Electronic Supplementary information

Mechanism Behind the Photochromism and Photomagnetism of Biindenilidenediones type II: Multiconfigurational, Perturbative and Density Functional Theory Studies

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Section I: Gas phase

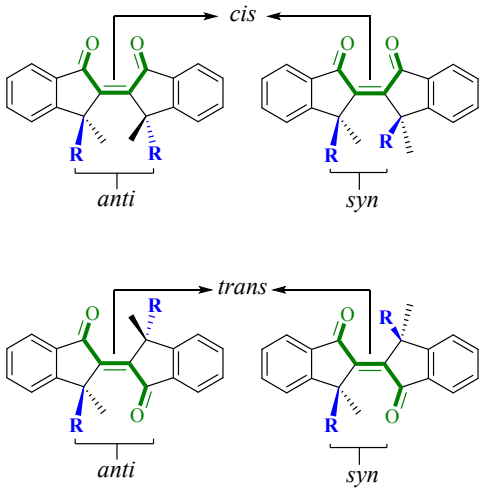


Figure S1. Possible isomers depending on the relative positions of the carbonyl groups and the equivalent substituents.

Criteria for the definition of the active space:

Based on the hydrogen migration involved in the Norrish type II reaction, we can classify the PES in the FC zone, TS zone and Product zone. In order to keep an active space with reasonable size that allow calculation times accessible, instead of increasing the active space, we have chosen the most important molecular orbitals to describe the electronic nature of the excited states depending on the zone of the PES that we were exploring.

We have used an active space (14,12) in all the calculations. However, they also were adapted to the PES zone according to Figure S3.

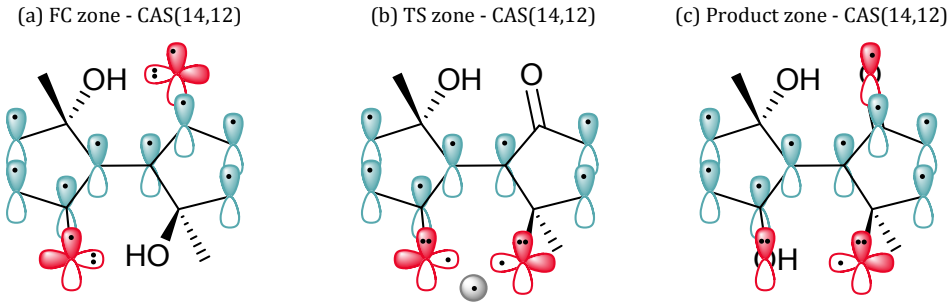


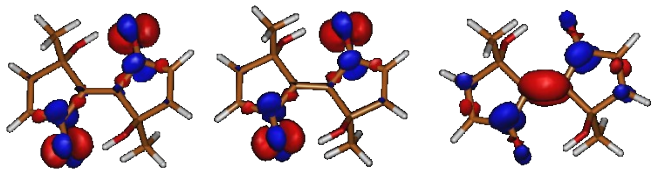
Figure S2. The active spaces used to study the hydrogen migration on BID-II derivatives

Initially, to study the transition state zone we included the π and π* of the carbonyl group obtaining a CAS(16,14). We also tried with the CAS(14,12) as shown in Figure S3b, which lead to the same qualitatively results for the target states, so we decided to use the last active space mentioned in order to decrease the computation time.

The ideal situation would be to calculate the whole stationary points using CAS(16,14) such as in the transition state zone. Nevertheless, the molecular symmetry in the Franck-Condon geometry compels to include also the *n* on the other carbonyl plus the σ, σ* and P_O orbitals of the other HO group. This leads to an increase of the active space to (22,18) which is unaffordable with computation tools currently available in our group.

DDCI Space

This space was defined based in computational affordability and similar size of the configuration space in Model 1 and 2. Once it was confirmed that all relevant valence MO were included, we additionally included the maximum number of empty MO as long as the CPU time was accessible.



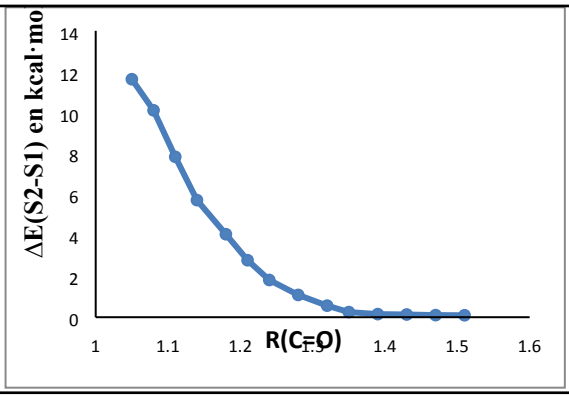
(a) (b) (c)

Figure S3. The electronic density differences between ground state and: (a) (Ag)1nπ*, (b) (Au)1nπ* and (c) (Au)1nπ* at Franck-Condon geometry. Negative and positive differences are shown in red and blue, respectively.

		ΔΔE(B2 B2-Mod)		
Irred. Rep.	**Nature**	**ΔΔE (CASSCF)**	**ΔΔE (MS-CASPT2)**	**ΔΔE (IDDCI+DC)**
A_g	$^3n\pi^*$	-2.1 T_2	+4.7 T_1	+6.4 T_1
	$^1n\pi^*$	-1.8 S_1	+1.7 S_1	+6.8 S_1
A_u	$^3\pi\pi^*$	-5.5 T_1	+1.8 T_2	+3.6 T_2
	$^1\pi\pi^*$	-2.0 S_5	+11.9 S_3	+3.4 S_2
A_u	$^3n\pi^*$	-4.2 T_3	+3.2 T_3	+6.8 T_3
	$^1n\pi^*$	-3.1 S_2	+0.1 S_2	+6.5 S_3

Table S1. Excitation energy differences between Model-2 and Model-1 for the lower singlet and triplet states at FC geometry.

R(C=O)[b]	**ΔE[a](E_{Ag}-E_{Au})**
1.05	11.633
1.08	10.113
1.11	7.839
1.14	5.724
1.18	4.057
1.21	**2.786**
1.24	1.819
1.28	1.089
1.32	0.565
1.35	0.250
1.39	0.151
1.43	0.132
1.47	0.102
1.51	0.095



[a] Energies calculated at SA3-CASSCF(14,12) level.
[b] C=O distances (in Å) along symmetrical stretching.

Figure S4. The S_1-S_2 energy gap in kcal·mol^{-1} at the SA3-CASSCF(14,12) level in B2-Mod.

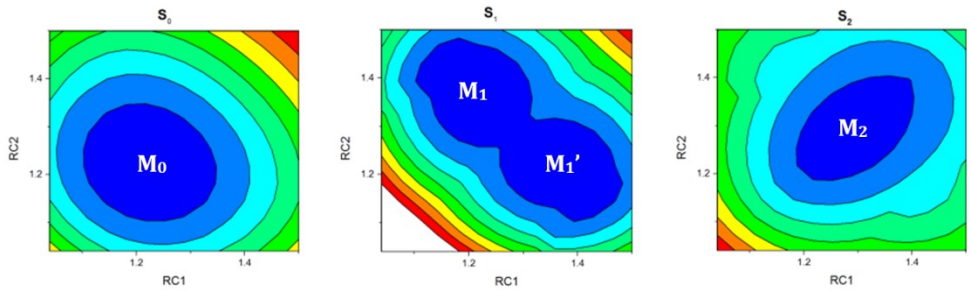


Figure S5. Contour diagrams calculated at CASSCF(14,12) level for the S_0, S_1 and S_2 PES for Model-1. RC1 and RC2 are the linear direction from FC to both mirror-image Min-$^1n\pi^*(S_1)$. M_i means minimum on the S_i.

