Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Trans-cis Photoisomerization of Biomimetic Cyclocurcumin Analogous Rationalized by Molecular Modelling

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Contents

1. Benchmark on different CASSCF active spaces.

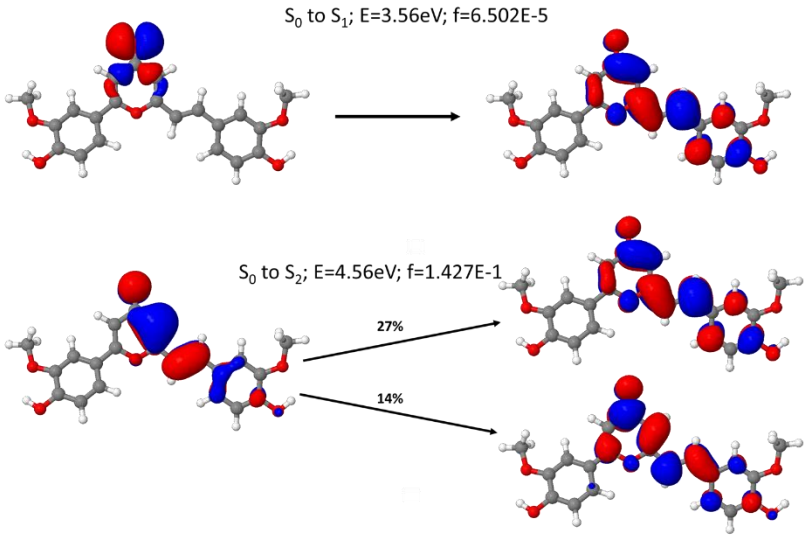

Figure SI1. MS-CASPT2(10,9) transitions in FC.

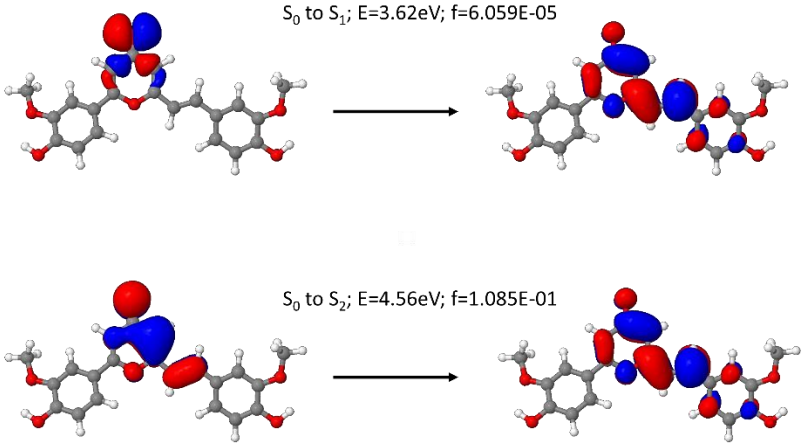

Figure SI2. MS-CASPT2(10,8) transitions in FC.

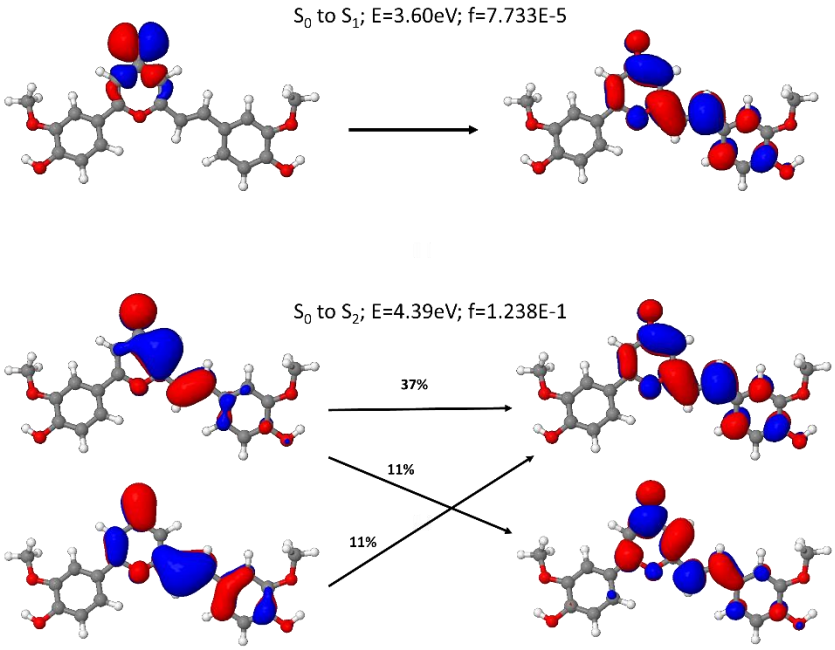

Figure SI3. MS-CASPT2(12,10) transitions in FC.

