Tracking the Stilbene Photoisomerization in the S_1 State by RASSCF

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Supporting Information.

Table S1. Computed geometrical parameters[a] of *cis*- and *trans*-stilbene minima in the S_0 and S_1(HOMO→LUMO) states optimized at the RASSCF and CASSCF level.

(a)

S_0 *trans* (**t**) and *cis* (**c**) equilibrium geometries

Isomer/Method	θ; ϕ	R(C_1=C'$_1$)	R(C_1-C_2)	R(C_2-C_3)	R(C_3-C_4)	R(C_4-C_5)	R(C_5-C_6)	R(C_6-C_7)	R(C_7-C_2)
t/RASSCF [b]	179°; 5°	1.352	1.485	1.391	1.385	1.383	1.387	1.387	1.383
t/CASSCF [c]	179°; 22°	1.361	1.482	1.400	1.388	1.390	1.395	1.382	1.401
c/RASSCF [b]	4°; 47°	1.351	1.487	1.392	1.385	1.386	1.385	1.385	1.392
c/CASSCF [c]	4°; 40°	1.353	1.483	1.402	1.391	1.389	1.396	1.388	1.399

(b)

S_1 π /π* (HOMO→LUMO) *trans* (**t***) and *cis* (**c***) equilibrium geometries

Isomer/Method	θ; ϕ	R(C_1=C'$_1$)	R(C_1-C_2)	R(C_2-C_3)	R(C_3-C_4)	R(C_4-C_5)	R(C_5-C_6)	R(C_6-C_7)	R(C_7-C_2)
t*/RASSCF [d]	180°;0°	1.399	1.407	1.436	1.371	1.396	1.400	1.368	1.430
c*/RASSCF [d]	35°; 12°	1.408	1.405	1.435	1.389	1.377	1.413	1.361	1.429

[a] Bond lengths in Å and angles in degrees; θ is the ethylenic C_1=C'$_1$ torsion angle and ϕ is the C_1-C_2 (C'$_1$-C'$_2$) twisting angle; [b] *RASSCF*/6-31G* Single State *(S_0) optimized geometry (the active space comprises the 14 π orbitals)*; [c] CASSCF/6-31G* Single State *(S_0) optimized geometry* (initial HF orbitals); [d] *RASSCF*/6-31G* two roots *(S_0 e S_1)* State Average (SA-2) *S_1 optimized geometry (the active space comprises both π and σ type orbitals, see discussion in the text)*.

Table S2. The lowest S_0→S_n (n≤4) vertical excitations by the SA-5 CASSCF(10, 10), SA-5 CASSCF(10,10)/CASPT2 with initial HF orbitals and the SA-5 RASSCF calculations at the *trans* (**t**/CASSCF) and *cis* (**c**/CASSCF) geometries. CASSCF and RASSCF wavefunction analysis is also reported.

State	ΔE CASSCF [a] kcal/mol	ΔE CASPT2[a] kcal/mol	Configuration *Weight* *CASSCF(10,10)*	ΔE RASSCF [a] kcal/mol	Configuration *Weight* *RASSCF(14,14)*
trans					
S_0	0	0	$(5\pi)^2$ $(6\pi^*)^0$ *0.823*	0	$(7\pi)^2$ $(8\pi^*)^0$ *0.874*
S_1	**151.1**	**101.5**	**$(5\pi)^1$ $(6\pi^*)^1$ *0.826*[b]**	**138.7**	**$(7\pi)^1$ $(8\pi^*)^1$ *0.882*[b]**