Figure S6 shows all the stationary points located around the FC geometry on the S_1 and T_1 PESs. The 3*N*-6 dimensional nuclear configuration space is projected into a 2D space formed by the two carbonyl distances.

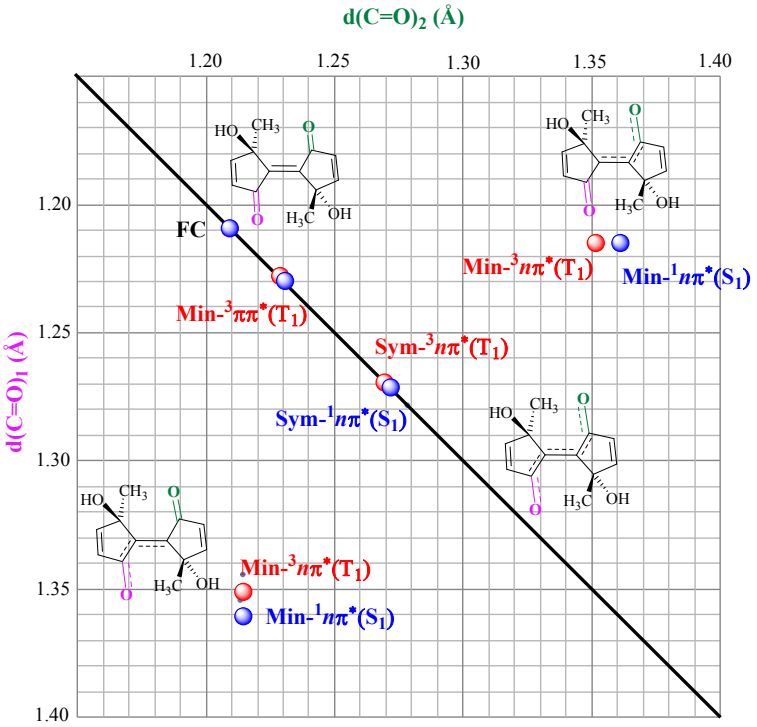


Figure S6. Stationary point located at CASSCF(14,12) on S_1 and T_1 in Model-1.

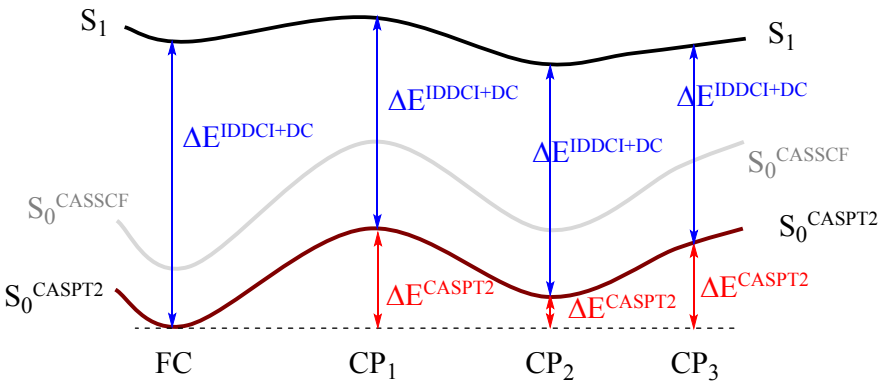


Figure S7. Graphical representation of the strategy used to get energy profiles at IDDCI+DC level. CP*i* means critical point *i*.

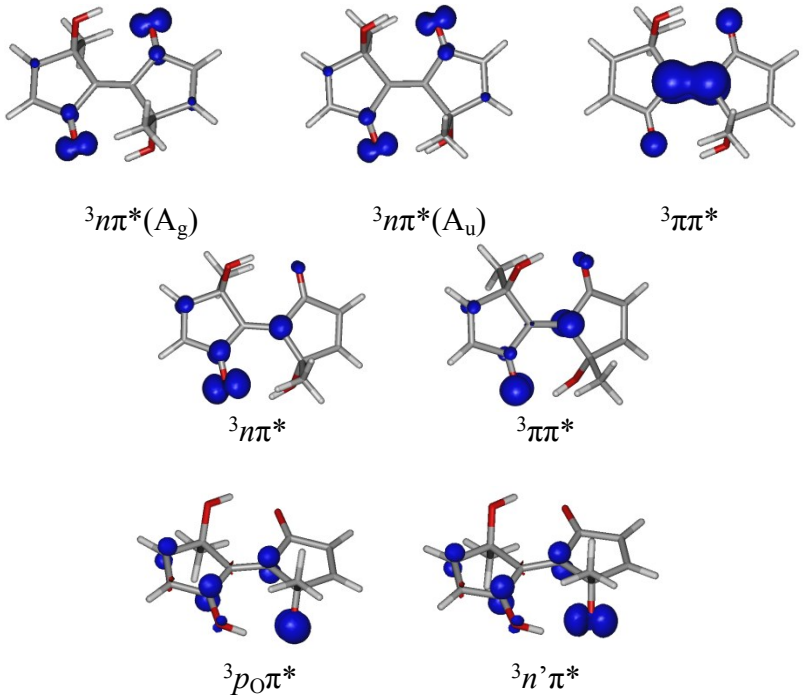
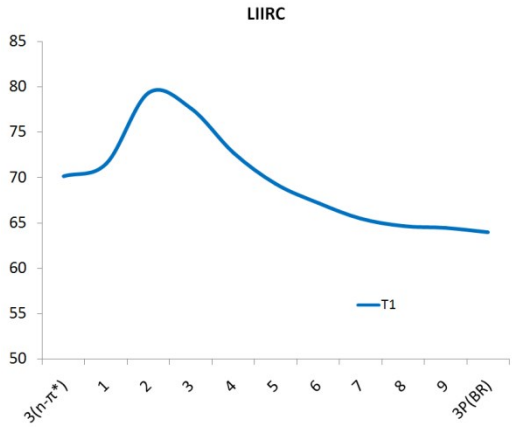
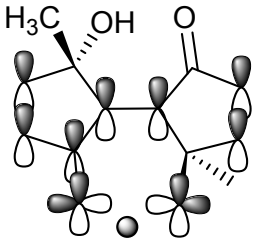


Figure S8. The spin density for the triplet states on the FC (first row), LM-$^1n\pi^*(S_1)$ (second row) and $^3P(p_O\pi^*)$ (third row).





MS2-CASPT2	LM-$^3n\pi^*$	1	2	3	4	5	6	7	8	9	$^3P(p_O\pi^*)$
T1	70.2	71.6	79.4	77.7	72.8	69.3	67.2	65.5	64.6	64.4	64.0

Figure S9. MS-CASPT2 energy profile along the coordinate connecting LM-$^3n\pi^*(T_1)$ and $^3P(p_O\pi^*)$.

```
zmat angstroms
 c
 c    1 cc2
 c    2 cc3          1 ccc3
 c    3 cc4          2 ccc4          1 dih4
 c    4 cc5          3 ccc5          2 dih5
 c    2 cc6          3 ccc6          4 dih6
 o    2 oc7          3 occ7          4 dih7
 o    5 oc8          4 occ8          3 dih8
 c    1 cc9          2 ccc9          6 dih9
 c    9 cc10         1 ccc10         2 dih10
 c   10 cc11         9 ccc11         1 dih11
 c   11 cc12        10 ccc12         9 dih12
 c   12 cc13        11 ccc13        10 dih13
 c   10 cc14         9 ccc14        13 dih14
 o   10 oc15         9 occ15        13 dih15
 o   13 oc16         9 occ16        10 dih16
variables:
```

