New insights into the by-product fatigue mechanism of the photo-induced ring-opening in diarylethenes

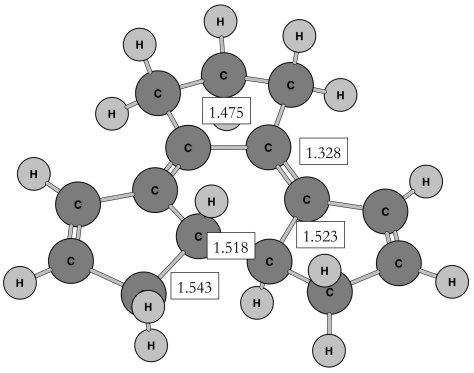
David Mendive-Tapia,*[a,b] Aurélie Perrier,[c] Michael J. Bearpark,[d] Michael A. Robb,[d] Benjamin Lasorne,[e] and Denis Jacquemin*[a,f]

Electronic Supplementary Information (ESI)

Contents

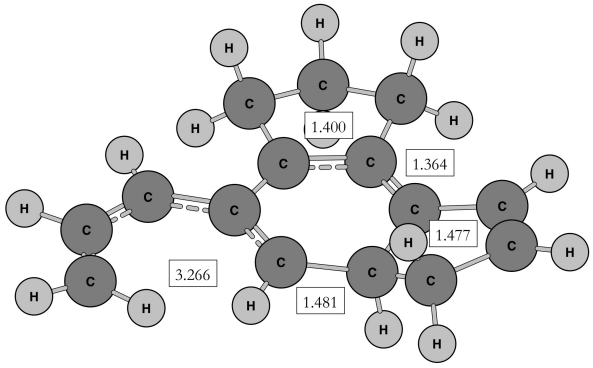
[a] *Chimie Et Interdisciplinarité, Synthèse, Analyse, Modélisation (CEISAM), UMR CNRS no. 6230, BP 92208, Université de Nantes, 2, Rue de la Houssinière, 44322 Nantes, Cedex 3, France. E-mail: denis.jacquemin@univ-nantes.fr, david.mendive@univ-nantes.fr.*
[b] *Research visitor, Department of Chemistry, Imperial College London, London SW7 2AZ, United Kingdom.*
[c] *Laboratoire Interfaces, Traitements, Organisation et Dynamique des Systèmes (ITODYS), CNRS UMR 7086, Université Paris 7 - Paris Diderot, Bâtiment Lavoisier, 15 rue Jean Antoine de Baïf, 75205 Paris Cedex 13, France.*
[d] *Department of Chemistry, Imperial College London, London SW7 2AZ, United Kingdom.*
[e] *Institut Charles Gerhardt Montpellier, UMR 5253, CNRS-UM2-ENSCM-UM1, CTMM, Université Montpellier 2, CC 1501, Place Eugène Bataillon, 34095 Montpellier, France.*
[f] *Institut Universitaire de France, 103, blvd Saint-Michel, F-75005 Paris Cedex 05, France.*

1 Ground state optimised structures (Å)



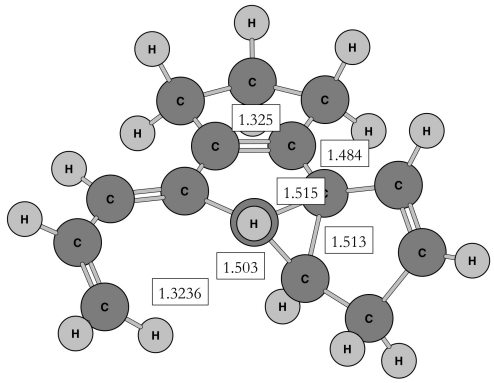
RHF/6-31++G(3df,3pd) CHD

(1) Closed S_0(1A)



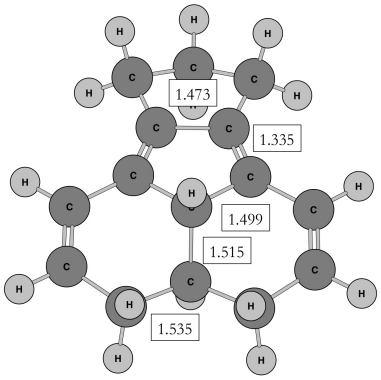
RHF/6-31++G(3df,3pd) PM

(2) Planar Minimum S_0(1A)



