

# Exploring the isomerization paths of push-pull hexatrienes

## Supporting Information

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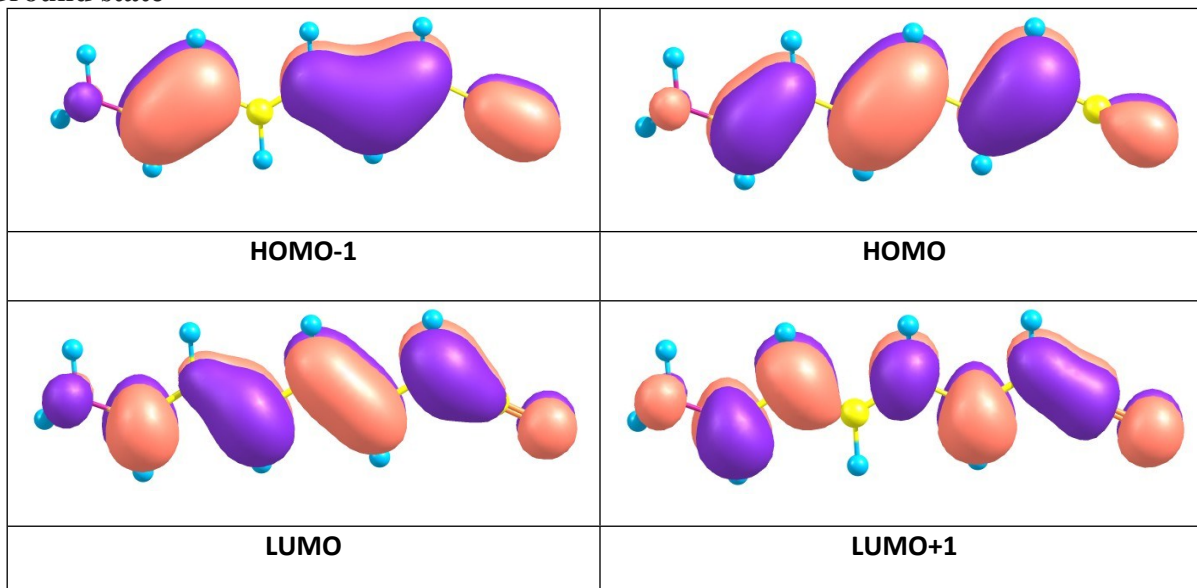
**Table S1.** A comparison of radiative transition properties of the different ground state isomers of **polyene I** and **polyene II**

polyene	Isomer	Transition moment (Debye)			Oscillator Strength			Einstein coefficient (in sec <sup>-1</sup> )		
		S <sub>0</sub> -S <sub>1</sub>	S <sub>0</sub> -S <sub>2</sub>	S <sub>1</sub> -S <sub>2</sub>	S <sub>0</sub> -S <sub>1</sub>	S <sub>0</sub> -S <sub>2</sub>	S <sub>1</sub> -S <sub>2</sub>	S <sub>0</sub> -S <sub>1</sub>	S <sub>0</sub> -S <sub>2</sub>	S <sub>1</sub> -S <sub>2</sub>
<b>I</b>	TTT	8.444	2.390	2.802	2.420	0.290	0.021	8.41(+9)	8.49(+8)	4.70(+5)
	CTT	7.605	3.290	1.601	1.935	0.394	0.007	6.53(+9)	1.57(+9)	1.90(+5)
	TCT	7.030	3.618	1.015	1.662	0.481	0.003	5.67(+9)	1.95(+9)	9.02(+4)
<b>II</b>	TTT	8.245	2.583	2.938	2.444	0.255	0.019	9.54(+9)	1.12(+9)	3.06(+5)
	CTT	7.888	2.960	2.310	2.225	0.329	0.010	8.59(+9)	1.41(+9)	1.07(+5)
	TCT	6.953	3.875	0.879	1.722	0.570	0.002	6.59(+9)	2.48(+9)	3.00(+4)