For $^3P(p_O\pi^*)$		For the S_0-FC		Differences	
cc2	1.533364	cc2	1.543617	cc2	-0.010253
cc3	1.514532	cc3	1.514452	cc3	0.000080
ccc3	103.425	ccc3	102.091	ccc3	1.334
cc4	1.337265	cc4	1.338301	cc4	-0.001036
ccc4	112.237	ccc4	113.698	ccc4	-1.461
dih4	-6.464	dih4	-6.645	dih4	0.181
cc5	1.481690	cc5	1.473990	cc5	0.007700
ccc5	109.877	ccc5	109.740	ccc5	0.137
dih5	1.624	dih5	1.751	dih5	-0.127
cc6	1.539062	cc6	1.533621	cc6	0.005441
ccc6	110.853	ccc6	109.773	ccc6	1.08
dih6	115.806	dih6	112.804	dih6	3.002
oc7	1.401832	oc7	1.395207	oc7	0.006625
occ7	110.488	occ7	106.620	occ7	3.868
dih7	-127.841	dih7	-126.425	dih7	-1.416
oc8	1.212674	oc8	1.210367	oc8	0.002307
occ8	123.906	occ8	125.262	occ8	-1.356
dih8	-175.233	dih8	-175.218	dih8	-0.015

cc9	1.386222		cc9	1.351774		cc9	0.034448	
ccc9	127.237		ccc9	128.133		ccc9	-0.896	
dih9	67.239		dih9	72.858		dih9	-5.619	
cc10	1.555429		cc10	1.543617		cc10	0.011812	
ccc10	125.638		ccc10	128.133		ccc10	-2.495	
dih10	-176.166		dih10	180.000		dih10	3.834	
cc11	1.512739		cc11	1.514452		cc11	-0.001713	
ccc11	102.446		ccc11	102.091		ccc11	0.355	
dih11	170.368		dih11	169.581		dih11	0.787	
cc12	1.352453		cc12	1.338301		cc12	0.014152	
ccc12	110.787		ccc12	113.698		ccc12	-2.911	
dih12	7.781		dih12	6.645		dih12	1.136	
cc13	1.436864		cc13	1.473990		cc13	-0.037126	
ccc13	109.491		ccc13	109.740		ccc13	-0.249	
dih13	-3.622		dih13	-1.751		dih13	-1.871	
cc14	1.536000		cc14	1.533621		cc14	0.002379	
ccc14	111.525		ccc14	112.428		ccc14	-0.903	
dih14	107.614		dih14	108.921		dih14	-1.307	
oc15	1.395025		oc15	1.395207		oc15	-0.000182	
occ15	113.770		occ15	113.920		occ15	-0.15	
dih15	-125.342		dih15	-123.160		dih15	-2.182	
oc16	1.341229		oc16	1.210367		oc16	0.130862	
occ16	129.629		occ16	127.622		occ16	2.007	
dih16	-174.954		dih16	-171.226		dih16	-3.728	

Table S2. z-matrices for the heavy atoms of the S_0-FC and the $^3P(p_O\pi^*)$ fully optimized structures.

Model-1

FC			
C	-0.57749	0.35104	0.00996
C	-0.76368	1.88188	-0.05797
C	-1.95893	-0.24793	0.06105
C	-2.25884	2.01088	-0.26149
C	-2.91593	0.84832	-0.17354
C	-0.35542	2.57937	1.24542
H	-2.69387	2.97648	-0.43631
H	-3.97260	0.68266	-0.24928
H	-0.86947	2.14780	2.09766
H	0.71096	2.50283	1.41206
H	-0.61314	3.63134	1.18243
H	0.78552	2.43976	-1.04842
O	-2.25626	-1.40315	0.26611
O	-0.15747	2.47691	-1.16479
C	0.57749	-0.35104	-0.00996
C	0.76368	-1.88188	0.05797
C	1.95893	0.24793	-0.06105
C	2.25884	-2.01088	0.26149
C	2.91593	-0.84832	0.17354
C	0.35542	-2.57937	-1.24542
H	2.69387	-2.97648	0.43631
H	3.97260	-0.68266	0.24928
H	0.86947	-2.14780	-2.09766
H	-0.71096	-2.50283	-1.41206
H	0.61314	-3.63134	-1.18243
H	-0.78552	-2.43976	1.04842
O	2.25626	1.40315	-0.26611
O	0.15747	-2.47691	1.16479

Sym-$^1n\pi^*(S_1)$			
C	-0.60247	0.34874	-0.03009
C	-0.77576	1.88466	-0.12614
C	-1.92964	-0.20275	-0.01066
C	-2.26824	2.03665	-0.32332
C	-2.91015	0.86077	-0.21530
C	-0.36273	2.59267	1.17132
H	-2.71035	2.99918	-0.48993
H	-3.96535	0.67955	-0.26926
H	-0.90721	2.19033	2.01818
H	0.69623	2.48635	1.36673
H	-0.58590	3.65103	1.08638
H	0.78932	2.49616	-1.09165
O	-2.27131	-1.41782	0.15643
O	-0.14642	2.45105	-1.23963
C	0.60247	-0.34874	0.03009
C	0.77576	-1.88466	0.12614
C	1.92964	0.20275	0.01066
C	2.26824	-2.03665	0.32332
C	2.91015	-0.86077	0.21530
C	0.36273	-2.59267	-1.17132
H	2.71035	-2.99918	0.48993
H	3.96535	-0.67955	0.26926
H	0.90721	-2.19033	-2.01818
H	-0.69623	-2.48635	-1.36673
H	0.58590	-3.65103	-1.08638
H	-0.78932	-2.49616	1.09165
O	2.27131	1.41782	-0.15643
O	0.14642	-2.45105	1.23963

Sym-$^3n\pi^*(T_1)$			
C	-0.598308	0.346792	-0.029199
C	-0.774467	1.882798	-0.123897
C	-1.931566	-0.20788	-0.009197
C	-2.267087	2.032541	-0.32167
C	-2.909762	0.857621	-0.215392
C	-0.360826	2.591087	1.173035
C	0.598308	-0.346792	0.029199
C	0.774467	-1.882798	0.123897
C	1.931566	0.20788	0.009197
C	2.267087	-2.032541	0.32167
C	2.909762	-0.857621	0.215392
C	0.360826	-2.591087	-1.173035
H	-2.709594	2.995159	-0.48727
H	-3.964941	0.677262	-0.271558
H	-0.904244	2.188486	2.020445
H	0.698398	2.485371	1.36748
H	-0.584566	3.649345	1.088181
H	0.789687	2.49279	-1.090737
H	2.709594	-2.995159	0.48727
H	3.964941	-0.677262	0.271558
H	0.904244	-2.188486	-2.020445
H	-0.698398	-2.485371	-1.36748
H	0.584566	-3.649345	-1.088181
H	-0.789687	-2.49279	1.090737
O	-2.271981	-1.418734	0.158624
O	-0.146445	2.449916	-1.237591
O	2.271981	1.418734	-0.158624
O	0.146445	-2.449916	1.237591

Min-$^3\pi\pi^*(T_1)$			
C	-0.71770	-0.25240	0.00250
C	-1.96980	0.62570	0.03660
C	-1.13140	-1.63700	-0.03010
C	-3.06520	-0.40810	0.21350
C	-2.60450	-1.66210	0.13740
C	-2.19233	1.39017	-1.27461
H	-4.08453	-0.10335	0.35098
H	-3.16270	-2.57589	0.19163
H	-3.14663	1.90381	-1.22603
H	-1.41928	2.12955	-1.43591
H	-2.20731	0.71365	-2.12246
H	-1.37840	2.18630	0.99270
O	-0.42084	-2.62555	-0.18530
O	-2.00347	1.48575	1.13825
C	0.71770	0.25240	-0.00250
C	1.96980	-0.62570	-0.03660
C	1.13140	1.63700	0.03010
C	3.06520	0.40810	-0.21350
C	2.60450	1.66210	-0.13740
C	2.19233	-1.39017	1.27461
H	4.08453	0.10335	-0.35098
H	3.16270	2.57589	-0.19163
H	3.14663	-1.90381	1.22603
H	1.41928	-2.12955	1.43591
H	2.20731	-0.71365	2.12246
H	1.37840	-2.18630	-0.99270
O	0.42084	2.62555	0.18530
O	2.00347	-1.48575	-1.13825