S_2	135.4	113.2	$(5\pi)^1\ (9\pi^*)^1$ *0.118* $(3\pi)^1(6\pi^*)^1$ *0.152*	145.6	$(7\pi)^0(8\pi^*)^2$ *0.295* $(7\pi)^1\ (10\pi^*)^1$ *0.203* $(6\pi)^1(8\pi^*)^1$ *0.251*
S_3	*135.9*	113.5	$(5\pi)^1(10\pi^*)^1$ *0.175* $(1\pi)^1\ (6\pi^*)^1$ *0.256*	177.1	$(3\pi)^1\ (8\pi^*)^1$ *0.314* $(4\pi)^0\ (8\pi^*)^2$ *0.192* $(7\pi)^1\ (8\pi^*)^1$ *0.147*
S_4	146.2	122.9	$(2\pi)^1\ (6\pi^*)^1$ *0.178* $(5\pi)^0\ (6\pi^*)^2$ *0.227*	178.8	$(5\pi)^1\ (8\pi^*)^1$ *0.478* $(6\pi)^1\ (7\pi)^1(8\pi^*)^1(9\pi^*)^1$*0.15*
cis					
S_0	0	0	$(5\pi)^2\ (6\pi^*)^0$ *0.822*	0	$(7\pi)^2\ (8\pi^*)^0$ 0.913
S_1	109.72	106.13	$(5\pi)^1\ (8\pi^*)^1$ *0.308* $(3\pi)^1(6\pi^*)^1$ *0.295*	139.05	$(7\pi)^1\ (10\pi^*)^1$ 0.213 $(6\pi)^1(8\pi^*)^1$ 0.289 $(7\pi)^0\ (8\pi^*)^2$ 0.219
S_2	**159.84**	**111.25**	**$(5\pi)^1\ (6\pi^*)^1$ *0.806*** [b]	**132.96**	**$(7\pi)^1\ (8\pi^*)^1$ 0.892** [b]
S_3	154.69	139.27	$(5\pi)^1(8\pi^*)^1$ *0.154* $(1\pi)^1\ (6\pi^*)^1$ *0.153*	163.06	$(7\pi)^1\ (10\pi^*)^1$ 0.447 $(6\pi)^1(8\pi^*)^1$ 0.458
S_4	174.34	145.50	$(2\pi)^1(6\pi^*)^1$ *0.121* $(5\pi)^1\ (6\pi^*)^1$ *0.131*	182.20	$(7\pi)^0\ (8\pi^*)^2$ 0.119 $(7\pi)^1\ (10\pi^*)^1$ 0.197 $(6\pi)^1(8\pi^*)^1$ 0.132

[a]The states ordering follows the CASPT2 energies; [b] The HOMO-LUMO/5π-6π* configuration is highlighted in bold.

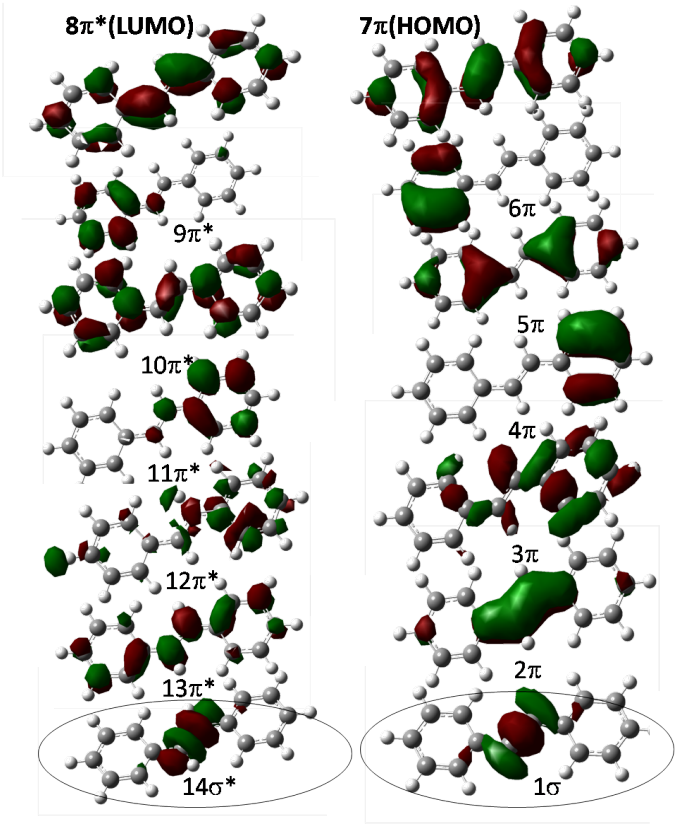

Figure S1. The 14 SA-2 RASSCF orbitals at the optimized RASSCF S_1 *trans* geometry (**t***) reported in Table 1.

