

Supporting Information:

**On Internal Conversion between Bright ($1^1B_u^+$)
and Dark($2^1A_g^-$) States in s-trans-Butadiene and
s-trans-Hexatriene**

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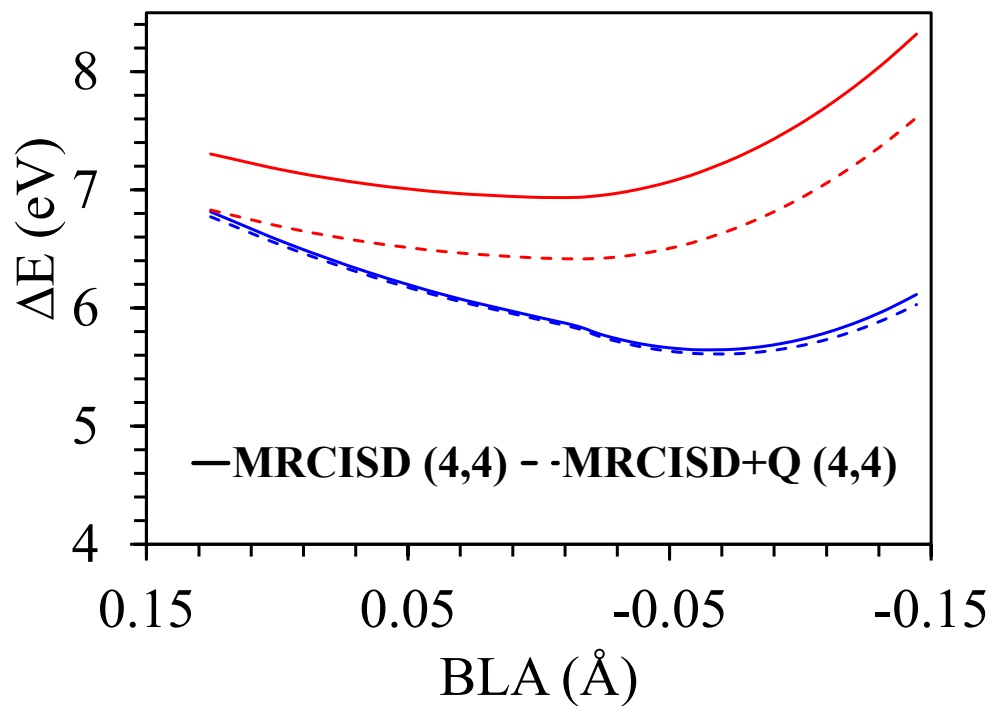
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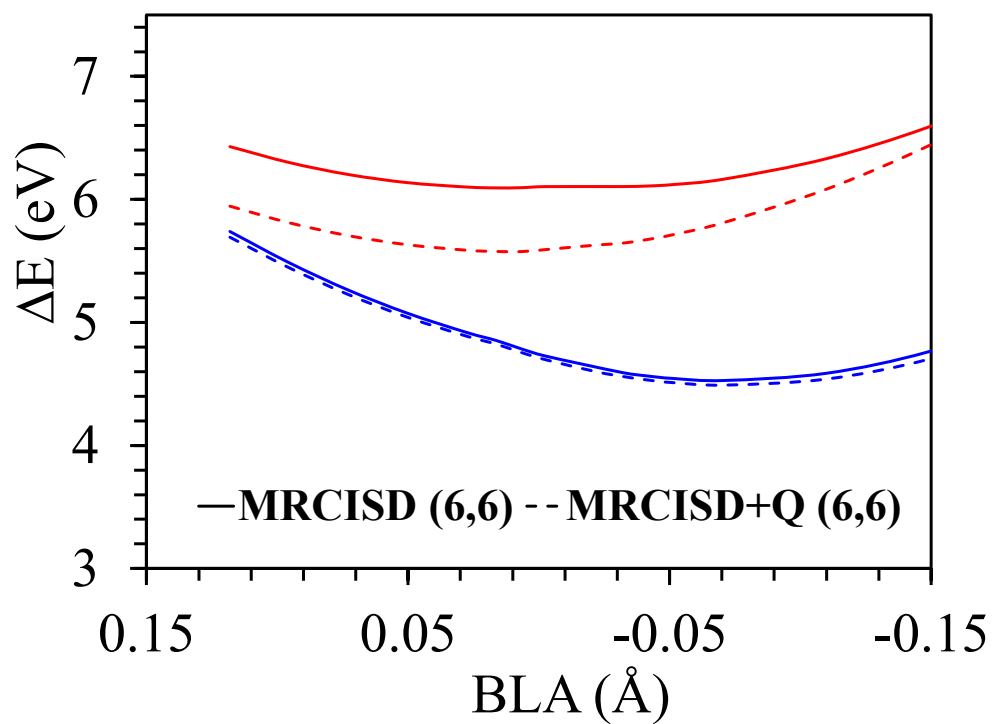
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Computational Details