Min-$^1n\pi^*(S_1)$			
C	-2.12089	0.93031	-0.62302
C	-2.30054	2.45180	-0.76084
C	-3.47378	0.33459	-0.57246
C	-3.79181	2.57705	-0.99716
C	-4.44163	1.41624	-0.86084
C	-1.21642	-1.93686	-1.92558
C	-1.92032	3.22206	0.50994
C	-0.74526	-1.32372	-0.59927
C	0.75440	-1.49666	-0.47903
C	1.38715	-0.30167	-0.53779
C	0.38708	0.73047	-0.62022
C	-0.91441	0.22459	-0.60093
H	1.20685	-2.46458	-0.39948
H	2.44332	-0.11845	-0.51198
H	-4.22562	3.53469	-1.21370
H	-5.49656	1.23955	-0.93620
H	-0.99838	-2.99943	-1.92112
H	-2.28216	-1.81380	-2.06379
H	-0.70461	-1.48062	-2.76598
H	-2.46477	2.84093	1.36615
H	-0.86180	3.14703	0.72724
H	-2.16611	4.27153	0.38316
H	-2.28377	-1.87513	0.40667
H	-0.75673	3.19075	-1.70715
O	0.75351	2.04125	-0.66860
O	-3.77921	-0.81431	-0.32262
O	-1.34001	-1.95053	0.49473
O	-1.66384	2.98967	-1.89129

Min-$^3n\pi^*(T_1)$			
C	-2.11858	0.93639	-0.62357
C	-2.29948	2.45775	-0.75639
C	-3.47545	0.33606	-0.57628
C	-3.79053	2.57955	-0.99545
C	-4.44093	1.41764	-0.86512
C	-1.22431	-1.93349	-1.92705
C	-1.92326	3.22641	0.51681
C	-0.74523	-1.31859	-0.60389
C	0.75556	-1.48651	-0.49330
C	1.38820	-0.29291	-0.53902
C	0.39203	0.74260	-0.62545
C	-0.91443	0.22771	-0.61039
H	1.20831	-2.45420	-0.40943
H	2.44401	-0.10953	-0.50474
H	-4.22522	3.53662	-1.21276
H	-5.49563	1.24174	-0.94499
H	-1.00035	-2.99479	-1.92337
H	-2.29167	-1.81686	-2.05632
H	-0.72113	-1.47569	-2.77187
H	-2.46085	2.83793	1.37454
H	-0.86318	3.16260	0.73029
H	-2.17787	4.27375	0.39296
H	-2.27530	-1.87134	0.41233
H	-0.72943	3.05539	-1.74112
O	0.73940	2.04911	-0.62252
O	-3.77504	-0.81342	-0.32564
O	-1.33060	-1.94716	0.49388
O	-1.66535	2.99998	-1.88331

$^3P(p_O\pi^*)$			
C	-2.18615	0.94423	-0.67205
C	-2.32842	2.49029	-0.76595
C	-3.51041	0.43948	-0.62751
C	-3.81363	2.66790	-0.99176
C	-4.46375	1.48951	-0.85802
C	-1.26061	-1.96640	-1.94590
C	-1.93566	3.17349	0.55249
C	-0.80832	-1.27975	-0.64488
C	0.68112	-1.45414	-0.43286
C	1.33695	-0.28923	-0.46687
C	0.37838	0.82295	-0.66587
C	-0.99067	0.24271	-0.65460
H	1.10754	-2.43167	-0.30859
H	2.39332	-0.12587	-0.38273
H	-4.24226	3.63531	-1.16236
H	-5.52087	1.31630	-0.90889
H	-1.04861	-3.02925	-1.89872
H	-2.31850	-1.82579	-2.11519
H	-0.71268	-1.54102	-2.77709
H	-2.50761	2.77022	1.38117
H	-0.88233	3.04982	0.76669
H	-2.14139	4.23588	0.47549
H	-3.29790	-1.33247	0.02263
H	-0.72178	3.01881	-1.67558
O	0.70710	1.98026	-0.81800
O	-3.94086	-0.81897	-0.45450
O	-1.52711	-1.91439	0.37772
O	-1.65501	3.05205	-1.85086

$^1I^c(n'\pi^*)$			
C	-2.17761	0.95351	-0.70514
C	-2.32839	2.49798	-0.76929
C	-3.49868	0.43874	-0.65247
C	-3.81734	2.66893	-0.97991
C	-4.46089	1.48386	-0.85243
C	-1.24431	-1.97267	-1.97144
C	-1.92951	3.15953	0.55840
C	-0.82734	-1.27109	-0.67563
C	0.65701	-1.45342	-0.41280
C	1.32240	-0.29286	-0.44962
C	0.38251	0.82665	-0.68801
C	-0.98724	0.24923	-0.71092
H	1.07604	-2.43144	-0.27294
H	2.37999	-0.14565	-0.35130
H	-4.25400	3.63520	-1.13586
H	-5.51770	1.30673	-0.89512
H	-1.02002	-3.03164	-1.89815
H	-2.30424	-1.85669	-2.14897
H	-0.70333	-1.55828	-2.81419
H	-2.49058	2.73709	1.38497
H	-0.87333	3.03938	0.76071
H	-2.14315	4.22162	0.50278
H	-3.39386	-1.30431	0.14168
H	-0.72846	3.03861	-1.68410
O	0.71942	1.98048	-0.84492
O	-3.90379	-0.83873	-0.51217
O	-1.48007	-1.84271	0.42185
O	-1.66367	3.08223	-1.84759

$^3I^c(n'\pi^*)$			
C	-2.17167	0.95030	-0.68553
C	-2.32480	2.49468	-0.76351
C	-3.49822	0.43426	-0.63624
C	-3.81048	2.66234	-0.99412
C	-4.45382	1.47604	-0.86792
C	-1.26294	-1.96640	-1.95563
C	-1.93859	3.16686	0.56216
C	-0.82195	-1.26826	-0.66714
C	0.66860	-1.45337	-0.43486
C	1.33477	-0.29392	-0.46889
C	0.39159	0.82921	-0.67894
C	-0.97966	0.25434	-0.68831
H	1.09084	-2.43279	-0.31424
H	2.39351	-0.14745	-0.38361
H	-4.24759	3.62730	-1.15646
H	-5.50987	1.29787	-0.92354
H	-1.04305	-3.02714	-1.88891
H	-2.32443	-1.84595	-2.11943
H	-0.73215	-1.55563	-2.80696
H	-2.50773	2.75123	1.38662
H	-0.88441	3.04726	0.77548
H	-2.15103	4.22860	0.49592
H	-3.39846	-1.33988	0.10084
H	-0.71613	3.03516	-1.66446
O	0.72811	1.98497	-0.82045
O	-3.92072	-0.84048	-0.51327
O	-1.47051	-1.81799	0.44923
O	-1.64937	3.06912	-1.84040

