Electronic Supplementary Information (ESI)

Sudden polarization and zwitterions formation as a pseudo Jahn-Teller effect: A new insight in photochemistry of alkenes

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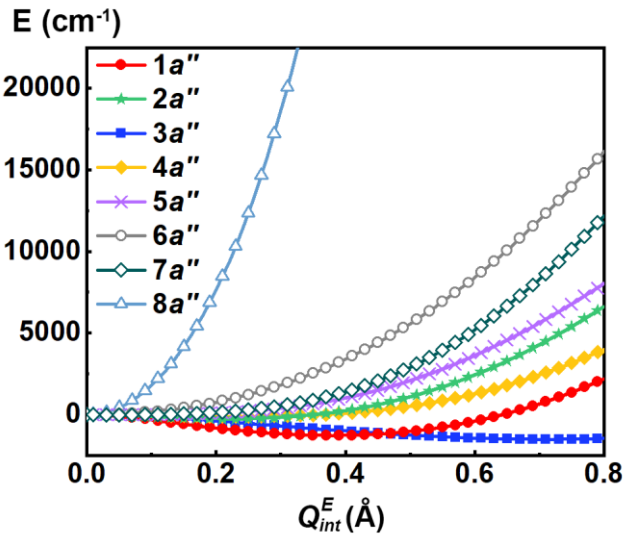


Figure S1. (Color online). Calculated potential energy profiles of the excited state S_1 (^{1}A") of butadiene along all its *a"* polar modes; only four of them contribute to lowering the energy by distortion.

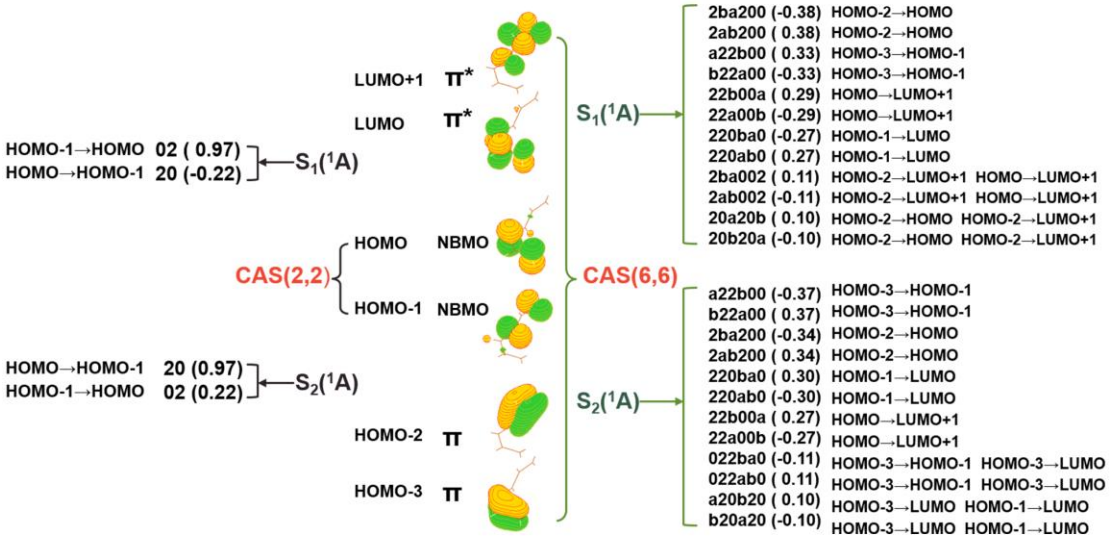


Figure S2. Elctronic configuration and corresponding orbital excitations for the $S_1(1^1A)$ and $S_2(2^1A)$ states of perpendicular *s-cis,s-trans*-diallyl, calculated with CAS(2,2) (left) and CAS(6,6) (right) methods. The coefficient for each configuration is given in the parentheses. Related molecular orbitals are dipicted in the middle of the figure.