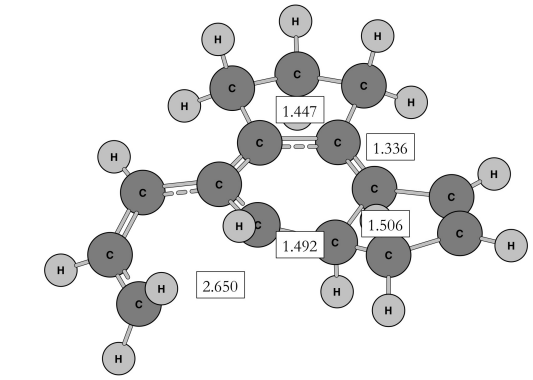
RHF/6-31++G(3df,3pd) BCH

(3) Bicyclohexane S_0(1A)

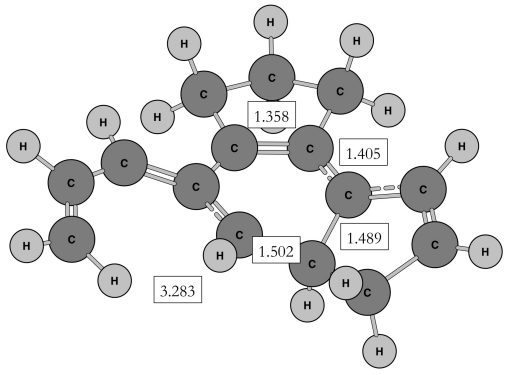


RHF/6-31++G(3df,3pd) BP

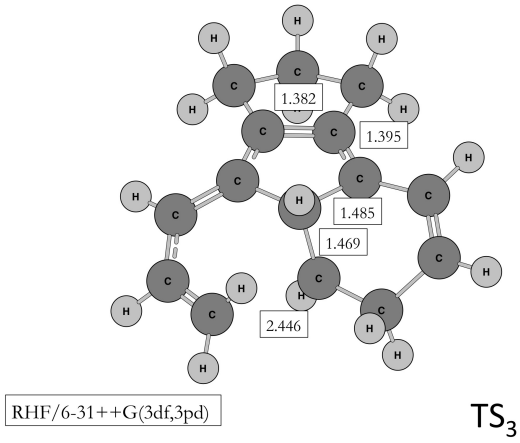
(4) By-product S_0(1A)



(5) TS_1 S_0(1A)



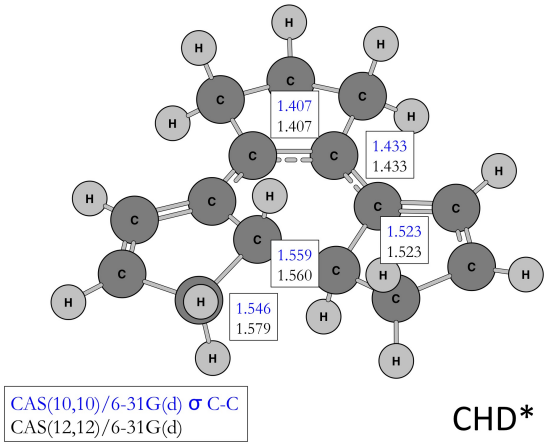
(6) TS_2 S_0(1A)



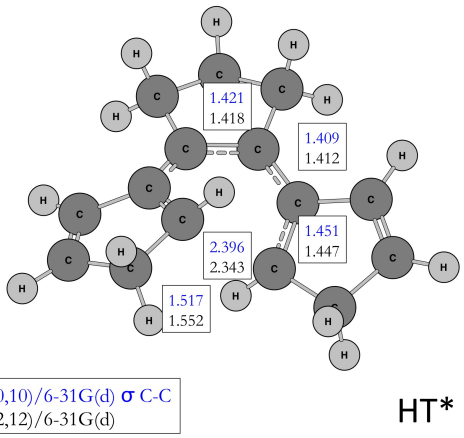
(7) TS_3 S_0(1A)