$^1P(n'\pi^*)$			
C	-2.15634	0.95311	-0.73652
C	-2.32596	2.49676	-0.73990
C	-3.46253	0.41769	-0.67889
C	-3.82825	2.66010	-0.83635
C	-4.44868	1.45584	-0.75757
C	-1.14858	-2.04026	-1.90068
C	-1.83692	3.11977	0.57536
C	-0.78057	-1.26336	-0.63071
C	0.71069	-1.39397	-0.36064
C	1.35803	-0.22965	-0.49036
C	0.39626	0.85212	-0.80019
C	-0.96193	0.25421	-0.75500
H	1.14791	-2.35174	-0.15225
H	2.41392	-0.05852	-0.41385
H	-4.28848	3.62429	-0.91838
H	-5.50926	1.28166	-0.76662
H	-0.88746	-3.08521	-1.77073
H	-2.20684	-1.97222	-2.10106
H	-0.60325	-1.64809	-2.75203
H	-2.32659	2.66002	1.42716
H	-0.76710	3.01025	0.69276
H	-2.06745	4.17983	0.57277
H	-4.63609	-1.04959	-0.37395
H	-0.80621	3.04237	-1.77705
O	0.70835	1.99605	-1.05792
O	-3.73745	-0.90035	-0.63564
O	-1.40814	-1.81652	0.48056
O	-1.75121	3.12568	-1.84492

$^3P(n'\pi^*)$			
C	-2.15372	0.94881	-0.72963
C	-2.32359	2.49354	-0.73396
C	-3.46429	0.41566	-0.68115
C	-3.82404	2.65908	-0.84014
C	-4.44643	1.45712	-0.76688
C	-1.16255	-2.05392	-1.87069
C	-1.84117	3.11707	0.58364
C	-0.76598	-1.26052	-0.61872
C	0.73185	-1.38884	-0.38709
C	1.37190	-0.22103	-0.51493
C	0.39945	0.85972	-0.79605
C	-0.95754	0.25645	-0.74147
H	1.17369	-2.34710	-0.19076
H	2.42763	-0.04336	-0.45325
H	-4.28193	3.62457	-0.92058
H	-5.50740	1.28490	-0.78348
H	-0.88548	-3.09466	-1.74143
H	-2.22560	-1.99713	-2.04492
H	-0.64189	-1.65899	-2.73580
H	-2.33744	2.65932	1.43268
H	-0.77239	3.00516	0.70809
H	-2.06943	4.17767	0.57841
H	-4.67607	-1.03293	-0.46675
H	-0.79912	3.04756	-1.76044
O	0.70723	2.00726	-1.04296
O	-3.75476	-0.89883	-0.64339
O	-1.38704	-1.81901	0.49571
O	-1.74404	3.12272	-1.83667

$^1P(Epox)$			
C	-2.184373	0.991333	-0.9409
C	-2.327589	2.526685	-0.78238
C	-3.448177	0.499179	-0.895901
C	-3.801383	2.738611	-1.061318
C	-4.44754	1.566716	-1.063574
C	-1.434515	-2.245199	-1.691373
C	-2.053831	2.96937	0.667035
C	-0.683813	-1.243704	-0.847901
C	0.815925	-1.428784	-0.806696
C	1.436956	-0.261351	-0.59374
C	0.438035	0.830178	-0.555652
C	-0.948849	0.200481	-0.659192
H	1.278502	-2.394098	-0.888182
H	2.48679	-0.079519	-0.475656
H	-4.213746	3.723407	-1.16083
H	-5.498227	1.379532	-1.165113
H	-1.405317	-3.216571	-1.205333
H	-2.460245	-1.976152	-1.873841
H	-0.930382	-2.33875	-2.647288
H	-2.68487	2.428487	1.362461
H	-1.021099	2.815566	0.948276
H	-2.2688	4.029042	0.75612
H	-3.265608	-1.167395	-0.041691
H	-0.675856	3.273758	-1.42542
O	0.703512	2.006302	-0.548806
O	-3.881954	-0.7515	-0.634531
O	-1.146014	-0.853751	0.413348
O	-1.587666	3.298403	-1.684509

$^1I^*(n'\pi^*)$			
C	-2.17761	0.95351	-0.70514
C	-2.32839	2.49798	-0.76929
C	-3.49868	0.43874	-0.65247
C	-3.81734	2.66893	-0.97991
C	-4.46089	1.48386	-0.85243
C	-1.24431	-1.97267	-1.97144
C	-1.92951	3.15953	0.55840
C	-0.82734	-1.27109	-0.67563
C	0.65701	-1.45342	-0.41280
C	1.32240	-0.29286	-0.44962
C	0.38251	0.82665	-0.68801
C	-0.98724	0.24923	-0.71092
H	1.07604	-2.43144	-0.27294
H	2.37999	-0.14565	-0.35130
H	-4.25400	3.63520	-1.13586
H	-5.51770	1.30673	-0.89512
H	-1.02002	-3.03164	-1.89815
H	-2.30424	-1.85669	-2.14897
H	-0.70333	-1.55828	-2.81419
H	-2.49058	2.73709	1.38497
H	-0.87333	3.03938	0.76071
H	-2.14315	4.22162	0.50278
H	-3.39386	-1.30431	0.14168
H	-0.72846	3.03861	-1.68410
O	0.71942	1.98048	-0.84492
O	-3.90379	-0.83873	-0.51217
O	-1.48007	-1.84271	0.42185
O	-1.66367	3.08223	-1.84759

$^3I^*(n'\pi^*)$			
C	-2.17167	0.95030	-0.68553
C	-2.32480	2.49468	-0.76351
C	-3.49822	0.43426	-0.63624
C	-3.81048	2.66234	-0.99412
C	-4.45382	1.47604	-0.86792
C	-1.26294	-1.96640	-1.95563
C	-1.93859	3.16686	0.56216
C	-0.82195	-1.26826	-0.66714
C	0.66860	-1.45337	-0.43486
C	1.33477	-0.29392	-0.46889
C	0.39159	0.82921	-0.67894
C	-0.97966	0.25434	-0.68831
H	1.09084	-2.43280	-0.31424
H	2.39351	-0.14745	-0.38361
H	-4.24759	3.62730	-1.15646
H	-5.50987	1.29787	-0.92354
H	-1.04305	-3.02714	-1.88892
H	-2.32443	-1.84595	-2.11944
H	-0.73215	-1.55563	-2.80697
H	-2.50773	2.75123	1.38662
H	-0.88441	3.04726	0.77548
H	-2.15103	4.22860	0.49592
H	-3.39846	-1.33988	0.10084
H	-0.71613	3.03516	-1.66446
O	0.72811	1.98497	-0.82045
O	-3.92072	-0.84048	-0.51327
O	-1.47051	-1.81799	0.44923
O	-1.64937	3.06912	-1.84040

$^1P(EpoxRot)$			
C	-2.35949	0.63598	-0.330648
C	-2.48364	1.97568	-1.06386
C	-3.548985	0.336369	0.220752
C	-3.956987	2.294701	-0.893236
C	-4.552123	1.366927	-0.130708
C	-0.859473	-1.114821	-2.654114
C	-1.616781	3.07655	-0.446407
C	-0.432135	-0.942964	-1.223049
C	1.033882	-0.973467	-0.857445
C	1.24829	-0.332225	0.304317
C	-0.026663	0.252779	0.799692
C	-1.109927	-0.142915	-0.19292
H	1.769633	-1.501638	-1.434411
H	2.172272	-0.246031	0.842086
H	-4.402726	3.169041	-1.325651
H	-5.580098	1.34563	0.181456
H	-0.628999	-2.124064	-2.981101
H	-1.921561	-0.947489	-2.760379
H	-0.329643	-0.424684	-3.303056
H	-1.809406	3.181646	0.613677
H	-0.560212	2.851692	-0.569466
H	-1.81538	4.020726	-0.942428
H	-4.747228	-0.802601	1.156067
H	-1.28343	1.863664	-2.588596
O	-0.17000	0.948233	1.772759
O	-3.81604	-0.722541	1.005545
O	-1.20329	-1.604838	-0.255518
O	-2.22000	1.880932	-2.445944

