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

Supporting Information

Performance of TDDFT with and without spin-flip in trajectory surface hopping dynamics: Cis-trans azobenzene photoisomerization

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Scheme Photoisomerization mechanism of azobenzene following excitation to the $S_1(n\pi^*)$ state with potential energy profiles along minimum energy path of rotational transition state on S_0 state. Cis-Min S_0 electronic structure is in the left bottom, trans-Min S_0 in the right bottom, TS-rot S_0 in the left middle, CI-inv S_0/S_1 in the right middle, and CI-rot S_0/S_1 in the top.



Fig. S1 The stereoview of the superposition for TS-inv-rot optimized by SF-TDDFT and TDDFT.



Fig. S2 The two-dimensional potential energy surfaces in vicinity of conical intersections. Left panel is CI-rot S_0/S_1 in terms of NNCC1 and CNNC dihedral angles and right panel is CI-inv S_0/S_1 in terms of CNN and NNC bond angles. (a) and (b) calculated by SF-TDDFT. (c) and (d) calculated by SA2-CAS(6,6).



Fig. S3 The two-dimensional potential energy surfaces in terms of NNCC1 and CNNC dihedral angles in vicinity of cis-min S_1 (actually stands for double cone conical intersection) calculated by TDDFT.



Fig. S4 The time evolution of the average population of the S_0 and S_1 states for the cis-to-trans photoisomerization simulated by Tully's fewest switches algorithm at SF-TDDFT level.

SF-TDDFT 150 150 120 120 -90 90 60 60 NNCC2 (deg) NNCC1 (deg) 30 -30 -0 -0 -30 --30 --60 --60 -90 -90 -120 -120 -150 -150 30 -30 0 60 150 120 150 -90 -60 90 120 -150 -120 -90 -60 -30 0 30 60 90 -150 -120 CNNC (deg) CNNC (deg) 150 -150 120 120 -90 -90 -60 60 NNCC1 (deg) NNCC2 (deg) 30 -30 -0 -0 -



Fig. S5 The left (right) panel stands simulated cis-to-trans photoisomerization results from SF-TDDFT method in THS-LS algorithm in terms of CNNC/NNCC1 (left panel) and CNNC/NNCC2 (right panel). Top panel is for hopping spots and bottom panel is for product distributions.



Fig. S6 The S_1 PESs along the rotation of the CNNC dihedral angle by SF-TDDFT and TDDFT methods.

trans-azobenzene S ₀ Min									
SF-TDDFT					TDDFT				
N	-0.003	0.488	0.391	Ν	0.000	0.488	0.393		
С	-0.002	0.184	1.780	С	0.000	0.186	1.776		
С	-0.001	1.280	2.632	С	0.000	1.282	2.632		
С	0.001	1.089	4.006	С	0.000	1.090	4.006		
С	0.002	-0.200	4.524	С	0.000	-0.199	4.523		
С	0.001	-1.296	3.666	С	0.000	-1.296	3.664		
С	-0.001	-1.111	2.294	С	0.000	-1.110	2.293		
Н	-0.002	2.264	2.200	Н	0.001	2.267	2.199		
Н	0.002	1.938	4.668	Η	0.000	1.938	4.668		
Н	0.004	-0.352	5.590	Η	0.000	-0.351	5.589		
Н	0.001	-2.294	4.071	Η	-0.001	-2.294	4.068		
Н	-0.002	-1.943	1.615	Η	0.000	-1.942	1.613		
Ν	-0.003	-0.487	-0.391	Ν	0.000	-0.488	-0.393		
С	-0.002	-0.183	-1.779	С	0.000	-0.186	-1.776		
С	-0.001	-1.280	-2.632	С	0.000	-1.282	-2.632		
С	0.001	-1.089	-4.006	С	0.000	-1.090	-4.006		
С	0.002	0.199	-4.524	С	0.000	0.199	-4.523		
С	0.001	1.296	-3.667	С	0.000	1.296	-3.664		
С	-0.001	1.111	-2.295	С	0.000	1.110	-2.293		
Н	-0.002	-2.264	-2.198	Η	0.001	-2.267	-2.199		
Η	0.002	-1.938	-4.667	Η	0.000	-1.938	-4.668		
Н	0.004	0.351	-5.590	Η	0.000	0.351	-5.589		
Н	0.002	2.293	-4.072	Н	-0.001	2.294	-4.068		
Н	-0.002	1.943	-1.616	Н	0.000	1.942	-1.613		

 Table S1.Cartesian coordinates for all optimized geometries.