2 Excited state optimised structures (Å)

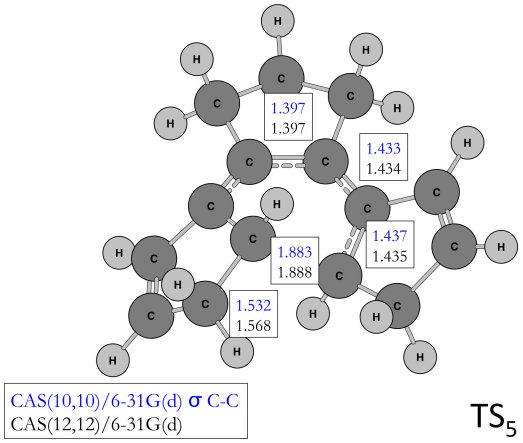
2.1 Model II



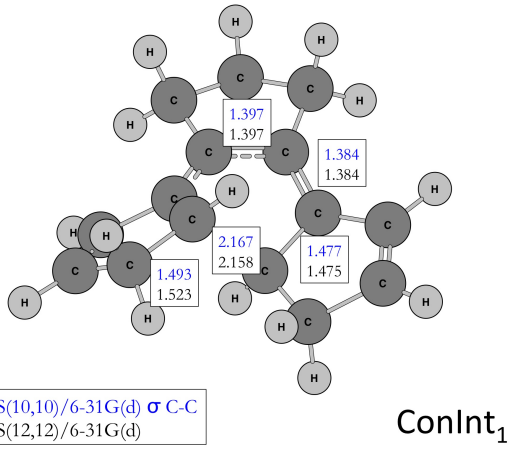
(8) Closed S_1(2A)



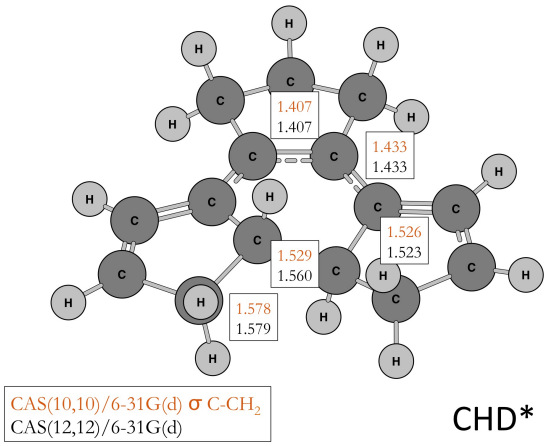
(9) Open S_1(2A)



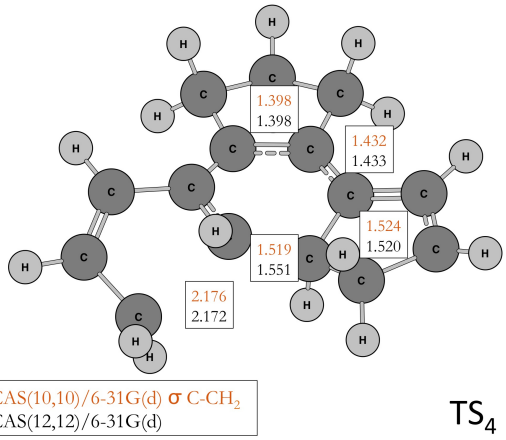
(10) TS_5 S_1(2A)



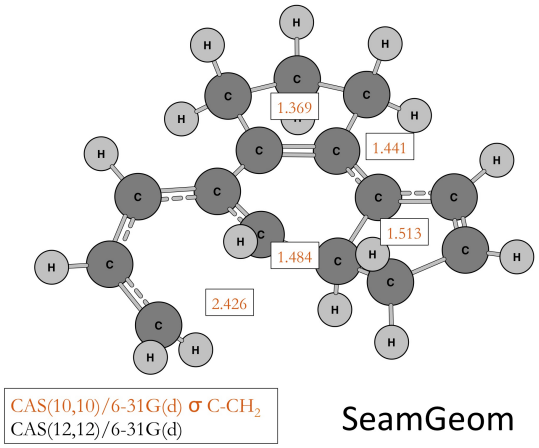
(11) $ConInt_1$ S_1(2A)/S_0(1A)



