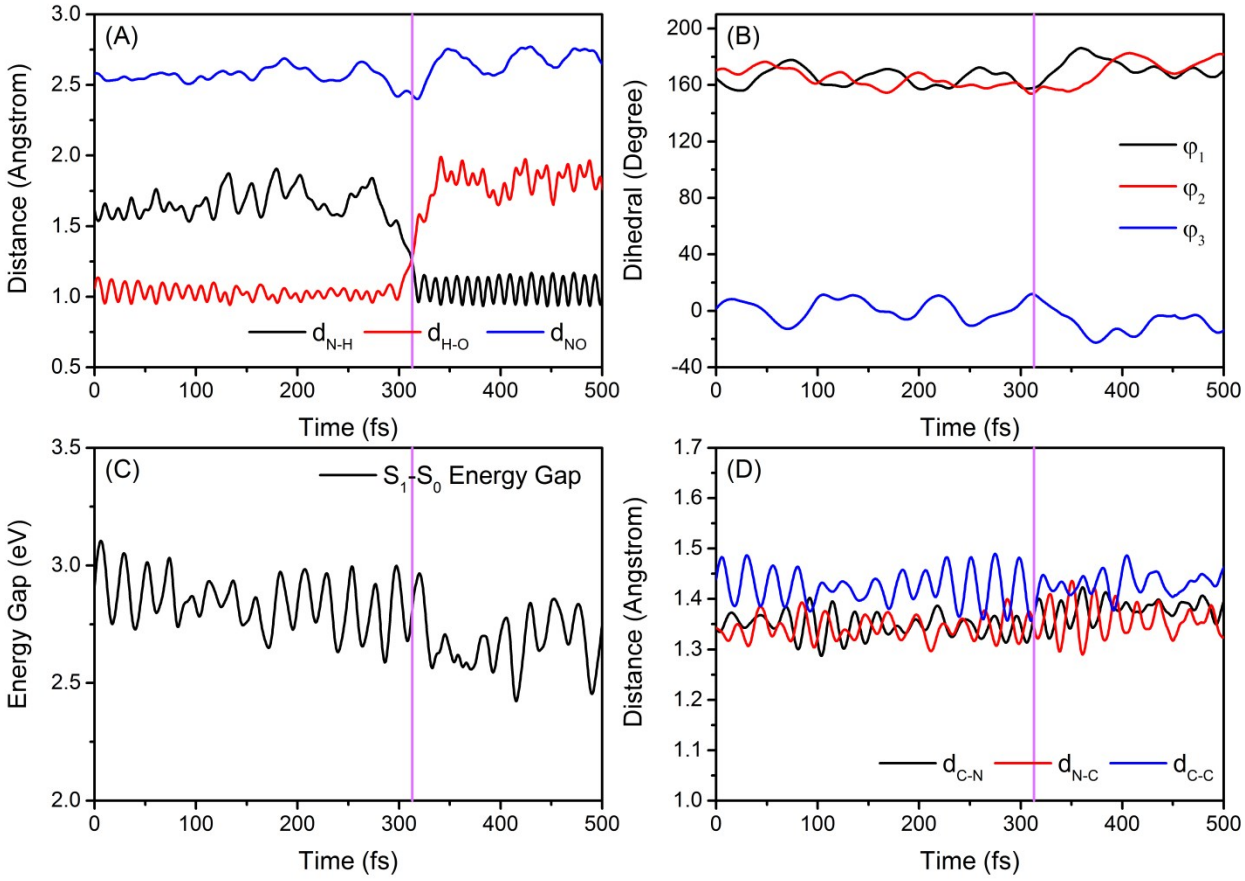

Fig. S3. Different properties vs. simulation time of a typical trajectory for (IIA)S_1 in acetonitrile solution. a) N–H, O–H and NO distances, b) φ_1, φ_1 and φ_3 dihedral angles, c) S_1/S_0 energy gap and d) C_1–N, N–C_3 and C_3–C_4 distances. The vertical lines indicate the ESIPT event.