We obtained the ground-state minimum (FC) and the minima on the $1^1B_u^+$ and $2^1A_g^-$ potentials, $1^1B_{u,min}^+$ and $2^1A_{g,min}^-$, respectively, by performing the CCSD/EOMCCSD geometry optimizations using the cc-pVTZ basis set. The minimum energy pathways (MEPs) connecting the FC, $1^1B_{u,min}^+$, and $2^1A_{g,min}^-$ structures were obtained using the geodesic interpolation.^{S1} The π valence molecular orbitals belonging to the a_u and b_g irreducible representations of the C_{2h} point group were used to define the relevant (4,4) (*s-trans*-butadiene) and (6,6) (*s-trans*-hexatriene) active spaces in multi-reference calculations. The post-CASSCF calculations for the $2^1A_g^-$ state were performed using the SA-CASSCF reference wave function averaging the two lowest CASSCF roots of the $1^1A_g^-$ symmetry. With the exception of the single-root MRMP2 computations, the post-CASSCF calculations for the $1^1B_u^+$ state were carried out using the SA-CASSCF reference wave function averaging the two lowest roots of the $1^1B_u^+$ symmetry. The SA-CASSCF, XMS-CASPT2, MRCI, and MRCI+Q calculations were performed with Molpro,^{S2} whereas the remaining results were obtained with GAMESS^{S3,S4} or, in the case of the DEA- and DIP-EOMCC methods, with the codes developed in Refs. S5,S6, interfaced with GAMESS. No level shift was applied in the multi-reference perturbation theory calculations, as no intruder states were encountered.

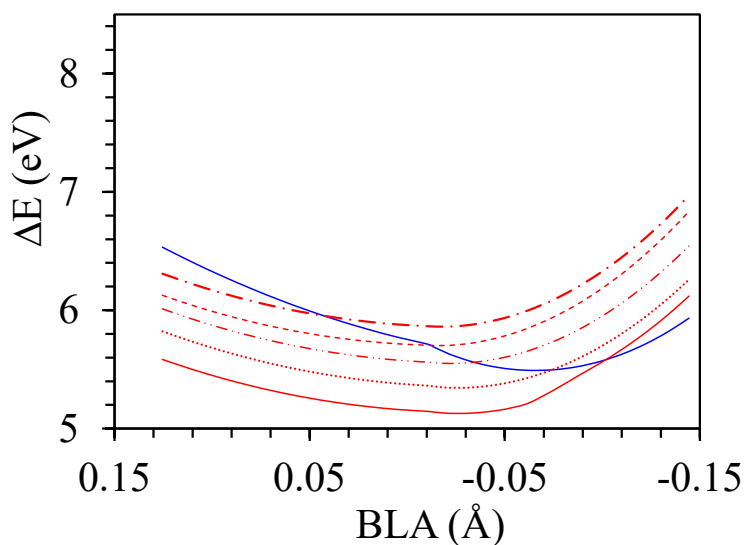


(a)