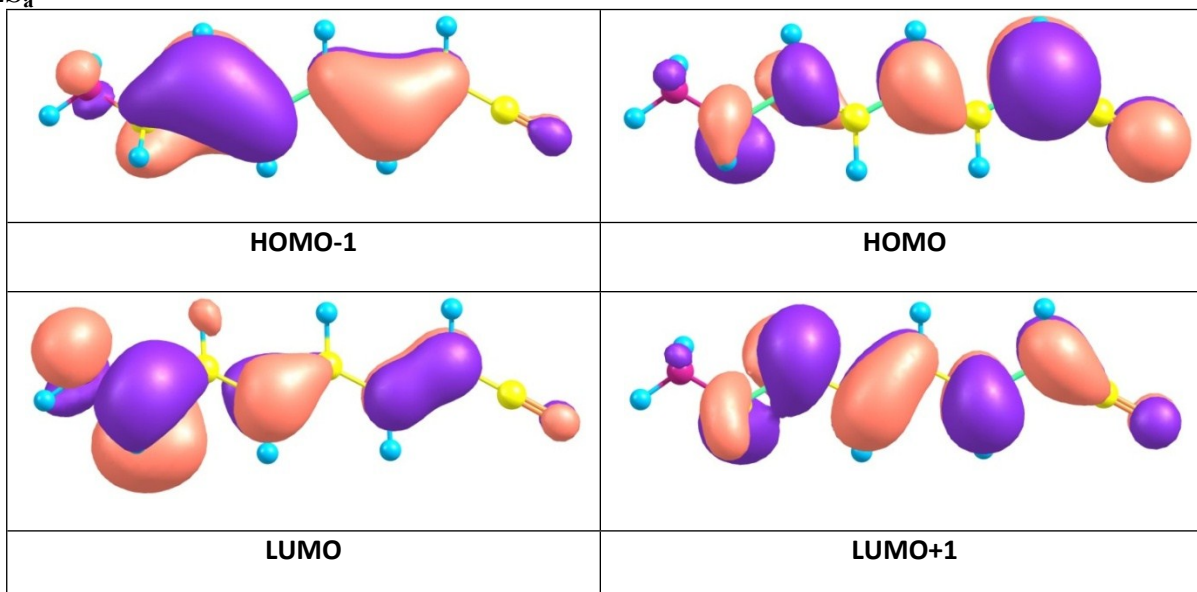
**Table S2.** Absolute energies (in Hartree) of first three low-lying states of some important points at CASPT2 level of calculation.

Geometries	polyene I			polyene II		
	CASPT2			CASPT2		
	E(S <sub>0</sub> )	E(S <sub>1</sub> )	E(S <sub>2</sub> )	E(S <sub>0</sub> )	E(S <sub>1</sub> )	E(S <sub>2</sub> )
GS (TTT)	-379.7652	-379.5964	-379.5920	-438.7522	-438.5749	-438.5734
ES <sub>a</sub>	-379.7253	-379.6226	-379.6059	-438.7189	-438.6051	-438.5723
TS <sub>a</sub>	-379.6827	-379.6204	-379.6067	-	-	-
ES <sub>b</sub>	-379.7226	-379.6215	-379.6075	-438.6903	-438.6031	-438.5794
ES <sub>b</sub> (90°)	-379.6899	-379.6251	-379.6186	-438.6645	-438.6036	-438.5854
ES <sub>c</sub>	-379.7257	-379.6185	-379.5997	-438.7206	-438.6053	-438.5739
ES <sub>d</sub>	-379.7257	-379.6185	-379.5997	-	-	-
CI <sub>a</sub>	-379.6149	-379.6106	-379.5069	-438.6059	-438.6052	438.4772
GS (CTT)	-379.7618	-379.5902	-379.5838	-438.7543	-438.5799	-438.5777
ES(S <sub>2</sub> )	-379.6950	-379.6147	-379.6073	-438.6772	438.5834	-438.57802
CI(S <sub>2</sub> /S <sub>1</sub> )	-379.6889	-379.5865	-379.5825	-438.6741	-438.5677	-438.5654
CI <sub>b</sub>	-379.6231	-379.6263	-379.5730	-	-	-
GS (CCT)	-379.7614	-379.5866	-379.5840	-	-	-
GS(TCT)	-379.7609	-379.5865	-379.5845	-438.7507	-438.5788	-438.5738
TS <sub>GS(TCT)</sub>	-379.6937	-379.6352	-379.5775	-438.6807	-438.6069	-438.5779
TS <sub>GS(CTT)</sub>	-379.6881	-379.6338	-379.5980	-438.6719	-438.6024	-438.5792
CI <sub>d</sub>	-379.6093	-379.6086	-379.4982	-438.5976	-438.5960	-438.4871
GS(TCC)	-379.7632	-379.5949	-379.5798	-	-	-