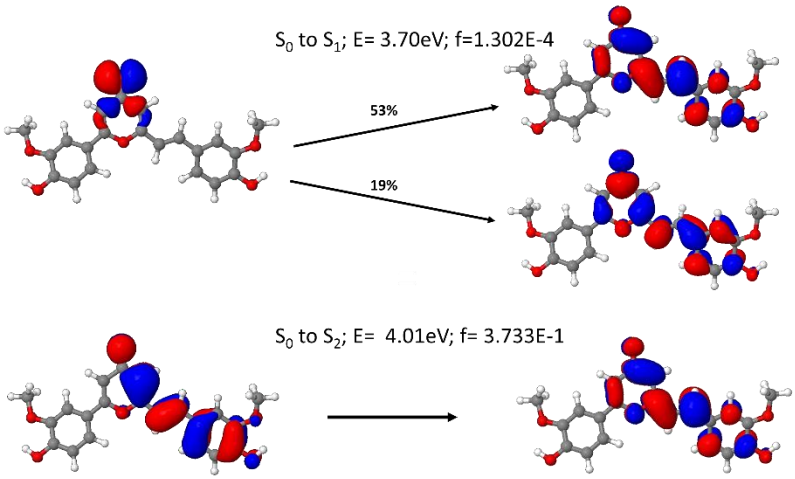

Figure SI4. MS-CASPT2(14,12) transitions in FC.

2. Orbitals in the chosen active space (10,9).

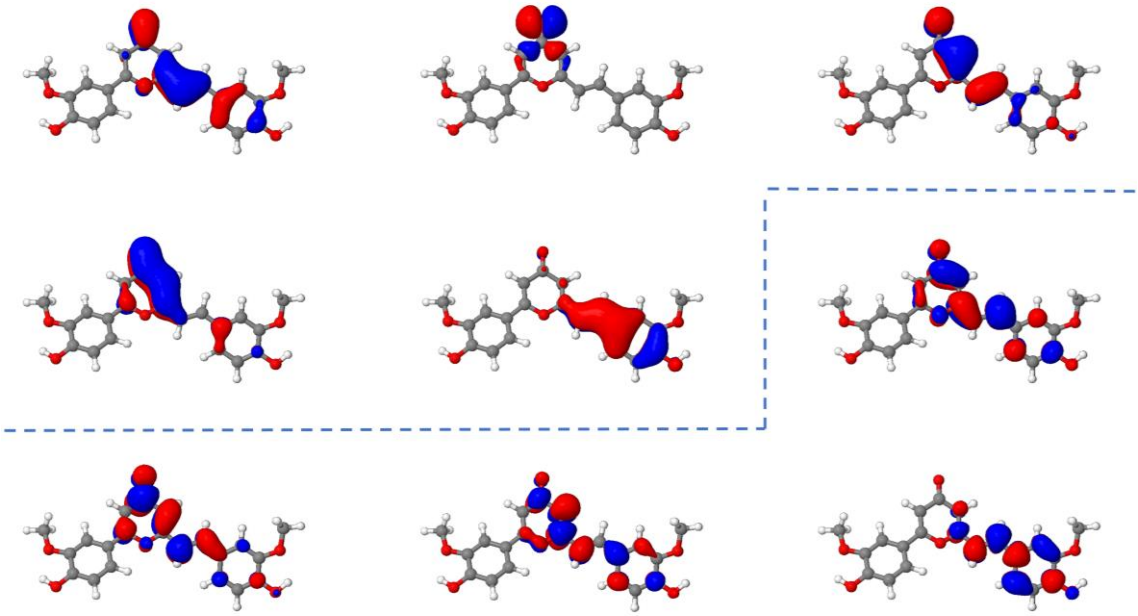

Figure SI5. Orbitals considered in the used (10,9) active space. Up, initially occupied orbitals and down, empty orbitals.