			trans-azobe	enzene S	S_1 Min				
		SF-TDDFT			TDDFT				
Ν	0.002	0.395	0.481	N	0.918	0.404	0.481		
С	0.001	0.160	1.843	С	0.441	0.207	1.766		
С	0.002	1.284	2.700	С	0.597	1.243	2.692		
С	0.000	1.099	4.066	С	0.138	1.081	3.986		
С	-0.001	-0.201	4.608	С	-0.469	-0.109	4.376		
С	-0.002	-1.285	3.766	С	-0.616	-1.141	3.455		
С	-0.001	-1.116	2.375	С	-0.167	-0.993	2.154		
Н	0.003	2.265	2.268	Н	1.072	2.154	2.376		
Н	0.001	1.951	4.718	Н	0.256	1.882	4.695		
Н	-0.002	-0.337	5.672	Н	-0.821	-0.232	5.386		
Н	-0.004	-2.280	4.167	Н	-1.083	-2.064	3.752		
Н	-0.002	-1.965	1.722	Н	-0.269	-1.785	1.433		
Ν	0.002	-0.395	-0.481	Ν	0.918	-0.404	-0.481		
С	0.001	-0.160	-1.843	С	0.441	-0.207	-1.766		
С	0.002	-1.284	-2.700	С	0.597	-1.243	-2.692		
С	0.000	-1.099	-4.066	С	0.138	-1.081	-3.986		
С	-0.001	0.201	-4.608	С	-0.469	0.109	-4.376		
С	-0.002	1.285	-3.766	С	-0.616	1.141	-3.455		
С	-0.001	1.116	-2.375	С	-0.167	0.993	-2.154		
Н	0.003	-2.265	-2.268	Н	1.073	-2.154	-2.376		
Н	0.001	-1.951	-4.718	Н	0.256	-1.882	-4.695		
Н	-0.002	0.337	-5.672	Н	-0.821	0.232	-5.386		
Н	-0.004	2.280	-4.167	Н	-1.083	2.064	-3.752		
Η	-0.002	1.965	-1.722	Н	-0.269	1.785	-1.433		

			cis-azober	nzene S	₀ Min				
SF-TDDFT					TDDFT				
Ν	1.902	0.002	0.623	N	1.883	0.007	0.625		
С	0.722	-0.055	1.446	С	0.711	-0.049	1.450		
С	0.690	0.801	2.540	С	0.704	0.792	2.559		
С	-0.368	0.738	3.435	С	-0.344	0.733	3.465		
С	-1.371	-0.209	3.262	С	-1.361	-0.200	3.294		
С	-1.312	-1.091	2.190	С	-1.326	-1.070	2.210		
С	-0.272	-1.015	1.276	С	-0.297	-0.996	1.283		
Н	1.496	1.499	2.678	Н	1.523	1.476	2.695		
Н	-0.401	1.412	4.273	Н	-0.357	1.397	4.312		
Н	-2.183	-0.270	3.965	Н	-2.165	-0.259	4.006		
Η	-2.075	-1.839	2.064	Н	-2.100	-1.808	2.087		
Н	-0.227	-1.698	0.447	Н	-0.272	-1.672	0.447		
Ν	1.904	-0.024	-0.621	Ν	1.884	-0.035	-0.621		
С	0.725	0.046	-1.445	С	0.714	0.037	-1.449		
С	0.680	-0.817	-2.533	С	0.695	-0.807	-2.556		
С	-0.377	-0.742	-3.429	С	-0.351	-0.733	-3.463		
С	-1.364	0.222	-3.264	С	-1.353	0.216	-3.295		
С	-1.291	1.111	-2.197	С	-1.306	1.088	-2.214		
С	-0.252	1.023	-1.282	С	-0.279	1.000	-1.285		
Н	1.474	-1.530	-2.666	Н	1.503	-1.504	-2.690		
Н	-0.421	-1.422	-4.262	Н	-0.373	-1.398	-4.309		
Н	-2.175	0.291	-3.967	Н	-2.155	0.286	-4.009		
Н	-2.042	1.872	-2.077	Н	-2.068	1.838	-2.093		
Н	-0.197	1.711	-0.458	Н	-0.244	1.677	-0.451		

cis-azobenzene S_1 Min						
		TDDFT				
Ν	1.359	-0.261	0.555			
С	0.573	0.012	1.637			
С	0.754	-0.782	2.784			
С	-0.019	-0.564	3.906			
С	-0.974	0.452	3.916			
С	-1.147	1.253	2.790			
С	-0.386	1.046	1.656			
Н	1.501	-1.554	2.754			
Н	0.120	-1.179	4.778			
Н	-1.571	0.622	4.795			
Н	-1.877	2.044	2.802			
Н	-0.504	1.670	0.789			
Ν	1.339	0.382	-0.559			
С	0.572	0.044	-1.643			
С	0.702	0.836	-2.796			
С	-0.060	0.560	-3.914			
С	-0.951	-0.512	-3.912			
С	-1.071	-1.311	-2.778			
С	-0.320	-1.045	-1.647			
Н	1.401	1.652	-2.776			
Н	0.040	1.174	-4.792			
Н	-1.538	-0.727	-4.787			
Н	-1.749	-2.146	-2.780			
Н	-0.397	-1.668	-0.775			