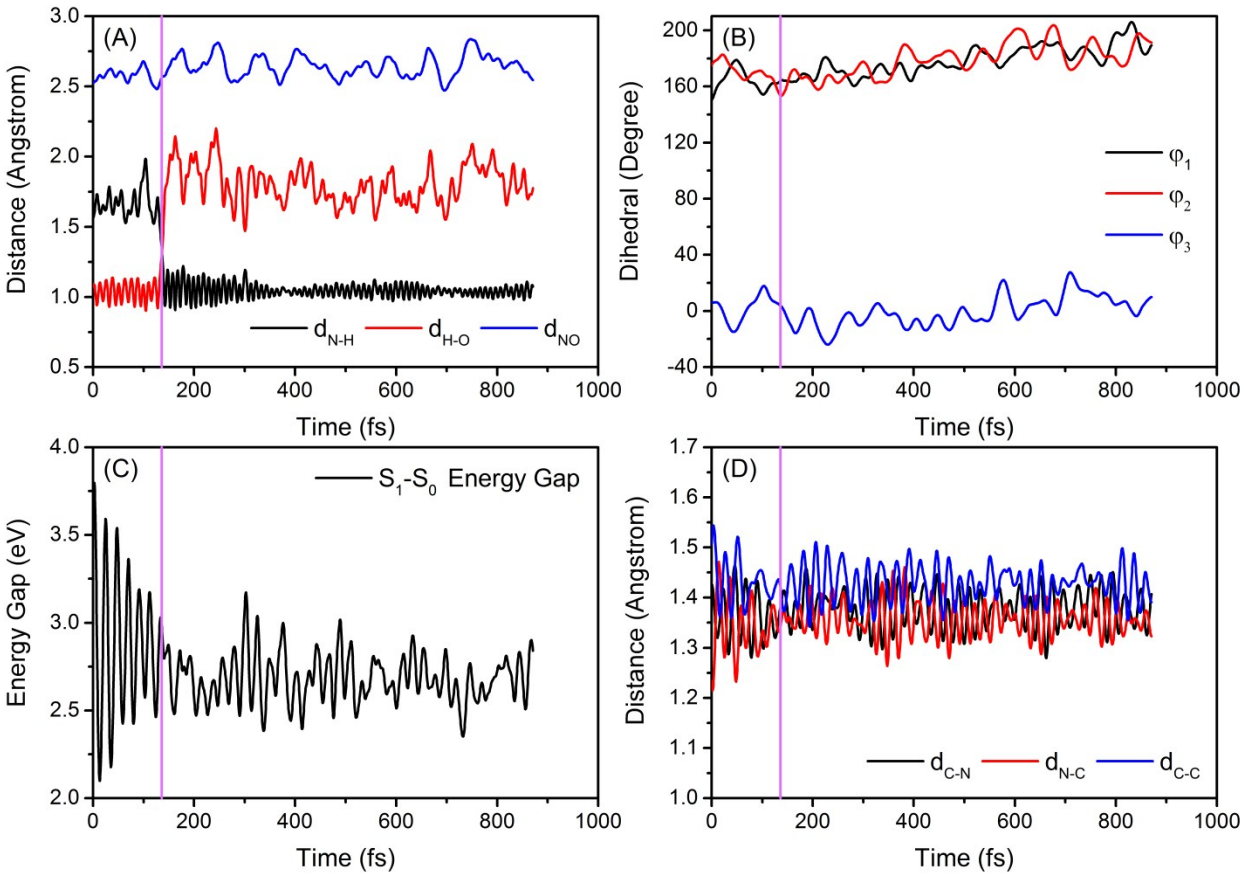

Fig. S4. Different properties vs. simulation time of a typical trajectory for (IIA)S_1 in acetonitrile solution. a) N–H, O–H and NO distances, b) φ_1, φ_1 and φ_3 dihedral angles, c) S_1/S_0 energy gap and d) C_1–N, N–C_3 and C_3–C_4 distances. The vertical lines indicate the ESIPT event.