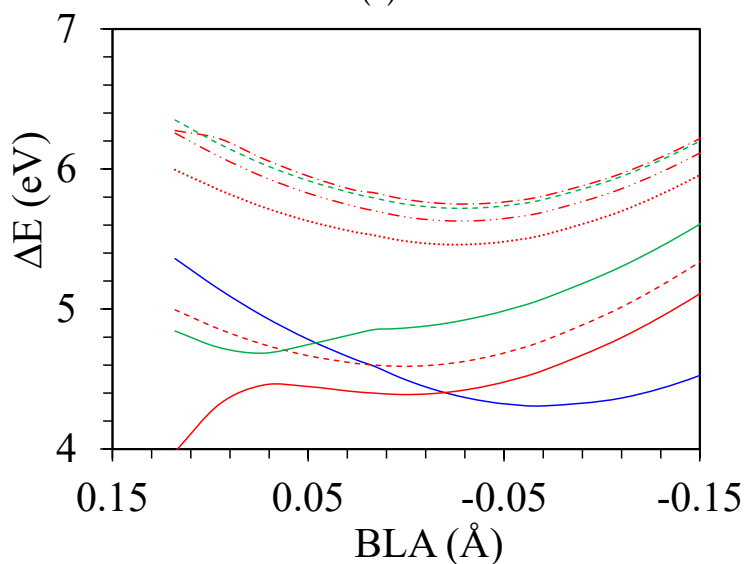


(b)

Figure S1: The MEPs on the $1^1B_u^+$ (red) and $2^1A_g^-$ (blue) PESs of (a) *s-trans*-butadiene and (b) *s-trans*-hexatriene obtained by MRCISD/cc-pVTZ (solid lines) and MRCISD+Q/cc-pVTZ (dashed lines).



(a)



(b)

Figure S2: MEPS on the $1^1B_u^+$ (red) and $2^1A_g^-$ (blue) PESs of (a) *s-trans*-butadiene and (b) -hexatriene. In the case of the latter molecule, additional $2^1B_u^+$ (green) state is also shown. In the calculation of $2^1A_g^-$ state, two state ($1^1A_g^-$ and $2^1A_g^-$) perturbation on the basis of two state SA-CASSCF with $1^1A_g^-$ and $2^1A_g^-$ seems to be natural. However, there are multiple choices are possible for the calculation of $1^1B_u^+$. The solid lines and dashed lines represent the two state XMCQDPT2 of $1^1B_u^+$ and $2^1B_u^+$ on the basis of two state SA-CASSCF either with $1^1A_g^-$ and $2^1A_g^-$ or with $1^1B_u^+$ and $2^1B_u^+$, respectively. The former choice of SA-CASSCF for *s-trans*-hexatriene yielded unphysical curves near FC. The dotted lines and dash-dotted lines represent state specific ($1^1B_u^+$) MP2 (MRMP2) on the basis of two state SA-CASSCF either with $1^1A_g^-$ and $2^1A_g^-$ or with $1^1B_u^+$ and $2^1B_u^+$, respectively. The dash-dotted-dotted lines represent the $1^1B_u^+$ by a state specific CASPT2 on the basis of two state SA-CASSCF with $1^1A_g^-$ and $2^1A_g^-$. In general, the state specific perturbation results overestimate $1^1B_u^+$ significantly.