Cartesian coordinates of key molecular structures discussed in the text

180°/t*

C	-1.838836	-3.624762	-0.011211
C	-1.010629	-2.511419	0.168450
H	-2.094922	-4.211630	0.851101
H	-0.743143	-1.930498	-0.694653
C	-0.481039	-2.066170	1.391413
C	-0.734923	-2.706894	2.647649
C	0.373387	-0.896237	1.417823
C	-0.179582	-2.218267	3.801903
H	-1.365839	-3.571269	2.695305
C	0.915149	-0.426326	2.583740
H	0.580688	-0.392107	0.489675
C	0.641498	-1.089008	3.792279
H	-0.381236	-2.714479	4.735222
H	1.544807	0.444653	2.567565
H	1.067402	-0.722653	4.707946
C	-2.380647	-4.070598	-1.230751
C	-2.141081	-3.432974	-2.488248
C	-3.227576	-5.230835	-1.246219
C	-2.707121	-3.923546	-3.636836
H	-1.509711	-2.569253	-2.543605
C	-3.781339	-5.700417	-2.406153
H	-3.425320	-5.735400	-0.316336
C	-3.527625	-5.052291	-3.618141
H	-2.510754	-3.428523	-4.571539
H	-4.410971	-6.571174	-2.381303
H	-3.961448	-5.420980	-4.529396

110°

C	-1.619566	-3.342357	-0.274624
C	-0.816449	-2.157773	-0.257702
H	-1.358318	-4.210357	0.383206
H	0.195741	-2.458318	-0.511853
C	-0.935842	-1.456269	0.989768
C	-2.111709	-1.452954	1.765958
C	0.167187	-0.733157	1.518125
C	-2.170758	-0.806045	2.984852
H	-2.994265	-1.944549	1.408338
C	0.089381	-0.081889	2.722309
H	1.083864	-0.698538	0.956396
C	-1.081109	-0.119243	3.488467
H	-3.087971	-0.848722	3.546767
H	0.951290	0.455329	3.083928
H	-1.131347	0.377181	4.438003
C	-2.820968	-3.644053	-1.019199
C	-3.410549	-2.648972	-1.829282

C	-3.436495	-4.912934	-0.903877
C	-4.595324	-2.913611	-2.498053
H	-2.900134	-1.695573	-1.884735
C	-4.601510	-5.170352	-1.581452
H	-2.981390	-5.670869	-0.283209
C	-5.171948	-4.172444	-2.363001
H	-5.067428	-2.165381	-3.106605
H	-5.072675	-6.132076	-1.503747
H	-6.096230	-4.387991	-2.878617

90°/tw*

C	-1.961328	-3.933193	0.382481
C	-1.067124	-2.817113	0.385314
H	-1.415746	-4.870089	0.445222
H	-0.297322	-2.677056	-0.403987
C	-1.066892	-1.701409	1.288461
C	-2.061512	-1.651739	2.284071
C	-0.140726	-0.649512	1.171845
C	-2.143740	-0.564634	3.129083
H	-2.751286	-2.481126	2.326819
C	-0.210764	0.425985	2.026445
H	0.616317	-0.693704	0.404468
C	-1.216700	0.465142	2.996378
H	-2.914938	-0.506683	3.876357
H	0.492619	1.235243	1.947808
H	-1.277381	1.318629	3.655256
C	-3.134202	-3.748096	-0.416422
C	-3.718747	-2.492287	-0.669539
C	-3.773277	-4.851356	-1.011182
C	-4.840099	-2.366324	-1.472988
H	-3.310401	-1.608512	-0.223708
C	-4.885489	-4.703465	-1.798951
H	-3.363540	-5.830929	-0.848503
C	-5.438085	-3.462382	-2.059249
H	-5.243258	-1.383767	-1.645277
H	-5.332918	-5.578195	-2.238556
H	-6.299101	-3.354574	-2.687677

Pyr-CI

C	-2.410284	-3.337398	0.161912
C	-1.927383	-1.990623	0.277382
H	-1.952272	-4.196920	0.738884
H	-0.980076	-2.632514	-0.078214
C	-1.382194	-1.200792	1.441948
C	-2.222404	-0.817359	2.492826
C	-0.062489	-0.767224	1.458680
C	-1.742571	-0.049553	3.536677
H	-3.254604	-1.112860	2.474251
C	0.415654	-0.004331	2.513356
H	0.597206	-1.027376	0.652744

C	-0.417869	0.359916	3.555306
H	-2.404963	0.238408	4.332574
H	1.443572	0.309963	2.512131
H	-0.044356	0.958714	4.364647
C	-3.508258	-3.678415	-0.764049
C	-4.500212	-2.709187	-1.005116
C	-3.639460	-4.928224	-1.346476
C	-5.588393	-2.991940	-1.794130
H	-4.370818	-1.731587	-0.573228
C	-4.735913	-5.211631	-2.153404
H	-2.900379	-5.692340	-1.166402
C	-5.708388	-4.251159	-2.374635
H	-6.338797	-2.240397	-1.965987
H	-4.832052	-6.185509	-2.600845
H	-6.557549	-4.480473	-2.995292