Fig. S5. Average bond distance in the aliphatic chain before and after the ESIPT reaction for (IA)S_1 (left panel) and (IIA)S_1 (right panel). R = Anthracene.

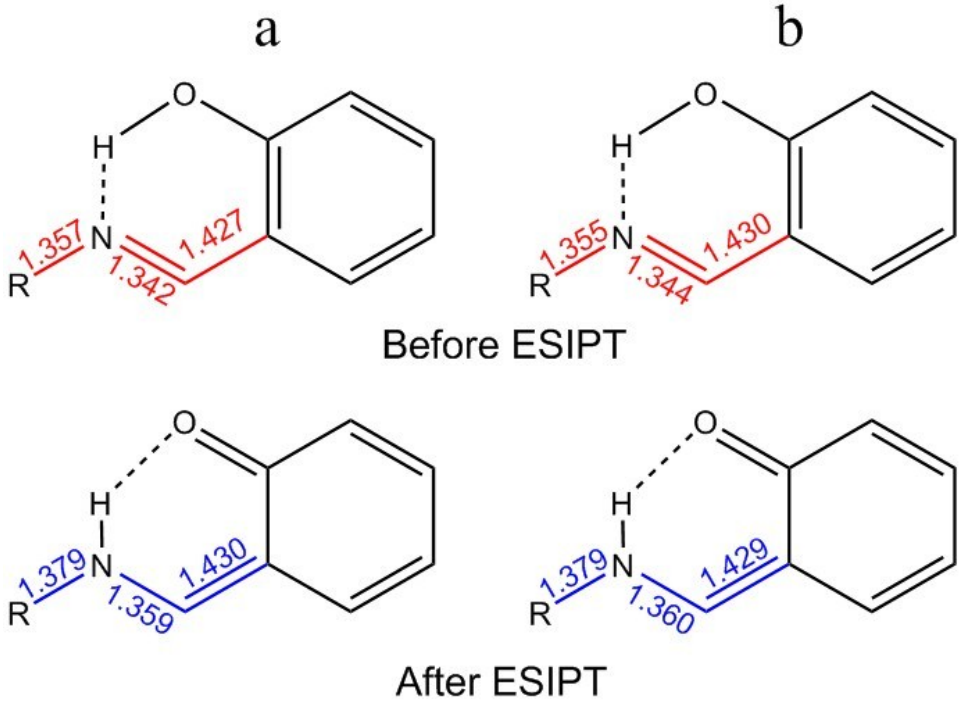

Fig. S6. Isosurface of HOMO (left) and LUMO (right) orbitals of IA (top) and IIA (bottom) in acetonitrile calculated at the PCM/ωB97XD level of theory using the same basis set as in the molecular dynamics. Isosurface value: 0.02 $a_0^{-3/2}$.

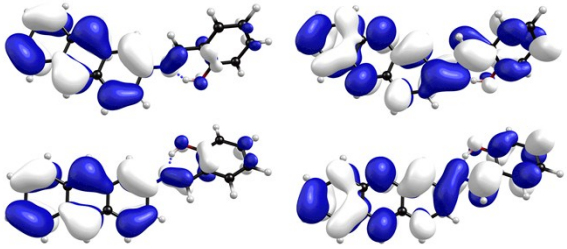

Fig. S7. N–H and O–H distances for the trajectory in which the ESIMPT is the fastest. The legends with an asterisk (blue and magenta)correspond to calculations with the basis set used for all dynamics. In red and black are the values for a trajectory with exactly the same initial conditions but with a a larger basis set: 6-311G(d,p) for all atom except for those in the anthracene (6-31G). Note that the proton-transfer-time agrees within 1fs.