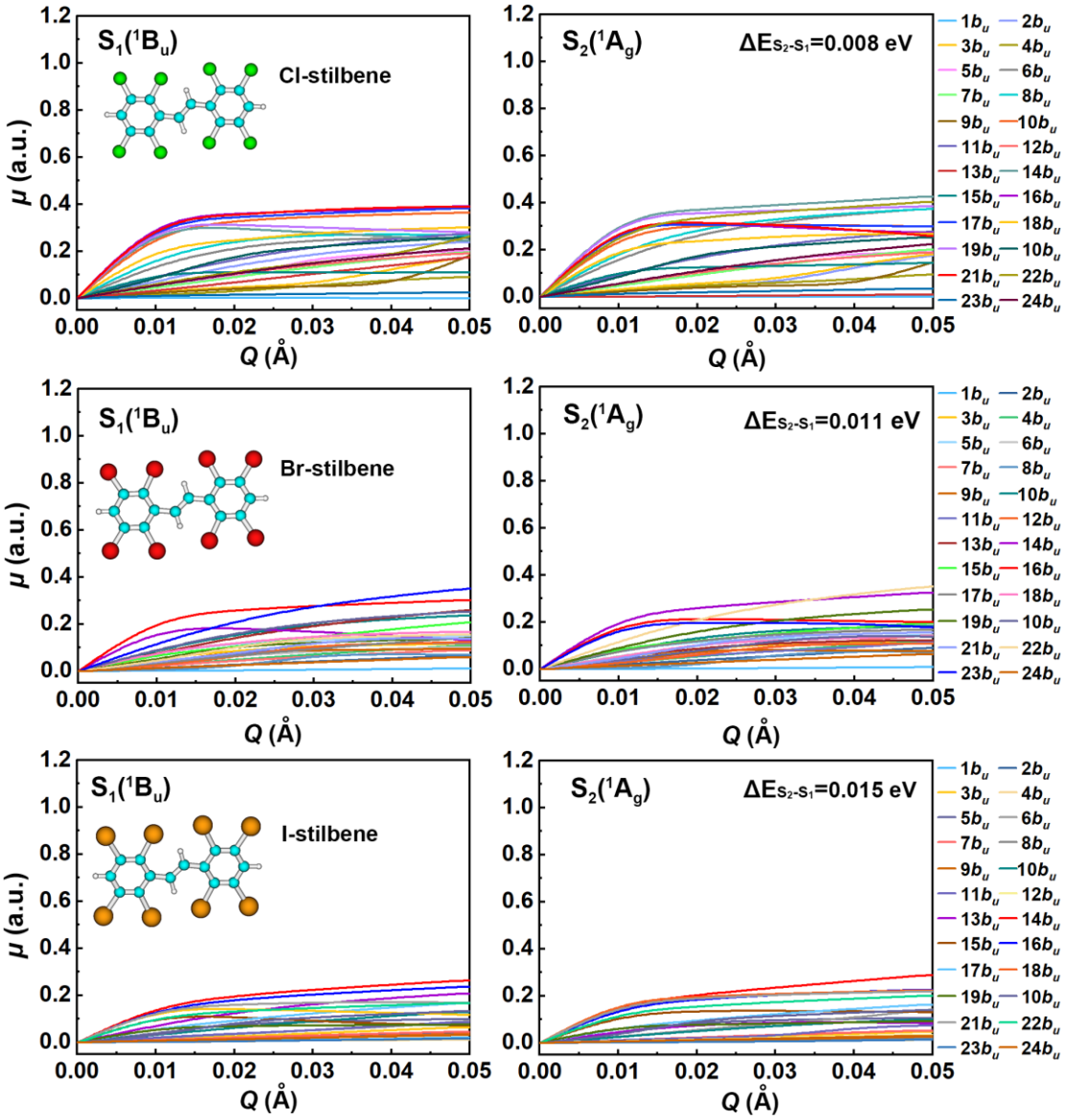
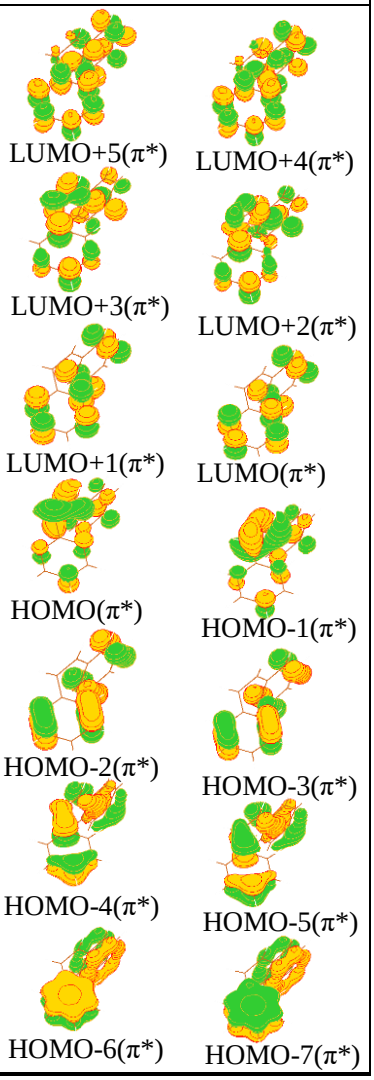


Figure S3. The dipole moment profiles of the $S_1(1^1B_u)$ and $S_1(2^1A_g)$ excited states along all the polar b_u modes for Cl/Br/I-stilbene. The values of their dipole moments are all much smaller than in F-stilbene, and decline with the increase of the shown energy gaps between the S_1 and S_2 states $\Delta E_{S2\text{-}S1}$.

Table S1. The main elctronic configurations (with CI coefficients in parenthesis) and the orbital excitations in the excited $S_1(^1B)$ state of perpendicular stilbene.

Active space	Electron configuration	Electron transition	Orbitals
CAS(2,2)	ba(-0.71)		
	ab(0.71)		
CAS(6,6)	22ba00(-0.69)		
	22ab00(0.69)		
CAS(10, 10)	222ba20000(-0.33)	HOMO-2→HOMO	
	222ab20000(0.33)	HOMO-2→HOMO	
	22b22a0000(0.32)	HOMO-3→HOMO-1	
	22a22b0000(-0.32)	HOMO-3→HOMO-1	
	22220ba000(-0.28)	HOMO-1→LUMO	
	22220ab000(0.28)	HOMO-1→LUMO	
	2222a00b00(-0.28)	HOMO→LUMO+1	
	2222b00a00(0.28)	HOMO→LUMO+1	
CAS(14, 14)	22222ba2000000(-0.31)	HOMO-2→HOMO	
	22222ab2000000(0.31)	HOMO-2→HOMO	
	2222b22a000000(0.31)	HOMO-3→HOMO-1	
	2222a22b000000(-0.31)	HOMO-3→HOMO-1	
	222222b00a0000(0.26)	HOMO→LUMO+1	
	222222a00b0000(-0.26)	HOMO→LUMO+1	
	2222220ba00000(-0.26)	HOMO-1→LUMO	
	2222220ab00000(0.26)	HOMO-1→LUMO	