3. Extended multistate CASPT2 (XMS-CASPT2) pathways.

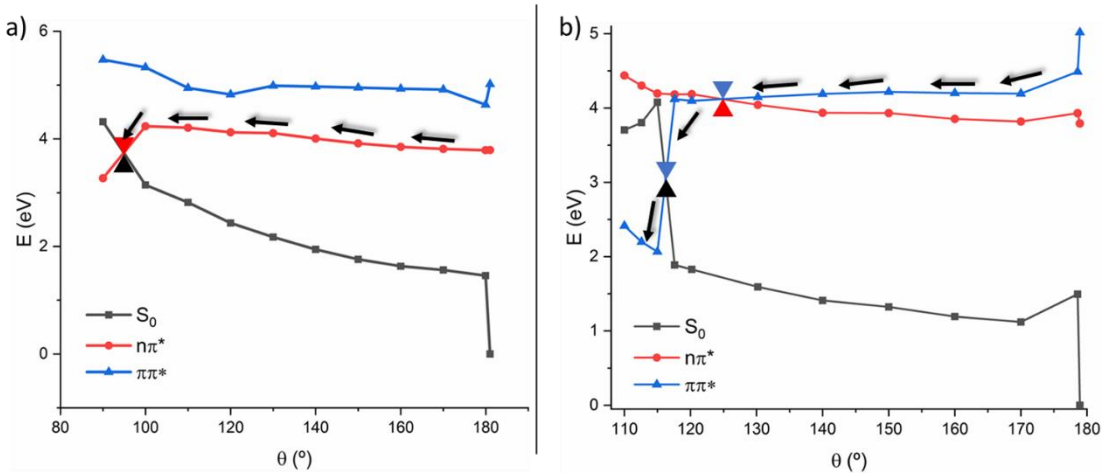

Figure SI6. Extended multistate CASPT2 (XMS-CASPT2) pathways following the ^{1}(n-π*) (a) and ^{1}(π-π*) (b) states.

4. Explicit solvent (water) pathway at MS-CASPT2/6-31G* following the $^1(\pi\ -\pi^*)$ state.

As example of the behavior found in polar solvents, the influence of explicit solvent is was evaluated adding two water molecules to the system and reoptimizing all the scan points relaxing in the $^1(\pi\ -\pi^*)$ state at the CASSCF/6-31G*. After that single point MS-CASPT2/6-31G* were performed. The inclusion of explicit water does not alter the main features of the isomerization profile, hence justifying our simplified approach for protic solvents.

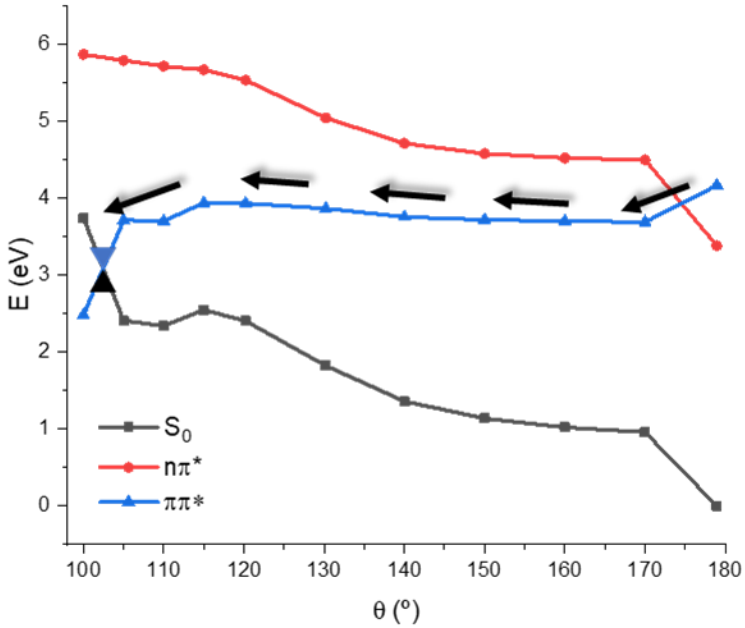

Figure SI7. Multistate CASPT2 (XMS-CASPT2) pathways following the $^1(\pi-\pi^*)$ state and considering explicitly two water molecules.