Model-2

FC			
C	-5.29861	0.96873	0.10950
C	5.29861	-0.96873	-0.10950
C	-4.07783	1.59946	-0.03530
C	4.07783	-1.59946	0.03530
C	-2.93112	0.80161	-0.07986
C	2.93112	-0.80161	0.07986
C	-2.98929	-0.56523	0.00186
C	2.98929	0.56523	-0.00186
C	-4.21702	-1.20765	0.15959
C	4.21702	1.20765	-0.15959
C	-5.36313	-0.43170	0.21156
C	5.36313	0.43170	-0.21156
C	-1.62362	-1.21934	-0.10996
C	1.62362	1.21934	0.10996
C	-1.52978	1.23693	-0.18379
C	1.52978	-1.23693	0.18379
C	-0.67024	0.00151	-0.06780
C	0.67024	-0.00151	0.06780
C	-1.50847	-1.97487	-1.44149
C	1.50847	1.97487	1.44149
H	-6.20395	1.54642	0.15278
H	6.20395	-1.54642	-0.15278
H	-3.99900	2.66847	-0.10398
H	3.99900	-2.66847	0.10398
H	-4.26890	-2.27621	0.25223
H	4.26890	2.27621	-0.25223
H	-6.32004	-0.90601	0.33618
H	6.32004	0.90601	-0.33618
H	-0.53157	-2.42815	-1.54741
H	0.53157	2.42815	1.54741
H	-2.25362	-2.76191	-1.47302
H	2.25362	2.76191	1.47302
H	-1.67366	-1.31071	-2.28280
H	1.67366	1.31071	2.28280
H	-0.65729	-2.52647	0.91208
H	0.65729	2.52647	-0.91208
O	-1.16583	2.38264	-0.33130
O	1.16583	-2.38264	0.33130
O	-1.49552	-2.08193	0.97729
O	1.49552	2.08193	-0.97729

Min-$^1n\pi^*(S_1)$			
C	-5.27946	1.00927	0.21146
C	-4.06381	1.62237	-0.01852
C	-2.93291	0.82090	-0.09015
C	-3.00171	-0.54757	0.04773
C	-4.21810	-1.16625	0.28948
C	-5.35086	-0.37548	0.36998
C	-1.64282	-1.20501	-0.12446
C	-1.52382	1.23238	-0.27161
C	-0.69706	0.01034	-0.16082
C	-1.61240	-2.00114	-1.43729
C	5.34023	-0.95933	-0.00221
C	4.10856	-1.59635	0.02220
C	2.96289	-0.79481	0.00917
C	3.03928	0.57589	-0.01247
C	4.27589	1.21094	-0.04888
C	5.41741	0.43824	-0.04396
C	1.65984	1.20778	0.02356
C	1.54705	-1.15367	-0.02431
C	0.71572	-0.02416	-0.08156
C	1.46354	1.93627	1.36151
H	-6.17639	1.59788	0.27783
H	-3.98424	2.68788	-0.13064
H	-4.28033	-2.23018	0.42385
H	-6.30469	-0.83388	0.56097
H	-0.63978	-2.44424	-1.61505
H	-2.34794	-2.79720	-1.39614
H	-1.84734	-1.36032	-2.27883
H	-0.76194	-2.68355	0.80221
H	6.24367	-1.54162	0.00249
H	4.04236	-2.66876	0.04179
H	4.33707	2.28257	-0.09331
H	6.38220	0.91171	-0.07626
H	0.47356	2.36678	1.43206
H	2.18633	2.74053	1.43978
H	1.60693	1.25910	2.19613
H	0.70647	2.50454	-1.02027
O	-1.15400	2.37186	-0.47667
O	-1.43583	-2.04255	0.98207
O	1.18560	-2.44778	-0.03750
O	1.56083	2.08658	-1.05335

Min-$^3n\pi^*(T_1)$			
C	-5.27092	1.003366	0.216967
C	-4.056531	1.618994	-0.009471
C	-2.924199	0.818971	-0.086205
C	-2.990841	-0.550019	0.043077
C	-4.20699	-1.171708	0.281234
C	-5.340255	-0.382969	0.366664
C	-1.632371	-1.207463	-0.129063
C	-1.517734	1.234616	-0.268412
C	-0.683712	0.008898	-0.164162
C	-1.602189	-2.00569	-1.440374
C	5.324698	-0.975556	-0.003263
C	4.08184	-1.602668	0.020805
C	2.945885	-0.796128	0.0103
C	3.031202	0.5852	-0.009778
C	4.264065	1.210835	-0.047308
C	5.416976	0.420046	-0.043215
C	1.652308	1.219013	0.023489
C	1.542148	-1.143992	-0.023573
C	0.70939	-0.017923	-0.082217
C	1.452257	1.947448	1.360484
H	-6.168698	1.590199	0.287268
H	-3.97798	2.685215	-0.115337
H	-4.267702	-2.236453	0.409087
H	-6.29352	-0.84377	0.55472
H	-0.63107	-2.452787	-1.615994
H	-2.339675	-2.799657	-1.398808
H	-1.833239	-1.365293	-2.283592
H	-0.701593	-2.625939	0.841151
H	6.220588	-1.569459	0.000323
H	4.005959	-2.674494	0.037187
H	4.333813	2.281849	-0.091771
H	6.384317	0.887465	-0.075222
H	0.462809	2.378751	1.429695
H	2.176531	2.750314	1.43951
H	1.594093	1.270384	2.195503
H	0.702067	2.513438	-1.024477
O	-1.152417	2.374124	-0.473691
O	-1.435732	-2.04299	0.980243
O	1.170308	-2.428926	-0.056769
O	1.556116	2.094756	-1.055006

Min-$^3\pi\pi^*(T_1)$			
C	-5.346174	0.97747	0.144532
C	5.346174	-0.97747	-0.144532
C	-4.139763	1.604876	0.00699
C	4.139763	-1.604876	-0.00699
C	-2.985442	0.80538	-0.032315
C	2.985442	-0.80538	0.032315
C	-3.052261	-0.563683	0.054102
C	3.052261	0.563683	-0.054102
C	-4.291851	-1.20413	0.203754
C	4.291851	1.20413	-0.203754
C	-5.419368	-0.429094	0.248163
C	5.419368	0.429094	-0.248163
C	-1.680718	-1.205606	-0.063681
C	1.680718	1.205606	0.063681
C	-1.568562	1.223422	-0.124474
C	1.568562	-1.223422	0.124474
C	-0.760468	0.023088	-0.038435
C	0.760468	-0.023088	0.038435
C	-1.568729	-1.97208	-1.39062
C	1.568729	1.97208	1.39062
H	-6.253067	1.553608	0.181788
H	6.253067	-1.553608	-0.181788
H	-4.064925	2.67422	-0.063982
H	4.064925	-2.67422	0.063982
H	-4.350148	-2.272758	0.295675
H	4.350148	2.272758	-0.295675
H	-6.381953	-0.893113	0.368208
H	6.381953	0.893113	-0.368208
H	-0.585333	-2.406258	-1.512558
H	0.585333	2.406258	1.512558
H	-2.297215	-2.775147	-1.398551
H	2.297215	2.775147	1.398551
H	-1.767498	-1.320413	-2.234487
H	1.767498	1.320413	2.234487
H	-0.67761	-2.519314	0.918754
H	0.67761	2.519314	-0.918754
O	-1.18063	2.379618	-0.249127
O	1.18063	-2.379618	0.249127
O	-1.499045	-2.053016	1.030161
O	1.499045	2.053016	-1.030161