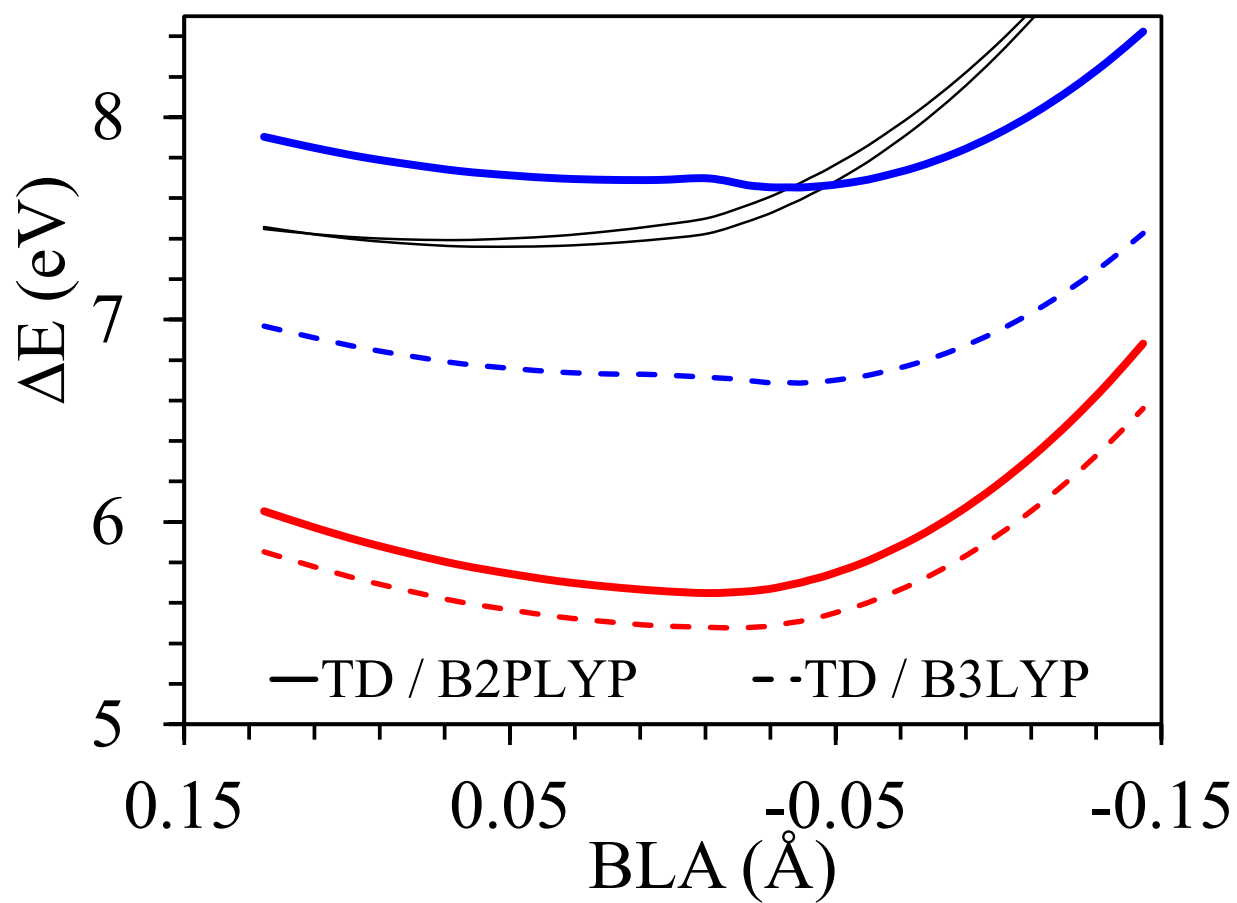
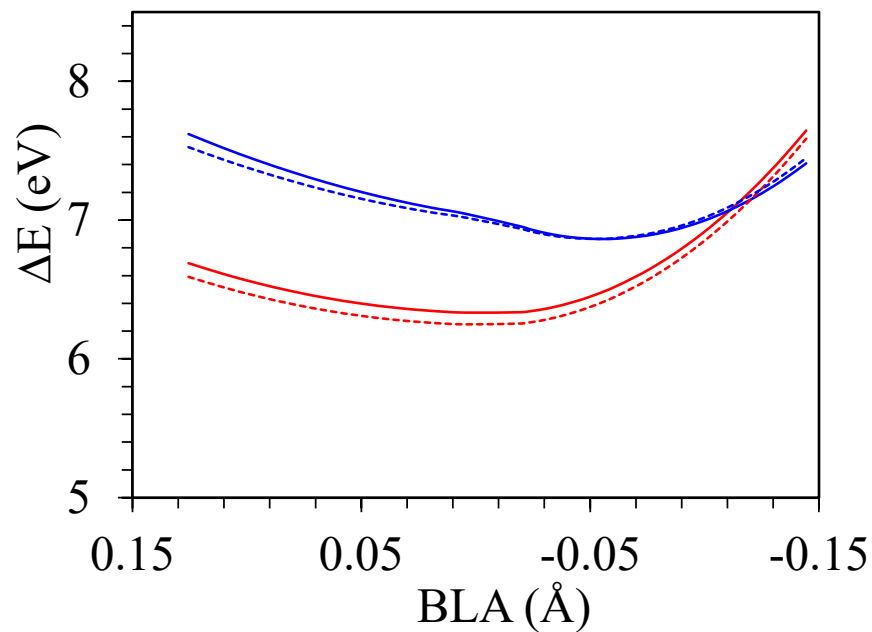