5. Cyclohexane pathway at CAM-B3LYP/6-31G* following the $^1(\pi\ -\pi^*)$ state.

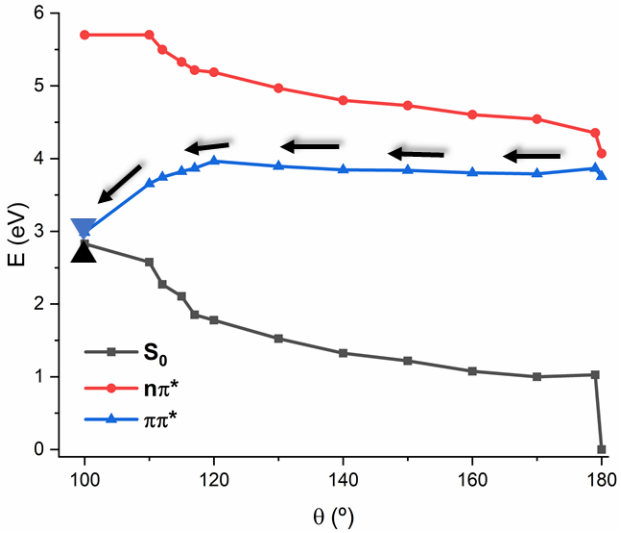

Figure SI8. Cyclohexane pathway at CAM-B3LYP/6-31G* following the $^1(\pi\ -\pi^*)$ state.

6. Solvent effect at CAM-B3LYP/6-31G* in the ^{1}(n-π*) state.

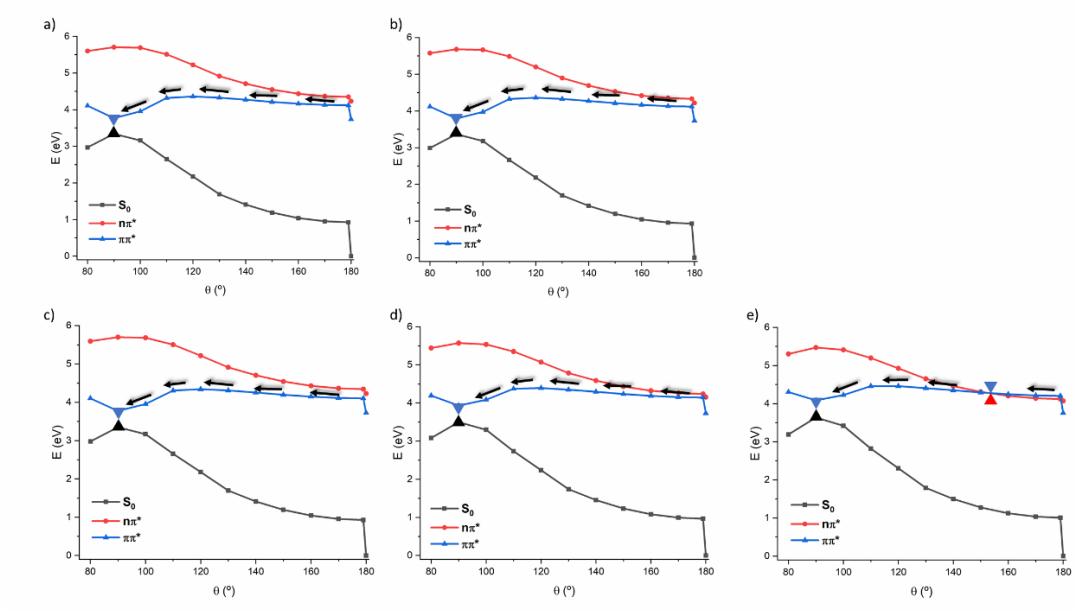

Figure SI9. ^{1}(n-π*) state pathways in different solvents, water (a), ethanol (b), dimethyl sulfoxide (c), chloroform (d) and cyclohexane (e) computed at the CAM-B3LYP/6-31G*.

7. Classical Molecular Dynamic and radial distribution analysis.

The choice of including two water molecules was based on the analysis of a 500 ns classical molecular dynamic simulation in which our chromophore represented by generalized amber force field was placed in a periodic water box. The analysis of the radial distribution function around the carbonyl oxygen revealed that only two solvent molecules were, in average, interacting with the chromophore.