CI-rot S ₀ /S ₁			CI-inv S ₀ /S ₁						
SF-TDDFT					SF-TDDFT				
Ν	-0.038	-1.413	0.596	N	0.000	-0.292	0.543		
С	-0.058	-0.546	1.703	С	0.000	-0.132	1.903		
С	-0.655	0.718	1.684	С	0.000	1.146	2.470		
С	-0.602	1.512	2.816	С	0.000	1.275	3.849		
С	0.034	1.053	3.967	С	0.000	0.161	4.676		
С	0.618	-0.210	3.986	С	0.000	-1.102	4.098		
С	0.568	-1.013	2.860	С	0.000	-1.261	2.725		
Н	-1.157	1.053	0.795	Н	0.000	2.011	1.838		
Н	-1.060	2.486	2.807	Н	0.000	2.260	4.275		
Н	0.069	1.675	4.844	Н	0.000	0.273	5.742		
Н	1.104	-0.565	4.878	Н	0.000	-1.976	4.721		
Н	1.005	-1.995	2.844	Н	0.000	-2.238	2.285		
Ν	-0.592	-1.087	-0.489	Ν	0.000	0.183	-0.569		
С	-0.236	-0.472	-1.652	С	0.000	0.100	-1.863		
С	-1.179	-0.354	-2.683	С	0.000	1.294	-2.678		
С	-0.833	0.273	-3.864	С	0.000	1.176	-4.060		
С	0.449	0.783	-4.051	С	0.000	-0.080	-4.685		
С	1.386	0.657	-3.034	С	0.000	-1.267	-3.870		
С	1.060	0.040	-1.839	С	0.000	-1.200	-2.530		
Н	-2.164	-0.758	-2.533	Н	0.000	2.253	-2.199		
Н	-1.565	0.361	-4.648	Н	0.000	2.067	-4.659		
Н	0.712	1.265	-4.975	Н	0.000	-0.163	-5.753		
Н	2.383	1.041	-3.170	Н	0.000	-2.226	-4.352		
Н	1.786	-0.063	-1.053	Н	0.000	-2.084	-1.923		

			TS-in	v-rot S)				
SF-TDDFT					TDDFT				
N	0.306	1.374	0.681	N	1.115	0.893	0.675		
С	0.104	0.484	1.814	С	0.433	0.303	1.810		
С	0.217	1.079	3.060	С	0.995	0.592	3.045		
С	0.039	0.311	4.202	С	0.419	0.076	4.197		
С	-0.248	-1.044	4.086	С	-0.713	-0.723	4.104		
С	-0.358	-1.633	2.829	С	-1.272	-1.009	2.860		
С	-0.182	-0.870	1.686	С	-0.700	-0.496	1.707		
Н	0.440	2.130	3.111	Н	1.872	1.215	3.076		
Н	0.124	0.764	5.174	Н	0.848	0.295	5.159		
Н	-0.386	-1.641	4.971	Н	-1.162	-1.125	4.996		
Н	-0.580	-2.682	2.745	Н	-2.149	-1.629	2.794		
Н	-0.263	-1.308	0.707	Н	-1.119	-0.707	0.739		
Ν	0.218	0.913	-0.444	Ν	0.666	0.673	-0.442		
С	0.118	0.403	-1.688	С	0.172	0.432	-1.666		
С	1.274	0.052	-2.403	С	0.615	-0.680	-2.408		
С	1.155	-0.472	-3.678	С	0.098	-0.908	-3.671		
С	-0.085	-0.641	-4.278	С	-0.853	-0.063	-4.230		
С	-1.223	-0.281	-3.569	С	-1.284	1.035	-3.494		
С	-1.140	0.228	-2.284	С	-0.790	1.295	-2.228		
Н	2.239	0.196	-1.953	Н	1.354	-1.336	-1.986		
Н	2.052	-0.742	-4.211	Н	0.450	-1.762	-4.225		
Н	-0.164	-1.042	-5.272	Н	-1.245	-0.252	-5.213		
Н	-2.196	-0.401	-4.015	Н	-2.018	1.705	-3.909		
Н	-2.027	0.498	-1.741	Н	-1.125	2.149	-1.669		