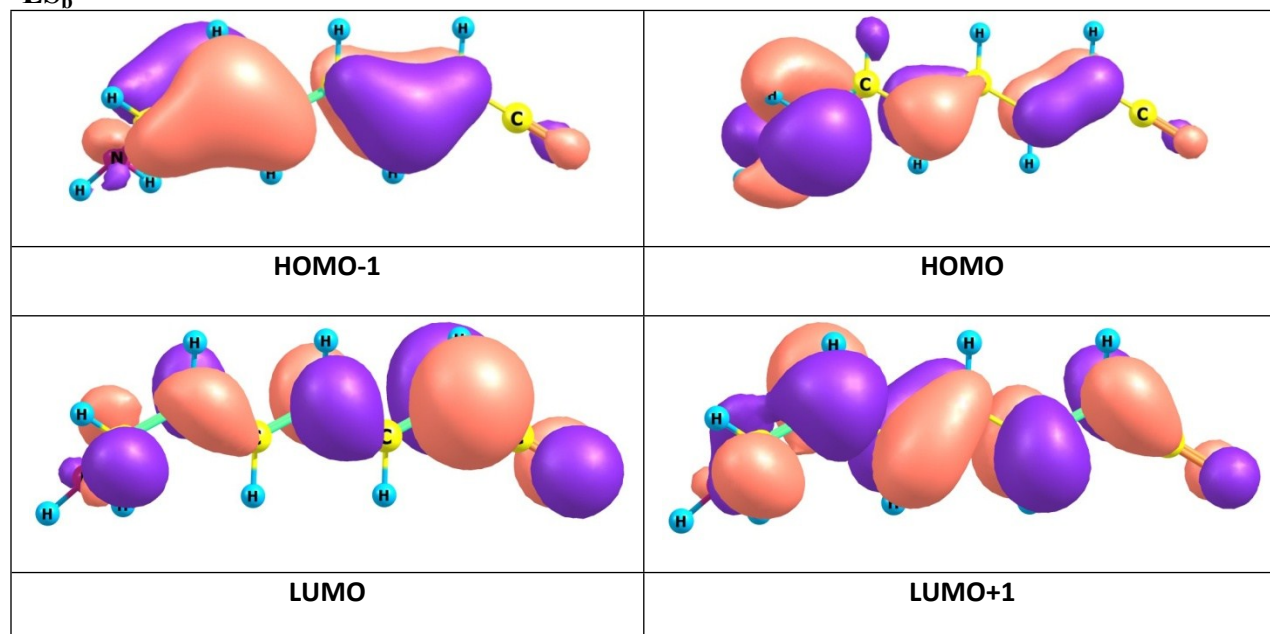
**Ground state**



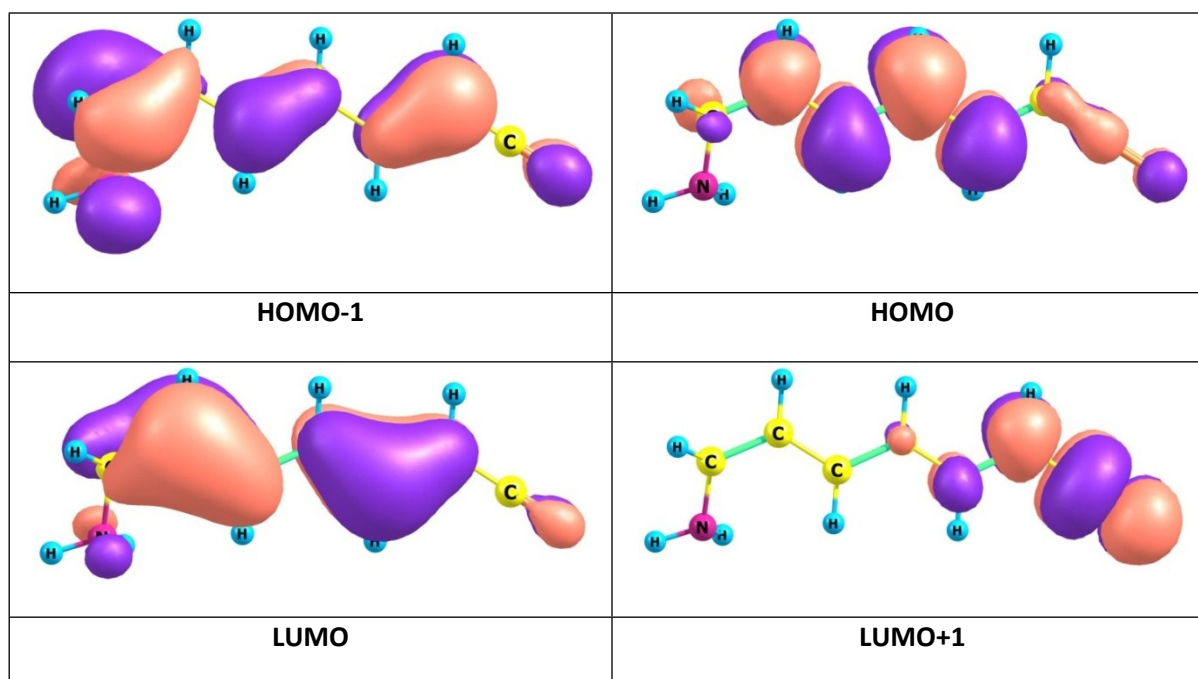
**ES<sub>a</sub>**



ES<sub>b</sub>



ES<sub>c</sub>



**Figure S1:** Some (10,10) active space