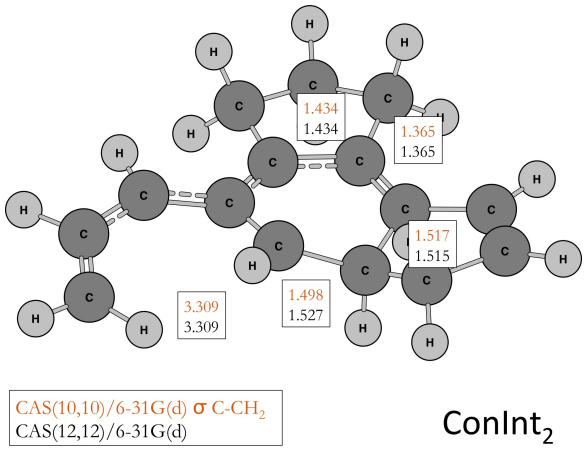
(12) Closed $S_1(2A)$



(13) TS_4 $S_1(2A)$

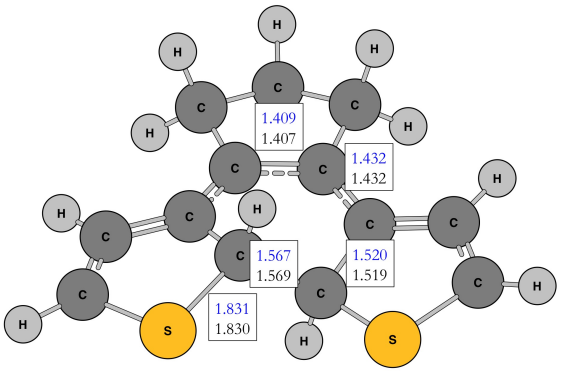


(14) SeamGeom $S_1(2A)/S_0(1A)$

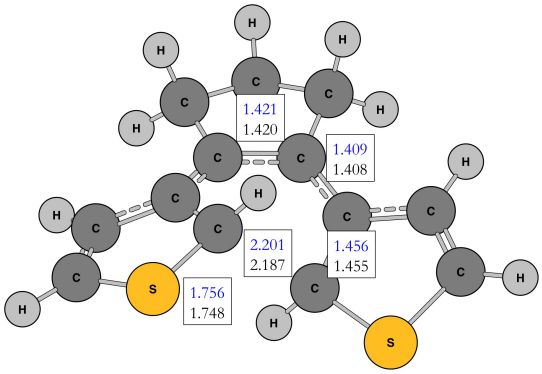


(15) $ConInt_2$ $S_1(2A)/S_0(1A)$

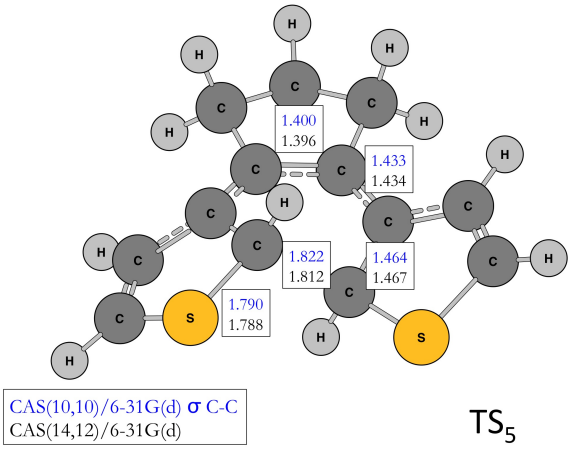
2.2 Model III



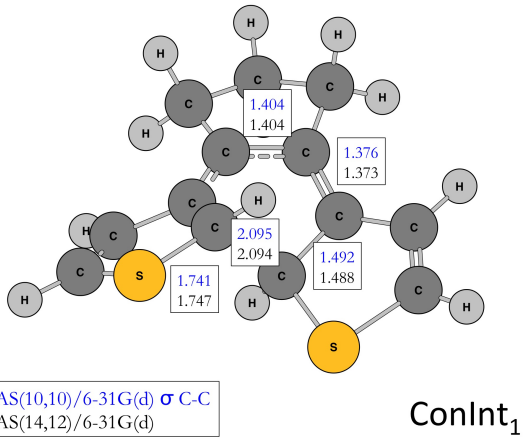
(16) Closed S_1(2A)