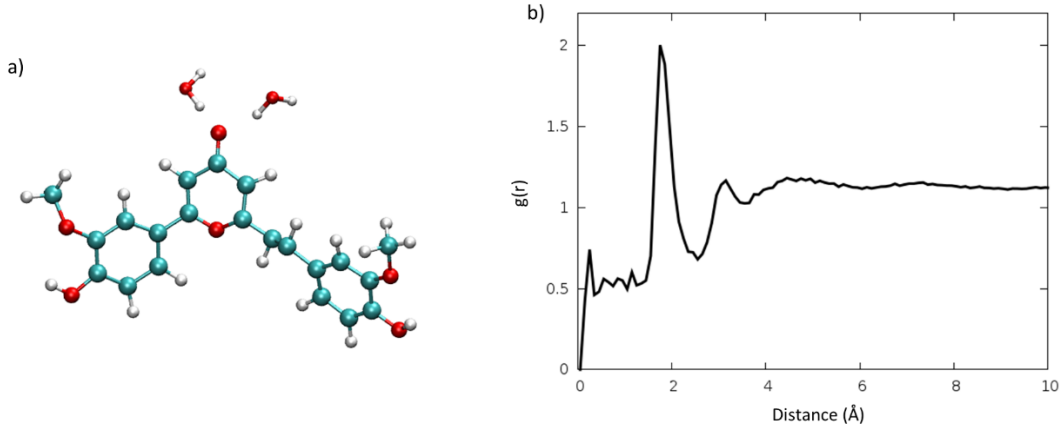

Figure SI10. Snapshot of the MD showing two water molecules interacting with the molecule (*left*), radial distribution function showing a maximum of two water molecules interacting (*right*).

8. Relevant 3D geometries along dihedral scan.

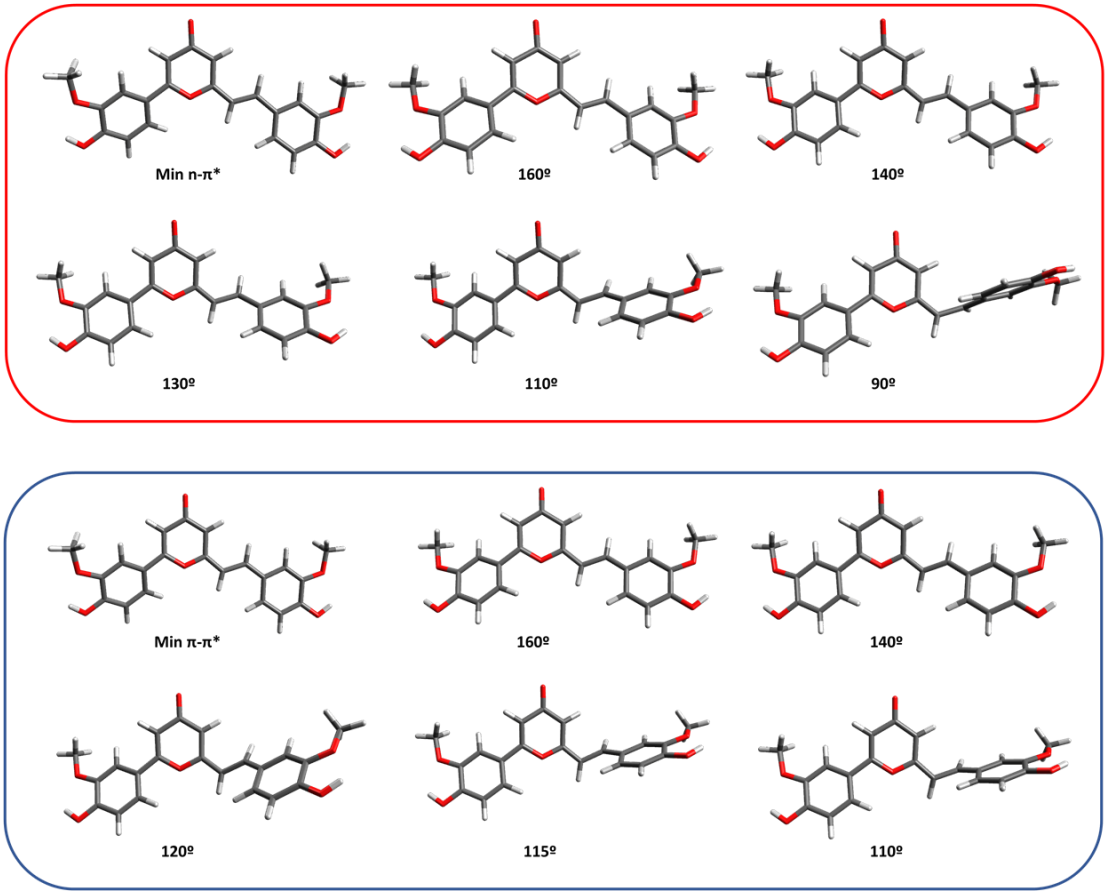

Figure SI11. 3D structures of the $^1(n\text{-}\pi^*)$ (top in red) and $^1(\pi\text{ -}\pi^*)$ (bottom in blue) excited-state pathways.