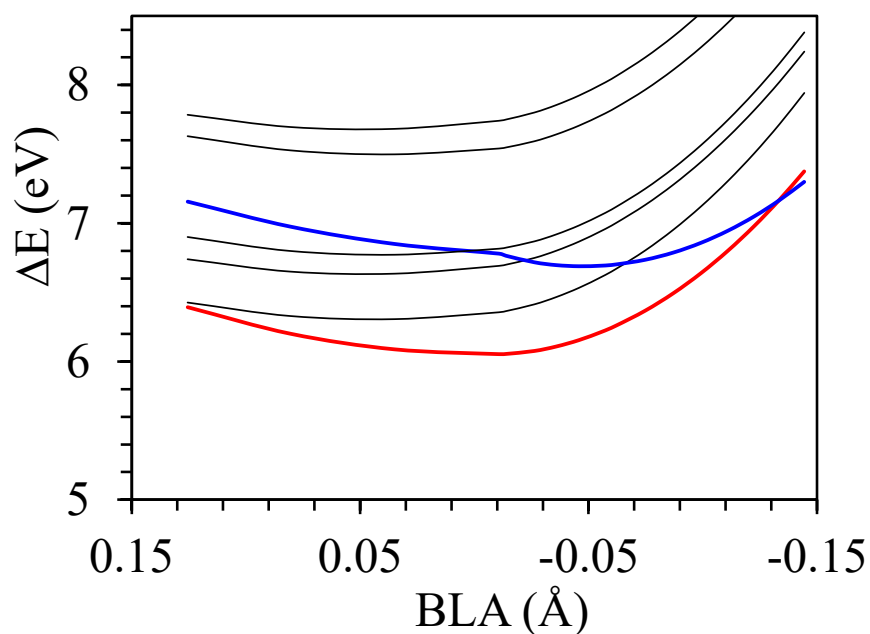