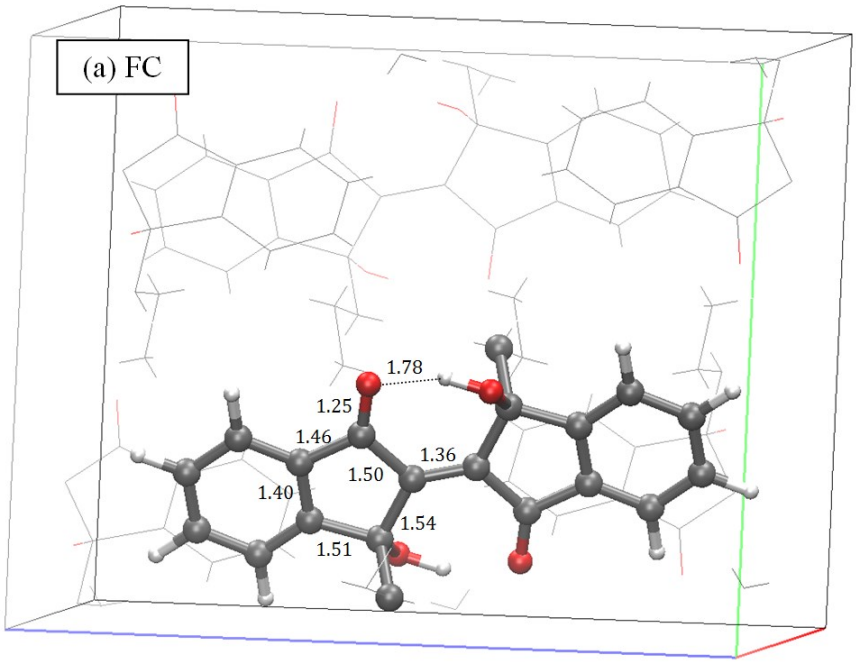
Sym-$^1n\pi^*(S_1)$			
C	-5.308837	0.954704	0.167276
C	5.308837	-0.954704	-0.167276
C	-4.1031	1.583414	0.025246
C	4.1031	-1.583414	-0.025246
C	-2.947341	0.783656	-0.010786
C	2.947341	-0.783656	0.010786
C	-3.017104	-0.586946	0.0815
C	3.017104	0.586946	-0.0815
C	-4.254365	-1.223707	0.237076
C	4.254365	1.223707	-0.237076
C	-5.384319	-0.449856	0.279308
C	5.384319	0.449856	-0.279308
C	-1.644119	-1.21907	-0.034589
C	1.644119	1.21907	0.034589
C	-1.5345	1.173949	-0.096482
C	1.5345	-1.173949	0.096482
C	-0.704484	0.016437	-0.022481
C	0.704484	-0.016437	0.022481
C	-1.539562	-1.985874	-1.36113
C	1.539562	1.985874	1.36113
H	-6.214593	1.532851	0.202854
H	6.214593	-1.532851	-0.202854
H	-4.035861	2.653105	-0.049091
H	4.035861	-2.653105	0.049091
H	-4.311194	-2.292036	0.334782
H	4.311194	2.292036	-0.334782
H	-6.346498	-0.913108	0.404183
H	6.346498	0.913108	-0.404183
H	-0.553727	-2.409714	-1.501032
H	0.553727	2.409714	1.501032
H	-2.260291	-2.796145	-1.364989
H	2.260291	2.796145	1.364989
H	-1.751379	-1.331891	-2.199212
H	1.751379	1.331891	2.199212
H	-0.685124	-2.582845	0.952629
H	0.685124	2.582845	-0.952629
O	-1.180542	2.393494	-0.206828
O	1.180542	-2.393494	0.206828
O	-1.474809	-2.068963	1.061838
O	1.474809	2.068963	-1.061838

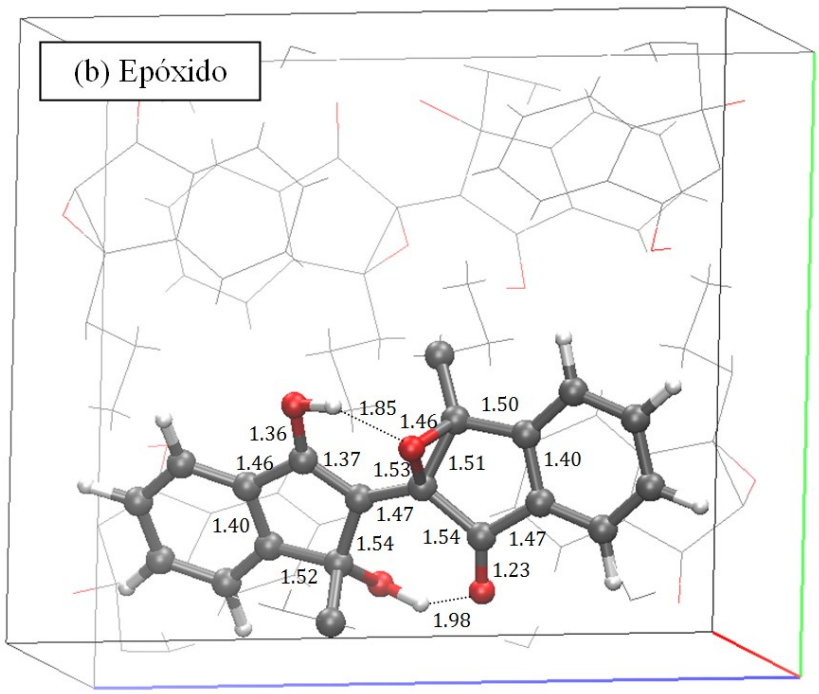
Sym-$^3n\pi^*(T_1)$			
C	-5.306657	0.95624	0.169083
C	5.306657	-0.95624	-0.169083
C	-4.101487	1.585946	0.02866
C	4.101487	-1.585946	-0.02866
C	-2.944737	0.787303	-0.008206
C	2.944737	-0.787303	0.008206
C	-3.013142	-0.583385	0.08195
C	3.013142	0.583385	-0.08195
C	-4.250558	-1.221174	0.235827
C	4.250558	1.221174	-0.235827
C	-5.381118	-0.448746	0.278584
C	5.381118	0.448746	-0.278584
C	-1.641223	-1.217355	-0.034722
C	1.641223	1.217355	0.034722
C	-1.533604	1.181635	-0.096556
C	1.533604	-1.181635	0.096556
C	-0.69764	0.015953	-0.022756
C	0.69764	-0.015953	0.022756
C	-1.537876	-1.986591	-1.35966
C	1.537876	1.986591	1.35966
H	-6.212822	1.533715	0.205205
H	6.212822	-1.533715	-0.205205
H	-4.034956	2.655754	-0.044223
H	4.034956	-2.655754	0.044223
H	-4.306427	-2.289694	0.331948
H	4.306427	2.289694	-0.331948
H	-6.342969	-0.913088	0.401871
H	6.342969	0.913088	-0.401871
H	-0.552557	-2.411633	-1.499483
H	0.552557	2.411633	1.499483
H	-2.259373	-2.796225	-1.361653
H	2.259373	2.796225	1.361653
H	-1.749467	-1.333991	-2.198838
H	1.749467	1.333991	2.198838
H	-0.685725	-2.582764	0.953735
H	0.685725	2.582764	-0.953735
O	-1.181338	2.395906	-0.208033
O	1.181338	-2.395906	0.208033
O	-1.473307	-2.065716	1.063179
O	1.473307	2.065716	-1.063179