9. Cartesian coordinates.

FC Ground state minimum

E (MP2/6-31G*) = -1254.81942218 hartree

No imaginary frequencies.

E (MS-CASPT2//SA(4)-CASSCF(10,9)/6-31G*) = -1258.543793 hartree

C	4.05106600	-2.34240700	-0.98249600
C	5.35615200	-2.04350300	-0.60529800
C	5.64819800	-0.78925600	-0.03132800
C	4.64225200	0.14996700	0.16390700
C	3.32709300	-0.15302000	-0.23591000
C	3.03779600	-1.40098400	-0.80202900
C	2.27338900	0.85237600	-0.06938200
O	1.04801700	0.27695000	0.15125800
C	-0.05068500	1.08656700	0.32229600
C	0.05051600	2.44294000	0.33081200
C	1.31788100	3.11753700	0.07771400
C	2.43057300	2.20094300	-0.13977400
O	1.43793000	4.35386300	0.04910900
C	-3.73325400	-0.00813300	0.38060900
O	6.34716600	-2.96326500	-0.78261800
O	6.97232300	-0.64529000	0.31031000

C	-4.84727900	0.30827800	-0.42437200
C	-6.04032000	-0.38714400	-0.26712700
C	-6.14801000	-1.41009400	0.69608500
C	-5.05532900	-1.71412200	1.50267100
C	-3.85870900	-1.01570400	1.34969300
O	-7.20091100	-0.19116500	-0.98074500
O	-7.32162300	-2.08771400	0.85057400
C	7.35701600	0.60739400	0.87909200
C	-7.18153700	0.83967300	-1.96830600
C	-1.25371900	0.28896600	0.50777200
C	-2.48777200	0.72361700	0.16635900
H	3.84926400	-3.31405900	-1.42489100
H	4.84853700	1.10079200	0.64472100
H	2.02157800	-1.63091600	-1.10768900
H	-0.82714700	3.04734200	0.53616900
H	3.40420200	2.62083700	-0.37042300
H	7.16965400	-2.55162100	-0.45055800
H	-4.75302300	1.09262500	-1.17038500
H	-5.16715600	-2.48989000	2.25528500
H	-3.02584600	-1.23610300	2.01265400
H	-7.94595600	-1.71090400	0.19914600
H	8.42974500	0.53177500	1.05103700
H	7.14758100	1.42937500	0.18748000
H	6.84049300	0.77974100	1.82842600
H	-8.17803500	0.84100300	-2.40788900
H	-6.97552600	1.81303900	-1.51212000
H	-6.43574300	0.62623500	-2.74044900
H	-1.10491700	-0.70941700	0.91472100
H	-2.57282500	1.68976700	-0.33427300

Min$_{n\pi^*}$

E (MS-CASPT2//SA(4)-CASSCF(10,9)/6-31G*) = -1258.42013597 hartree

C	-2.92550140	-2.25523511	-1.31449874
C	-4.28014430	-2.45321190	-1.17709918
C	-5.11033403	-1.36830447	-0.87056264
C	-4.57374584	-0.11266429	-0.71352789
C	-3.19739712	0.09296314	-0.86592458
C	-2.38351440	-0.98716207	-1.15521772
C	-2.62462638	1.44922009	-0.72797214
O	-1.33799587	1.42357073	-0.32153520
C	-0.58278362	2.57823477	-0.17909944
C	-1.23722415	3.83524070	-0.39865535
C	-2.53261516	3.84040391	-0.78308260
C	-3.26050525	2.58829968	-0.98305967
O	-3.22946175	4.97848424	-1.00707599
C	3.09683661	3.07839330	0.81153948
O	-4.79728466	-3.68496817	-1.32751157
O	-6.42244988	-1.69205930	-0.73989092
C	3.95435024	4.20757749	0.97122980
C	5.25181001	4.05464096	1.34194353
C	5.78436804	2.76055433	1.57915885
C	4.98378647	1.67257086	1.43280947
C	3.63739545	1.82274319	1.04926809
O	6.15465856	5.05115274	1.52365043
O	7.07490055	2.62601141	1.94644902
C	-7.35687346	-0.69511437	-0.42997652