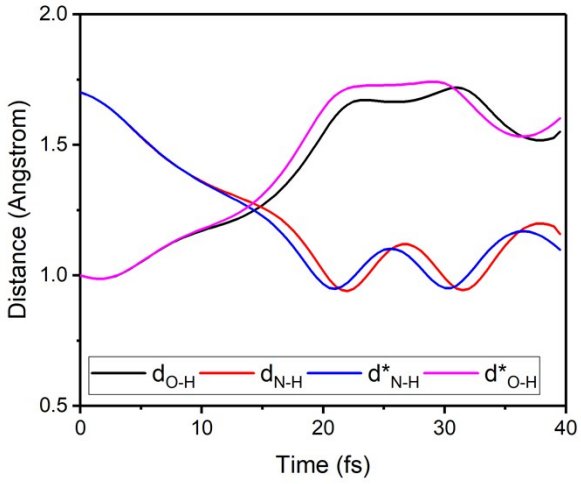

Table S1. Selected geometrical parameters of the optimized ground state rotamers and tautomers of 2-AntSA in acetonitrile solution, calculated at the PCM/ωB97XD/6-311+G(d,p) level of theory. Bond lengths are in Å, angles in degrees and ΔE in kcal/mol .

Conformer	d_{O-H}	d_{N-H}	d_{N-O}	d_{C1-N}	d_{N-C3}	d_{C3-C4}	ϕ_1	ϕ_2	ϕ_3	ΔE
(IA)S_0	0.988	1.738	2.624	1.408	1.281	1.454	45.48	-176.7	0.678	0.000
(IB)S_0	1.752	1.035	2.631	1.411	1.318	1.399	25.87	-178.0	-0.179	3.130
(IC)S_0	4.714	1.011	4.085	1.413	1.329	1.384	21.69	-176.1	-178.8	10.24
(IIA)S_0	0.990	1.732	2.620	1.409	1.282	1.454	147.6	178.3	-0.152	0.460
(IIB)S_0	1.727	1.037	2.601	1.409	1.317	1.401	180.0	180.0	0.000	3.280
(IIC)S_0	4.702	1.011	4.082	1.412	1.327	1.386	-180.0	180.0	180.0	10.58
(7)S_0	0.961	3.749	2.816	1.406	1.274	1.466	51.16	-178.1	8.390	9.640
(8)S_0	0.961	3.739	2.805	1.409	1.274	1.466	140.5	179.1	-6.028	10.32
(9)S_0	0.959	3.758	4.225	1.408	1.274	1.468	143.6	178.7	-178.1	10.13
(10)S_0	0.959	3.690	4.178	1.406	1.274	1.467	49.87	-175.0	-163.5	9.310
(11)S_0	0.960	3.441	4.014	1.410	1.272	1.482	64.44	5.870	-141.0	12.32
(12)S_0	0.960	2.564	3.269	1.411	1.274	1.486	54.66	3.891	48.26	11.60
(13)S_0	0.960	3.436	4.011	1.412	1.273	1.482	-124.3	6.789	-140.1	12.36
(14)S_0	4.471	1.010	4.041	1.426	1.329	1.390	128.9	-12.26	173.1	12.94
(15)S_0	3.997	1.011	3.059	1.414	1.333	1.393	27.68	20.62	18.68	15.45

Table S2. Excitation energy (eV), oscillator Strength (*f*), dominant transitions and largest excitation coefficients for $(IA)S_0$ and $(IIA)S_0$ in ACN computed at the at the PCM/ωB97XD/6-311+G(d,p) level of theory.

Conformer	S_n	Dominant Transitions	Coefficient [a]	Energy	*f*
$(IA)S_0$	1	HOMO (78) → LUMO (79)	0.6593	3.5088	0.1391
	2	HOMO−1 (77) → LUMO+1 (80)	0.4337		
	3	HOMO−1 (77) → LUMO (79)	0.5267		
$(IIA)S_0$	1	HOMO (78) → LUMO (79)	0.6580	3.4686	0.2087
	2	HOMO (78) → LUMO+1 (80)	0.52309		
	3	HOMO−1 (77) → LUMO (79)	0.56547		

[a] Only transitions with excitation coefficients higher than 0.4 were taken into consideration.