orbitals of **polyene I** (TTT isomer) at different geometries.

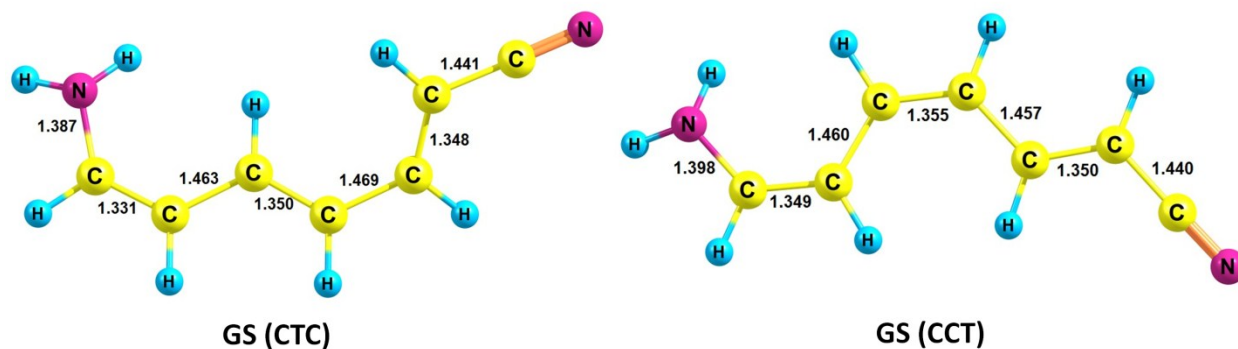


Figure S2: Optimized ground state geometries of some less stable isomers of polyene I.