			TS-pla	nar-inv	S_0			
		SF-TDDFT		TDDFT				
N	0.000	1.386	0.660	N	0.000	1.403	0.668	
С	0.000	0.512	1.821	С	0.000	0.517	1.811	
С	0.000	1.182	3.037	С	0.000	1.180	3.034	
С	0.000	0.466	4.224	С	0.000	0.460	4.218	
С	0.000	-0.924	4.194	С	0.000	-0.930	4.183	
С	0.000	-1.593	2.974	С	0.000	-1.593	2.959	
С	0.000	-0.876	1.788	С	0.000	-0.872	1.775	
Н	0.000	2.258	3.023	Н	0.000	2.256	3.023	
Н	0.000	0.985	5.167	Н	0.000	0.976	5.163	
Н	0.000	-1.483	5.114	Н	0.000	-1.493	5.100	
Н	0.000	-2.669	2.952	Н	0.000	-2.670	2.932	
Н	0.000	-1.382	0.842	Н	0.000	-1.380	0.830	
Ν	0.000	0.906	-0.481	Ν	0.000	0.926	-0.483	
С	0.000	0.342	-1.729	С	0.000	0.350	-1.720	
С	0.000	1.192	-2.845	С	0.000	1.194	-2.844	
С	0.000	0.676	-4.130	С	0.000	0.672	-4.126	
С	0.000	-0.700	-4.324	С	0.000	-0.706	-4.313	
С	0.000	-1.556	-3.231	С	0.000	-1.558	-3.215	
С	0.000	-1.043	-1.944	С	0.000	-1.039	-1.930	
Н	0.000	2.251	-2.666	Н	0.000	2.255	-2.671	
Н	0.000	1.341	-4.975	Н	0.000	1.332	-4.975	
Н	0.000	-1.103	-5.322	Н	0.000	-1.114	-5.309	
Н	0.000	-2.622	-3.382	Н	0.000	-2.624	-3.361	
Н	0.000	-1.709	-1.102	Н	0.000	-1.703	-1.087	

		TS-rot S ₀		
		SF-TDDFT		
Ν	1.394	0.379	0.543	
С	0.567	0.099	1.604	
С	0.662	0.944	2.723	
С	-0.145	0.732	3.822	
С	-1.049	-0.328	3.834	
С	-1.137	-1.179	2.735	
С	-0.340	-0.976	1.626	
Н	1.373	1.749	2.690	
Н	-0.072	1.386	4.674	
Η	-1.674	-0.494	4.695	
Η	-1.827	-2.005	2.751	
Η	-0.392	-1.639	0.781	
Ν	1.398	-0.356	-0.546	
С	0.564	-0.089	-1.604	
С	0.668	-0.932	-2.723	
С	-0.144	-0.733	-3.820	
С	-1.064	0.313	-3.831	
С	-1.162	1.163	-2.732	
С	-0.360	0.973	-1.624	
Η	1.392	-1.727	-2.692	
Η	-0.063	-1.386	-4.672	
Η	-1.693	0.470	-4.690	
Н	-1.865	1.978	-2.746	
Η	-0.420	1.635	-0.780	

			TS	rot S ₁					
SF-TDDFT					TDDFT				
N	1.086	0.581	0.540	N	1.149	0.549	0.543		
С	0.444	0.207	1.721	С	0.470	0.200	1.712		
С	0.474	1.116	2.781	С	0.519	1.103	2.777		
С	-0.151	0.801	3.974	С	-0.137	0.807	3.959		
С	-0.798	-0.423	4.124	С	-0.835	-0.390	4.093		
С	-0.815	-1.332	3.072	С	-0.872	-1.293	3.036		
С	-0.196	-1.028	1.872	С	-0.222	-1.009	1.847		
Н	0.984	2.053	2.643	Н	1.068	2.018	2.651		
Н	-0.133	1.504	4.788	Н	-0.104	1.506	4.777		
Н	-1.279	-0.667	5.055	Н	-1.341	-0.618	5.015		
Н	-1.310	-2.281	3.189	Н	-1.407	-2.221	3.140		
Н	-0.189	-1.725	1.054	Н	-0.232	-1.703	1.026		
Ν	1.133	-0.130	-0.497	Ν	1.196	-0.139	-0.504		
С	0.469	-0.034	-1.705	С	0.502	-0.042	-1.701		
С	0.788	-0.937	-2.722	С	0.841	-0.907	-2.744		
С	0.127	-0.867	-3.935	С	0.153	-0.840	-3.943		
С	-0.844	0.104	-4.157	С	-0.868	0.089	-4.121		
С	-1.151	1.008	-3.148	С	-1.197	0.954	-3.085		
С	-0.507	0.946	-1.923	С	-0.524	0.894	-1.874		
Н	1.546	-1.678	-2.541	Н	1.638	-1.613	-2.595		
Н	0.373	-1.568	-4.713	Н	0.416	-1.510	-4.743		
Н	-1.351	0.157	-5.104	Н	-1.396	0.140	-5.057		
Н	-1.896	1.767	-3.313	Н	-1.981	1.680	-3.218		
Н	-0.734	1.645	-1.138	Н	-0.767	1.565	-1.069		