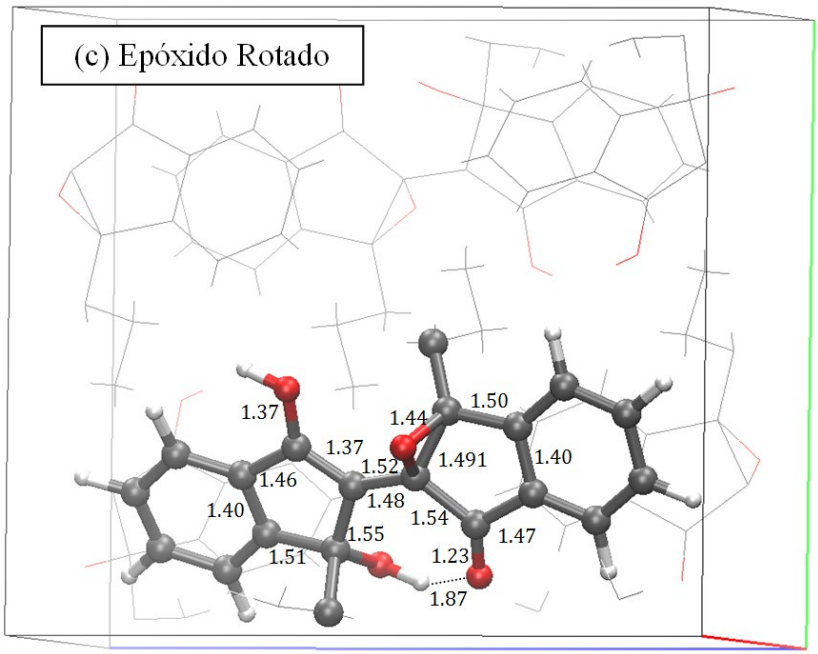
Table S3. Cartesian coordinates of the fully optimized structures of Model-1 and Model-2.

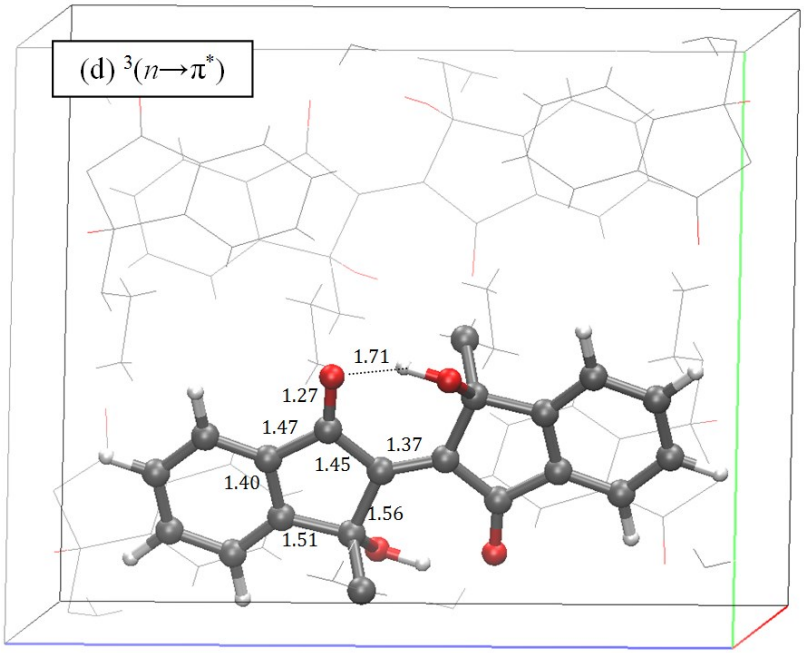
Section II: Crystal phase

Geometries optimized at the PBE+D2 in the crystal phase






(c) Epóxido Rotado
1.37
1.37
1.46
1.40
1.52
1.48
1.55
1.51
1.44
1.50
1.491
1.40
1.54
1.47
1.23
1.87


(d) $^3(n\rightarrow\pi^*)$
1.71
1.27
1.47
1.40
1.45
1.37
1.56
1.51

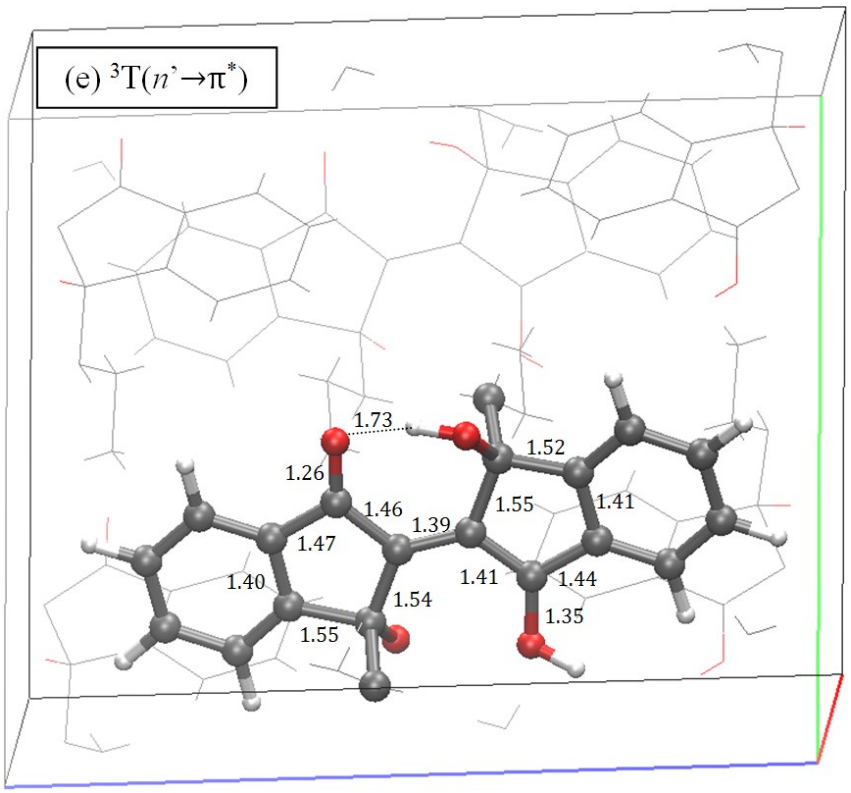
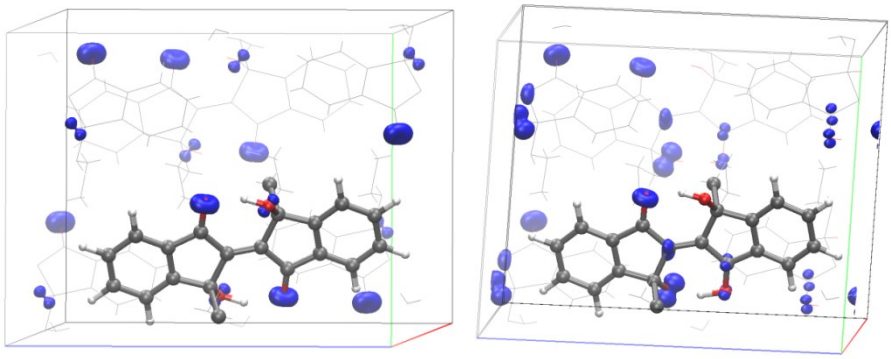
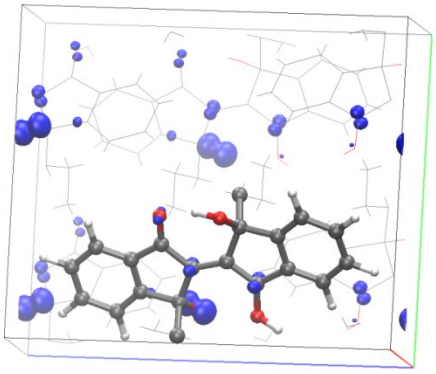


Figure S10. Geometries of the stationary points located at the PBE+D2 level using PBC.



(a) Sym-$^3n\pi^*$ (b) $^3P(p_0\pi^*)$



(c) $^3P(n'\pi^*)$

Figure S11. Spin densities of T_1 at the different stationary points located on T_1