C	5.76440377	6.38154260	1.32600919
C	0.74126208	2.34973509	0.19559035
C	1.71539832	3.32113109	0.41163926
H	-2.30249760	-3.09889544	-1.54557782
H	-5.20418080	0.71175785	-0.44709391
H	-1.32631640	-0.84594561	-1.26321055
H	-0.69490650	4.74812127	-0.25499442
H	-4.26352007	2.60214541	-1.35600280
H	-5.73641178	-3.64886137	-1.19280784
H	3.55361679	5.18701688	0.79199465
H	5.39529567	0.69715240	1.61527043
H	3.03758223	0.93875313	0.94645338
H	7.47388874	3.48536966	1.99794711
H	-8.31868128	-1.18304285	-0.38669203
H	-7.14209570	-0.24196384	0.53138627
H	-7.37918396	0.07219058	-1.19598828
H	6.63499402	6.98757788	1.52675174
H	5.44066055	6.54586037	0.30430343
H	4.96825852	6.66020107	2.00733612
H	0.99483186	1.31345253	0.32005684
H	1.45060785	4.35452041	0.27681837

Min$_{\pi\pi^*}$

E (MS-CASPT2//SA(4)-CASSCF(10,9)/6-31G*) = -1258.39484124 hartree

C	-2.95420761	-2.27554979	-1.29806329
C	-4.31200745	-2.45327514	-1.16502767
C	-5.12745816	-1.35545565	-0.86600681
C	-4.57388113	-0.10708533	-0.71119040
C	-3.19371870	0.07857777	-0.85831389
C	-2.39440667	-1.01473545	-1.14166632
C	-2.60794361	1.42929008	-0.72434935
O	-1.31409410	1.38806833	-0.33517528
C	-0.53899024	2.49273498	-0.16793622
C	-1.17901112	3.78513262	-0.37708359
C	-2.50060709	3.83360607	-0.77061841
C	-3.22342458	2.58527655	-0.96299702
O	-3.11707726	4.96396003	-0.97765478
C	3.07928681	3.08915576	0.79019148
O	-4.84692419	-3.67733485	-1.31364853
O	-6.44429634	-1.66004747	-0.74112447
C	3.93538386	4.23973735	0.97066004
C	5.23010407	4.09914851	1.33050507
C	5.78488704	2.80592919	1.54174976
C	4.98268611	1.67825927	1.37528042
C	3.67512375	1.80071501	1.01260499
O	6.12490069	5.09835355	1.52840917
O	7.07161568	2.66752745	1.89902166
C	-7.36646935	-0.64821238	-0.44162326
C	5.72065993	6.42918695	1.35643355
C	0.76503598	2.22633769	0.19401227
C	1.74672939	3.27135258	0.41858771
H	-2.34302315	-3.12908417	-1.52458071
H	-5.19467492	0.72755935	-0.45377118
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H	-0.63225368	4.69210573	-0.22918739
H	-4.23397528	2.62152633	-1.31441606
H	-5.78609937	-3.62564801	-1.18446774

H	3.51477330	5.21408148	0.81068969
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H	3.08472834	0.91356535	0.89336024
H	7.47025065	3.52677921	1.96788386
H	-8.33520814	-1.12250674	-0.40206700
H	-7.15086870	-0.19402480	0.51898242
H	-7.37283007	0.11553931	-1.21126973
H	6.58623241	7.03971858	1.56441237
H	5.39071904	6.60736968	0.33926475
H	4.92484559	6.68642536	2.04618815
H	1.02855148	1.19502132	0.30853733
H	1.42449832	4.28706809	0.28352228