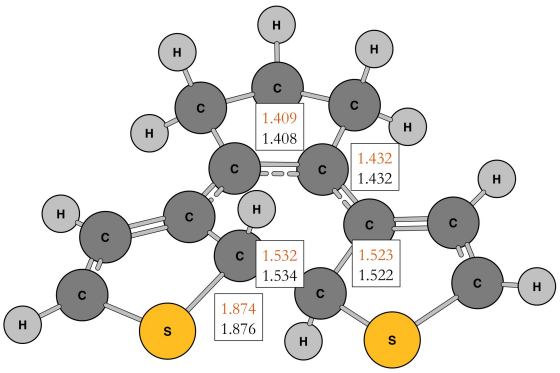
(17) Open S_1(2A)



(18) TS_5 S_1(2A)



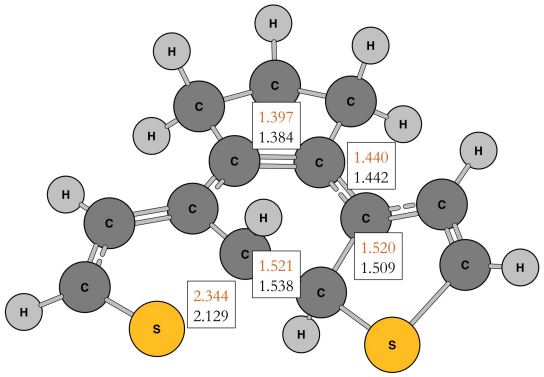
(19) $ConInt_1$ S_1(2A)/S_0(1A)



CAS(10,10)/6-31G(d) σ C-S
CAS(14,12)/6-31G(d)

CHD*

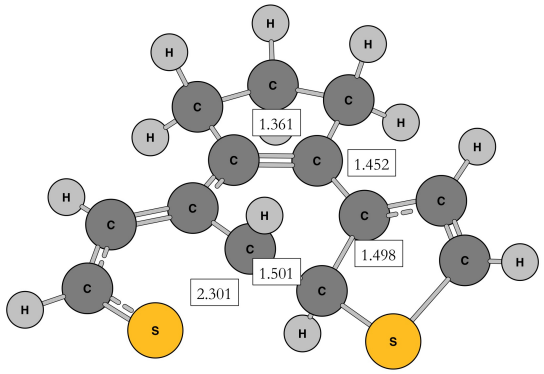
(20) Closed $S_1(2A)$



SA-CAS(10,10)/6-31G(d) σ C-S
CAS(14,12)/6-31G(d)

TS_4

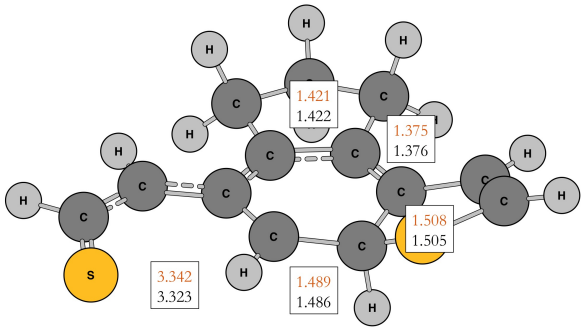
(21) TS_4 $S_1(2A)$



CAS(10,10)/6-31G(d) σ C-S
CAS(14,12)/6-31G(d)

SeamGeom

(22) SeamGeom $S_1(2A)/S_0(1A)$

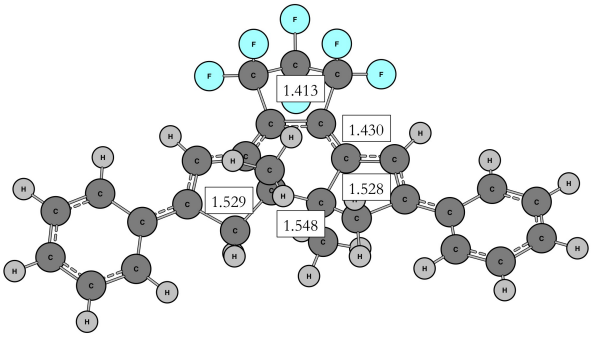


CAS(10,10)/6-31G(d) σ C-S
CAS(14,12)/6-31G(d)