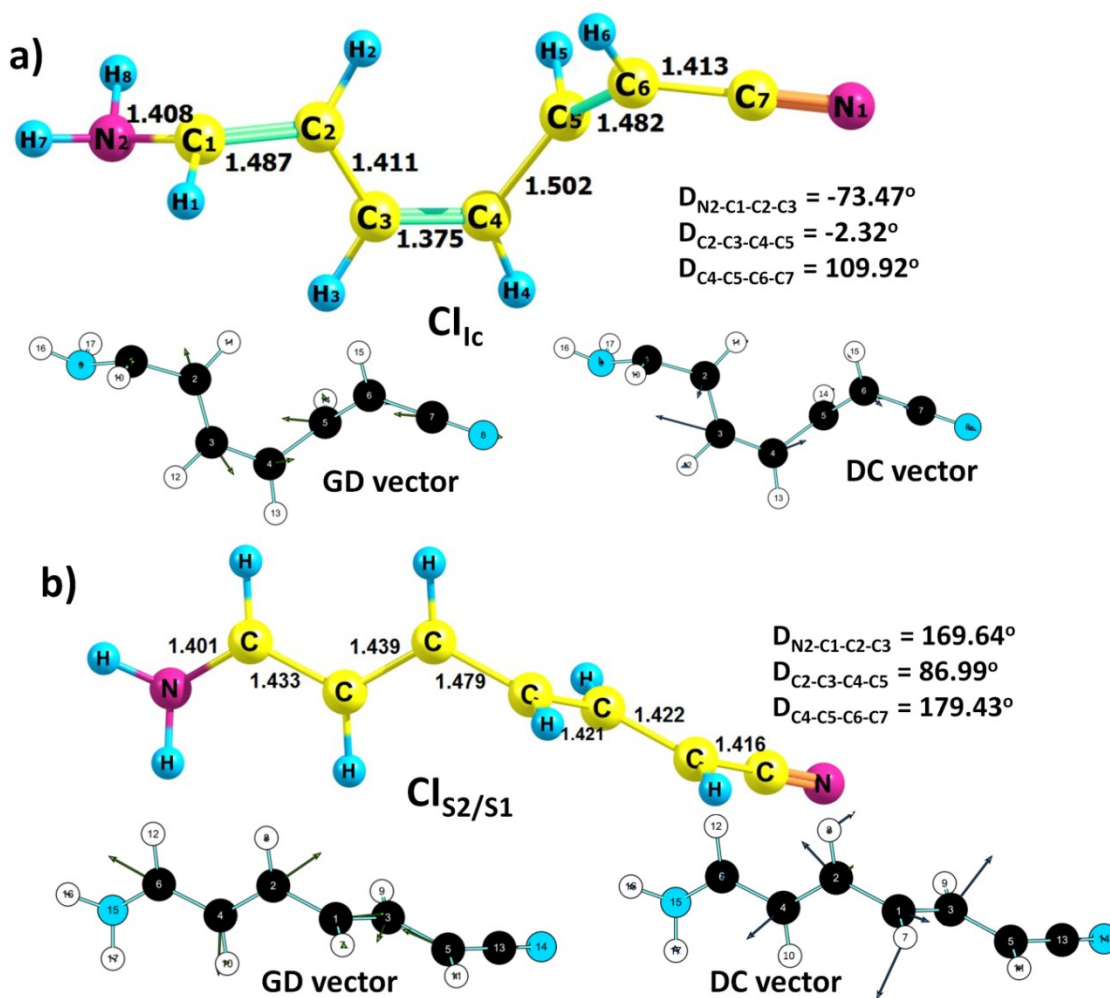
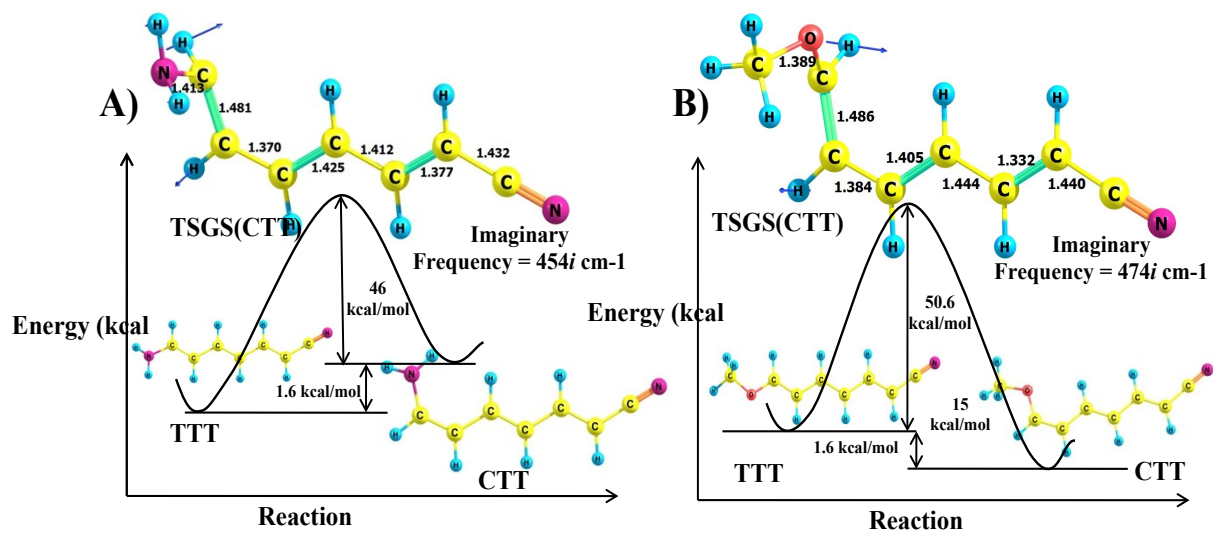


Figure S3: (a) Optimized conical intersection  $CI_{Ic}$  and (b)  $CI_{S2/S1}$  of polyene I with their gradient difference (GD) and derivative coupling (DC) vectors.



**Figure S4.** A schematic representation of the possible thermal *cis-trans* isomerization (TTT isomer to CTT isomer) of A) **polyene I** and B) **polyene II**