Min$_{n\pi^*}$ at CAM-B3LYP level

E (CAM-B3LYP/6-31G*) = -1261.73847490 hartree

C	-4.19204000	-2.40306900	-0.51422100
C	-5.48817400	-2.00455000	-0.24062000
C	-5.74372200	-0.66303700	0.09764700
C	-4.71480600	0.25357400	0.15515000
C	-3.39858700	-0.14763000	-0.13665600
C	-3.15266400	-1.48116800	-0.46054400
C	-2.29759100	0.81880800	-0.10467400
O	-1.07762200	0.22506600	-0.02179000
C	0.08789500	0.98780600	-0.02322700
C	-0.00344600	2.36277600	-0.05960400
C	-1.24511400	2.98730800	-0.12833200
C	-2.42569100	2.16264400	-0.17187700
O	-1.38569000	4.28784800	-0.15522500
C	3.74575700	-0.19129300	0.07128700
O	-6.50754100	-2.89136800	-0.28578300
O	-7.06171300	-0.41200400	0.36165500
C	4.99862400	0.44611900	-0.02439400
C	6.17069200	-0.28322600	0.02970400
C	6.13432300	-1.67696400	0.18239200
C	4.90839900	-2.31519300	0.28028200
C	3.73049000	-1.58274100	0.22669400
O	7.44096000	0.22451600	-0.05323800
O	7.29034600	-2.38530200	0.23505100
C	-7.43238600	0.90357900	0.71803000
C	7.58982800	1.61875200	-0.20951500
C	1.26236200	0.18699900	0.02718700
C	2.54524400	0.62757900	0.00394200
H	-4.01070300	-3.44100500	-0.76982300
H	-4.91602100	1.27518300	0.45083000
H	-2.14080600	-1.79727300	-0.67911800
H	0.89655300	2.96182000	-0.03501500
H	-3.39396300	2.62813300	-0.28037000
H	-7.31911100	-2.40798200	-0.05699000
H	5.03031900	1.52332800	-0.14405800
H	4.89498200	-3.39293700	0.40146300
H	2.78628000	-2.10891500	0.31230400
H	8.01670600	-1.74588300	0.14950600
H	-8.51102900	0.88605200	0.87346300
H	-6.93635100	1.21740900	1.64367600
H	-7.19116300	1.61267400	-0.08226300
H	8.66232200	1.80985700	-0.25384900
H	7.11977500	1.96674600	-1.13676300

H	7.15851700	2.16177500	0.63957400
H	1.05957000	-0.87849800	0.08814500
H	2.72785100	1.69702500	-0.07799400

$Min_{\pi\pi^*}$ at CAM-B3LYP level

E (CAM-B3LYP/6-31G*) = -1261.74053344 hartree

C	-4.20936500	-2.42597800	-0.35754400
C	-5.50591000	-1.99532900	-0.13774900
C	-5.75027800	-0.63089200	0.10640600
C	-4.71175100	0.27499900	0.12601100
C	-3.39295400	-0.15783500	-0.10700900
C	-3.16045600	-1.51436300	-0.33994200
C	-2.28429800	0.80153600	-0.10706900
O	-1.07036100	0.17888400	-0.06092000
C	0.09097100	0.91254800	-0.06781300
C	0.03615700	2.30279800	-0.10460600
C	-1.20863500	3.02005700	-0.14747300
C	-2.38275100	2.14680800	-0.15883400
O	-1.29560300	4.25303600	-0.17925900
C	3.72688300	-0.15428700	0.01999400
O	-6.53659300	-2.86972600	-0.14890800
O	-7.07073500	-0.34756600	0.32011000
C	5.00489700	0.48294600	0.01542100
C	6.15614200	-0.25944500	0.05827600
C	6.10212600	-1.67841900	0.10811600
C	4.86683100	-2.32162000	0.11373100
C	3.70291700	-1.58583000	0.07083000
O	7.43067900	0.21718300	0.05926500
O	7.24397500	-2.38569400	0.14930000
C	-7.43218000	0.99576100	0.56967500
C	7.62018100	1.62018900	0.01177700
C	1.24460500	0.11953200	-0.02871000
C	2.55450300	0.63037300	-0.02435200
H	-4.03650700	-3.48026100	-0.54292000
H	-4.90656400	1.31765700	0.33917300
H	-2.14916800	-1.85705400	-0.51592600
H	0.95282400	2.87898700	-0.10362700
H	-3.34991200	2.62757900	-0.22686800
H	-7.34541200	-2.36003300	0.02767100
H	5.04280700	1.56530100	-0.02275600
H	4.85061800	-3.40533400	0.15250400
H	2.75192600	-2.10421100	0.07695300
H	7.98148700	-1.74960800	0.13699300
H	-8.51453700	1.00213900	0.69796600
H	-6.95474400	1.37045300	1.48217300
H	-7.16054300	1.64090500	-0.27350500
H	8.69753400	1.78238500	0.02119600
H	7.19230800	2.04061600	-0.90456200
H	7.16705500	2.10454000	0.88332400
H	1.07575300	-0.95109200	-0.00063500
H	2.68836300	1.70681100	-0.05867700