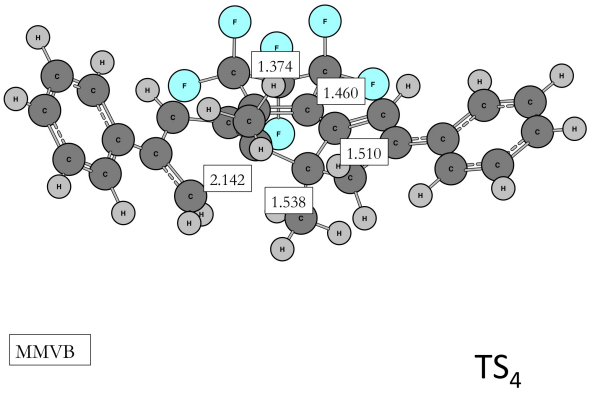
$ConInt_2$

(23) $ConInt_2$ $S_1(2A)/S_0(1A)$

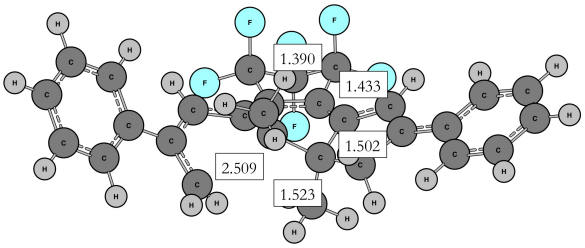
2.3 Model IV



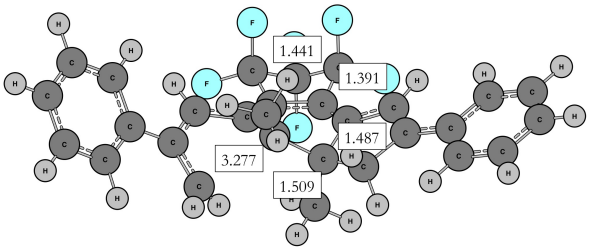
(24) Closed $S_1(2A)$



(25) TS_4 $S_1(2A)$



(26) SeamGeom $S_1(2A)/S_0(1A)$



(27) $ConInt_2$ $S_1(2A)/S_0(1A)$

3 Relative CASPT2 energies (kcal/mol)

3.1 Model II

Table 1 Vertical excitation energies calculated at the CASSCF(10,10)/6-31G(d) and CASPT2//CASSCF(10,10)/6-31G(d) levels of theory.

Structure	State	CASSCF	Description	CASPT2	Description
CHD	S_0	0.00	1A	0.00	1A
	S_1	111.99	2A	108.02	2A
	S_2	132.53	1B	119.21	1B
CHD*	S_0	18.27	1A	18.14	1A
	S_1	84.85	2A	82.50	2A
	S_2	117.67	1B	112.78	1B
TS_4	S_0	62.50	1A	61.84	1A
	S_1	131.53	2A	126.84	2A
	S_2	144.34	1B	136.60	1B
$ConInt_2$	S_0	70.14	1A	72.11	1A
	S_1	70.35	2A	72.84	2A
	S_2	119.49	1B	123.53	1B

3.2 Model III

Table 2 Vertical excitation energies calculated at the CASSCF(10,10)/6-31G(d) and CASPT2//CASSCF(10,10)/6-31G(d) levels of theory.

Structure	State	CASSCF	Description	CASPT2	Description
CHD	S_0	0.00	1A	0.00	1A
	S_1	128.32	2A	101.40	2A
	S_2	133.98	1B	117.83	1B
CHD*	S_0	19.97	1A	15.85	1A
	S_1	79.94	2A	74.02	2A
	S_2	115.33	1B	107.66	1B
TS_4	S_0	39.65	1A	38.59	1A
	S_1	101.75	2A	82.52	2A
	S_2	113.21	1B	104.65	1B
$ConInt_2$	S_0	75.27	1A	57.20	1B
	S_1	76.27	2A	64.59	1A
	S_2	84.13	1B	64.66	2A