Figure S3: The MEPs of *s-trans*-butadiene on the $1^1B_u^+$ (red), $2^1A_g^-$ (blue), and other different symmetry states (black) PESs by TDDFT/B2PLYP (solid lines) and TDDFT/B3LYP (dashed lines).



(a)



(b)

Figure S4: (a) The MEPs on the $1^1B_u^+$ (red) and $2^1A_g^-$ (blue) PESs of *s-trans*-butadiene obtained by EOMCCSD/cc-pVTZ (solid lines) and EOMCCSD/cc-pVQZ (dashed lines). (b) The MEPs of *s-trans*-butadiene on the $1^1B_u^+$ (red), $2^1A_g^-$ (blue), and other different symmetry states (black) PESs by EOMCCSD / aug-cc-pVTZ

Table S1: Vertical excitation energies of the two lowest singlet ($2^1A_g^-, 1^1B_u^+$) excited states of butadiene obtained with various methods in the gas phase.

Methods	$1^1B_u^+$	$2^1A_g^-$
DFT-SSMRPT(4,4) / ANO ^{a)}	5.41	6.41
DFT-SSMRPT(4,8) / ANO ^{a)}	6.47	6.46
DFT-SSMRPT(4,4) / cc-pV5Z ^{a)}	5.42	6.43
DFT-SSMRPT(4,4) / jul-cc-pVTZ ^{a)}	5.28	6.35
CASSCF-SSMRPT(4,4) / ANO ^{a)}	5.48	6.44
CASSCF-SSMRPT(4,4) / cc-pVQZ ^{a)}	6.00	6.39
HF-SSMRPT(4,4) / cc-pVQZ ^{a)}	5.19	6.36
MRMP2(4,8) / QZ3p ^{b)}	6.21	6.31
CASPT2(4,8) / cc-pVTZ ^{c)}	6.41	6.59
CASPT2(4,8) / jul-cc-pVTZ ^{c)}	6.75	6.42
MS-CASPT2(4,8) / cc-pVTZ ^{c)}	6.38	6.59
MS-CASPT2(4,8) / jul-cc-pVTZ ^{c)}	5.97	6.42
MCPDFT(4,8) / cc-pVTZ ^{c)}	4.75	6.69
MCPDFT(4,8) / jul-cc-pVTZ ^{c)}	6.07	6.46
MR-CISD / SA(3)-CAS(4,4) / daug'-cc-pVDZ ^{c)}	8.15	6.67
MR-CISD / SA(4)-CAS(4,4) / daug'-cc-pVDZ ^{c)}	6.65	6.63
CASSCF(4,8) / ANO ^{d)}	8.54	6.64
CASPT2(4,8) / ANO ^{d)}	6.23	6.27
RD-NEVPT2-SC(4,4) / 6-311G ^{**e)}	6.38	7.14
RD-NEVPT2-PC(4,4) / 6-311G ^{**e)}	6.36	6.88
NEVPT2-SC(4,4) / 6-311G ^{**e)}	6.75	6.88
NEVPT2-PC(4,4) / 6-311G ^{**e)}	6.73	6.90
RD-CASCI(6,14) / 6-311G ^{**e)}	6.48	7.59
SC-NEVPT2(4,4) / cc-pVDZ ^{f)}	6.46	6.91
cud-SC-NEVPT2(4,4) / cc-pVDZ ^{f)}	6.35	6.80
MR-CISD / SA(4)-CAS(4,4) / aug-cc-pVTZ ^{g)}	6.57	6.45
TDDFT / B3LYP / 6-311(2+,2+)G ^{**h)}	5.90	6.48
EOMCCSDT / (aPVTZ + experiment) ⁱ⁾	6.1	6.24
EOMCCSD / cc-pV5Z ^{j)}	6.47	7.33
Best estimate EOMCCSDT / CBS ^{j)}	6.21	6.41
t-MPS-NEVPT2 / cc-pVDZ ^{k)}	6.17	6.94
MR-AQCC ^{l)}	6.36	6.60
SAC-CI / DZP ^{m)}	6.33	6.56
NEVPT2 / aVTZ ⁿ⁾	6.68	6.70
FCI / 6-31+G(d) ⁿ⁾	6.41 ± 0.02	6.55 ± 0.04
Experiment	5.92, ^{S7-S14} 6.25 ^{S15}	

a) From Ref. S16 b) From Ref. S17 c) From Ref. S18 d) From Ref. S19 e) From Ref. S20 f) From Ref. S21 g) From Ref. S22 h) From Ref. S23 i) From Ref. S24 j) From Ref. S25 k) From Ref. S26 l) From Ref. S27 m) From Ref. S28 n) From Ref. S29

Table S2: Vertical excitation energies of the two lowest singlet ($2^1A_g^-$, $1^1B_u^+$) excited states of hexatriene obtained with various methods in the gas phase.