Table S3. Selected geometrical parameters of the optimized rotamers and tautomers of 2-AntSA in the low-lying excited-states, calculated at the PCM/ωB97XD/6-311+G(d,p) level of theory. Bond lengths are in Å, angles in degrees and ΔE in kcal/mol .

Conformer	d_{O-H}	d_{N-H}	d_{N-O}	d_{C1-N}	d_{N-C3}	d_{C3-C4}	ϕ_1	ϕ_2	ϕ_3	ΔE
(IA)S_1	1.006	1.650	2.566	1.358	1.342	1.427	0.000	180.0	0.000	4.930
(IA)$S_{1\text{-}Tw}$	0.974	1.894	2.701	1.363	1.389	1.434	-1.500	-88.22	-11.18	0.000
(IB)S_1	1.752	1.035	2.631	1.367	1.360	1.422	0.000	180.0	0.000	1.700
(IB)$S_{1\text{-}Tw}$	3.633	1.005	3.427	1.404	1.381	1.457	13.32	-169.3	91.14	2.660
(IC)S_1	4.641	1.011	4.039	1.389	1.351	1.426	3.720	-178.8	-176.5	5.020
(IIA)S_1	1.002	1.665	2.574	1.356	1.339	1.426	165.5	170.1	0.300	5.040
(IIA)$S_{1\text{-}Tw}$	0.975	1.878	2.690	1.372	1.381	1.437	-175.5	90.33	12.21	0.000
(IIB)S_1	1.753	1.035	2.634	1.371	1.359	1.425	180.0	180.0	0.000	0.710
(IIB)$S_{1\text{-}Tw}$	3.208	1.006	3.261	1.405	1.384	1.460	162.7	-178.9	80.59	1.580
(IIC)S_1	4.635	1.011	4.038	1.390	1.352	1.427	-180.0	-180.0	-180.0	3.820

Table S4. Summary of the excited-state dynamic simulations for conformers IA and IIA, calculated at the PCM/ωB97XD/6-311+G(d,p)/6-31G(d,p)/3-21G level of theory.

Conformer	Reaction			τ_{ESIPT} [fs]
	ESIPT	NO ESIPT	C=N torsion	
IA	19	1	0	77 ± 50
IIA	12	8	2	213 ± 80

Table S5. Atomic charges in the aliphatic and phenolic ring in the first excited-state or (IA)S1. Charges were assigned with the natural population analysis method. The wave function employed for the charge analysis was computed at the CIS/6-311++G(d,p) level of theory.,

	$(IA)S_1$	$(IA)S_{1\text{-}Tw}$	$(IB)S_1$	$(IB)S_{1\text{-}Tw}$	$(IIA)S_1$	$(IIA)S_{1\text{-}Tw}$	$(IIB)S_1$	$(IIB)S_{1\text{-}Tw}$
N	-0.30	-0.18	-0.23	-0.313	-0.276	-0.166	-0.237	-0.308
O	-0.35	-0.34	-0.35	-0.230	-0.350	-0.339	-0.348	-0.236
C1	0.11	0.07	0.13	0.156	0.108	0.066	0.128	0.156
C3	0.09	0.00	0.11	0.053	0.075	-0.012	0.111	0.057
C4	-0.08	-0.07	-0.05	0.012	-0.075	-0.063	-0.050	0.007
C5	0.23	0.17	0.20	0.149	0.217	0.171	0.190	0.148
C8	-0.12	-0.09	-0.11	-0.054	-0.116	-0.093	-0.113	-0.057
C9	0.00	-0.03	-0.04	-0.035	-0.003	-0.032	-0.042	-0.034
C10	-0.07	-0.062	-0.03	-0.008	-0.068	-0.061	-0.032	-0.012
C11	-0.02	-0.029	-0.05	-0.054	-0.019	-0.032	-0.050	-0.052