Methods	$1^1B_u^+$	$2^1A_g^-$
DFT-SSMRPT(6,6) / ANO ^{a)}	4.68	4.90
DFT-SSMRPT(6,6) / cc-pVQZ ^{a)}	4.78	4.99
DFT-SSMRPT(6,6) / jul-cc-pVTZ ^{a)}	4.64	5.12
CASSCF-SSMRPT(6,6) / cc-pVQZ ^{a)}	5.00	5.11
CASSCF(6,8) / ANO ^{b)}	7.36	5.65
CASPT2(6,8) / ANO ^{b)}	5.01	5.20
CASPT2(6,8) / ANO ^{c)}	5.45	4.89
CASPT2(6,8) / cc-pVTZ ^{c)}	6.01	5.11
RD-NEVPT2-SC(6,14) / 6-311G ^{**d)}	5.17	5.50
RD-NEVPT2-PC(6,14) / 6-311G ^{**d)}	5.15	5.16
NEVPT2-SC(6,14) / 6-311G ^{**d)}	5.57	5.78
NEVPT2-PC(6,14) / 6-311G ^{**d)}	5.56	5.75
RD-CASCI(6,14) / 6-311G ^{**d)}	6.48	7.59
SC-NEVPT2(6,6) / cc-pVDZ ^{e)}	5.35	5.60
cud-SC-NEVPT2(6,6) / cc-pVDZ ^{e)}	5.13	5.37
MRMP2(6,12) / DZ3p ^{f)}	5.10	5.09
CASCI-MRMP2(10,10) / cc-pVDZ ^{g)}	5.25	5.10
SF-CIS / 6-31G(d) ^{h)}	5.06	5.06
SF-ORMASCIS / 6-31G(d) ^{h)}	6.35	6.34
3SF-MRMP2 / 6-31G(d) ^{h)}	4.91	5.40
EOMCCSDT/aug-cc-pVDZ ⁱ⁾	5.40	5.63
Experiment	4.93, 4.95, 5.13 ^{S8,S30,S31}	5.21 ^{S32}

^{a)} From Ref. S16 ^{b)} From Ref. S19 ^{c)} From Ref. S33 ^{d)} From Ref. S20 ^{e)} From Ref. S21 ^{f)} From Ref. S17 ^{g)} From Ref. S34 ^{h)} From Ref. S35 ⁱ⁾ From Ref. S36

Table S3: The vertical and adiabatic excitation energies corresponding to the $1^1B_u^+$ and $2^1A_g^-$ states of *s-trans*-butadiene and *s-trans*-hexatriene obtained by the quantum chemistry methods employed in this study. The vertical and adiabatic excitation energies characterizing the $1^1B_u^+$ state are designated as $1^1B_u^+$ (FC) and $1^1B_u^+$ (min), respectively. The vertical and adiabatic excitation energies characterizing the $2^1A_g^-$ state are designated as $2^1A_g^-$ (FC) and $2^1A_g^-$ (min), respectively. All methods utilized the cc-pVTZ basis set.

Method	$1^1B_u^+$ (FC)	$2^1A_g^-$ (FC)	$1^1B_u^+$ (min)	$2^1A_g^-$ (min)
<i>trans</i> -butadiene				
EOMCCSD	6.69	7.62	6.33	6.86
δ -CR-EOMCC(2,3)	6.24	6.76	5.75	5.62
DIP-EOMCC(4h2p){3}	6.60	6.97	6.16	5.86
DEA-EOMCC(4p2h){3}	6.65	6.83	6.28	5.83
XMS-CASPT2	5.83	6.58	5.41	5.52
XMCQDPT2	6.13	6.53	5.70	5.50
MRCISD+Q	6.83	6.77	6.42	5.61
SA-CASSCF	8.34	6.74	7.97	5.47
MRMP2	6.31	-	5.86	-
MRSF / BH&HLYP	6.18	6.76	5.88	5.97
SSR(4,4)-wB97-X	6.14	6.87	5.78	6.03
TDDFT / PBE0	5.93	7.18	5.55	6.90
TDDFT / B3LYP	5.85	6.97	5.47	6.68
<i>trans</i> -hexatriene				
EOMCCSD	5.70	6.83	5.39	6.12
δ -CR-EOMCC(2,3)	5.20	5.86	4.77	4.70
DIP-EOMCC(4h2p){4}	5.63	5.85	5.25	4.70
DEA-EOMCC(3p1h,4p2h){4}	5.72	5.84	5.35	4.67
XMS-CASPT2	4.89	5.36	4.48	4.29
XMCQDPT2	4.99	5.36	4.59	4.31
MRCISD+Q	5.94	5.69	5.57	4.49
SA-CASSCF	6.90	5.74	6.05	4.42
MRMP2	6.28	-	5.75	-
MRSF / BH&HLYP	5.09	5.95	4.86	5.02
TDDFT / PBE0	4.87	6.03	4.55	5.76
TDDFT / B3LYP	4.80	5.82	4.48	5.55

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