
Topological transitions in orbital-symmetry-controlled chemical reactions

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I. DETAILS OF FIRST PRINCIPLE CALCULATIONS

A. Computational methods

We utilize the GAMESS program for geometry optimizations and frequency calculations at the CASSCF/def2-SVP level^{S1}. Transition structures are confirmed via intrinsic reaction coordinate (IRC) calculations. To calculate the total energy of the first excited state we used state-averaged CAS for two states.

To compute the Green's functions, we use PySCF to calculate the active space one- and two-electron integrals in the CAS active space (h_{PQ} and g_{PQRS} in Eq. S2)^{S2}. We used the natural orbitals from unrestricted second order MøllerPlesset perturbation theory (MP2) as a initial guess for the CAS-orbitals at the stationary points for each reaction. Subsequent calculations along the IRC towards reactants or products used interpolated CAS-orbitals from the previous geometry as initial guess. Custom Python scripts were used to generate plots and visualize orbitals.

After completing the CASSCF calculation, we construct the Hamiltonian of the active space. The definition of many-electron Hamiltonian in second quantized form^{S3}:

$$\hat{H} = \sum_{PQ} h_{PQ} a_P^\dagger a_Q + \frac{1}{2} \sum_{PQRS} g_{PQRS} a_P^\dagger a_R^\dagger a_S a_Q - \mu \sum_P a_P^\dagger a_P \quad (\text{S1})$$

$$h_{PQ} = \int \phi_P^*(\mathbf{x}) \left(-\frac{1}{2} \nabla^2 - \sum_I \frac{Z_I}{r_I} \right) \phi_Q(\mathbf{x}) d\mathbf{x} \quad (\text{S2})$$

$$g_{PQRS} = \iint \frac{\phi_P^*(\mathbf{x}_1) \phi_R^*(\mathbf{x}_2) \phi_Q(\mathbf{x}_1) \phi_S(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2 \quad (\text{S3})$$

$$\mu = -\frac{IP + EA}{2} \quad (\text{S4})$$

Z_I is the nuclear charge of atom I , r_I is the relative distance between electron-nucleus, r_{12} is the electron-electron distance and R_{IJ} is the internuclear separation. P, Q, R, S represent the index of orbitals included in the active space. And we adopt the definition of the Mulliken chemical potential (Eq. S4), where IP and EA represent ionization potential and electron affinity, respectively. With this convention, a pole at $\omega = 0$ corresponds to a vanishing charge gap (IP equal to EA in the reference used to set $\omega = 0$), whereas a zero at $\omega = 0$ corresponds to a self-energy pole and suppression of single-particle propagation without requiring a charge-gap closure. The molecular one-electron integral (Eq. S2), two-electron integral (Eq. S3), ionization potential and electron affinity are extracted from the previous CASSCF calculation.

Subsequently, we employed TRIQS to compute the Green's function along the reaction coordinate^{S4}. The Green's function heatmap plot displays the frequency(ω) versus reaction coordinate, with each point representing $\ln |\text{Det } G(\omega|\mathbf{R})|$ at a specific frequency and reaction coordinate to highlight poles and zeros at the same time.

To obtain the topological invariants for each subspace, we block diagonalize the Green's function into two blocks,

$$G(\omega|\mathbf{R}) = G^+(\omega|\mathbf{R}) \oplus G^-(\omega|\mathbf{R}) \quad (\text{S5})$$

The representations of the unitary matrices for this transformation were obtained from the irreducible representations of the CAS-orbitals through PySCF. For the conrotatory pathway, the relevant symmetry is a C_2 symmetry, while for the disrotatory the relevant symmetry is a mirror symmetry σ_v as highlighted in Fig. 4 in the main text. The corresponding topological invariants were defined as $N_+(\mathbf{R})$ and $N_-(\mathbf{R})$, respectively.

To calculate the topological invariant ($N_{+/-}(\mathbf{R})$), we select a cutoff by integrating ω within the interval $[-C, C]$. This interval is enclosed by connecting C and $-C$ through a semicircular path in the complex plane, as illustrated in Fig. S2.

We calculate $\text{Det } G(\omega|\mathbf{R})$ along this curve and plot $\text{Im} [\text{Det } G^{+/-}(\omega|\mathbf{R})]$ versus $\text{Re} [\text{Det } G^{+/-}(\omega|\mathbf{R})]$. The topological invariant (aka winding number) is determined by counting how many times the plot encircles the origin in a clockwise or counterclockwise direction. For particularly complex loops, it can be difficult to evaluate the winding number

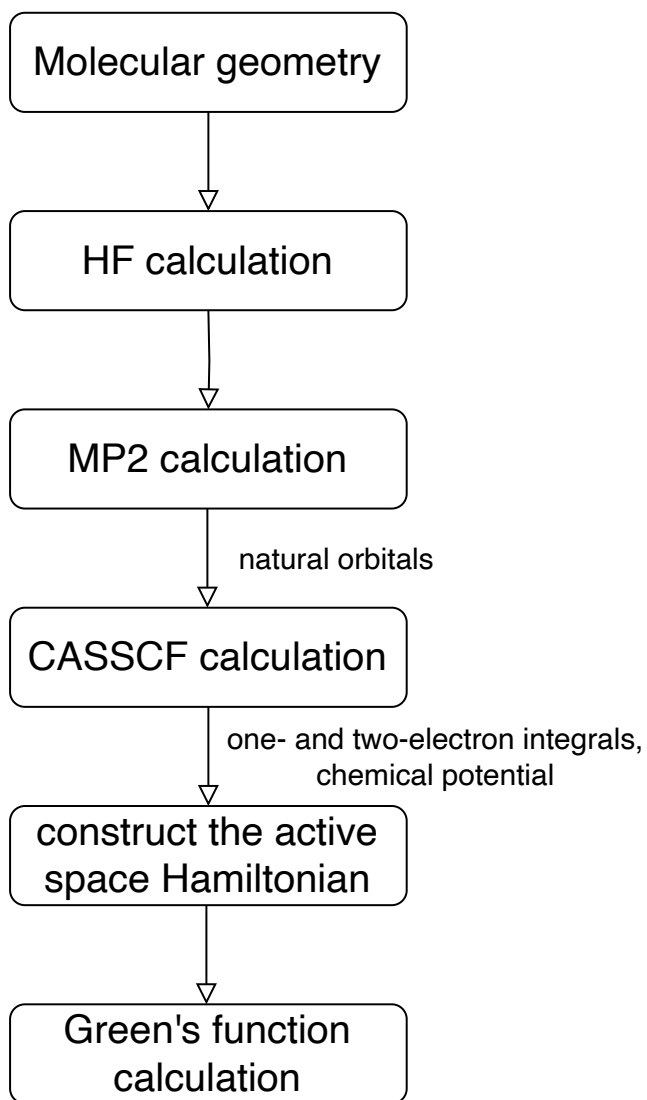


FIG. S1. flowchart: Green's function calculations

directly using this method. Therefore, we use the so-called crossing rule to evaluate the winding number, which works as follows: Initially, the winding number is zero. Pick a starting point outside the loop and move towards the origin in a straight line. If the loop is crossed, and the direction of the curve that is crossed goes from the left to the right, the winding number increases by one. If direction of the curve crossed is from right to the left, decreases the winding number by one. For more details about crossing rules, we refer to Ref. [S5](#).

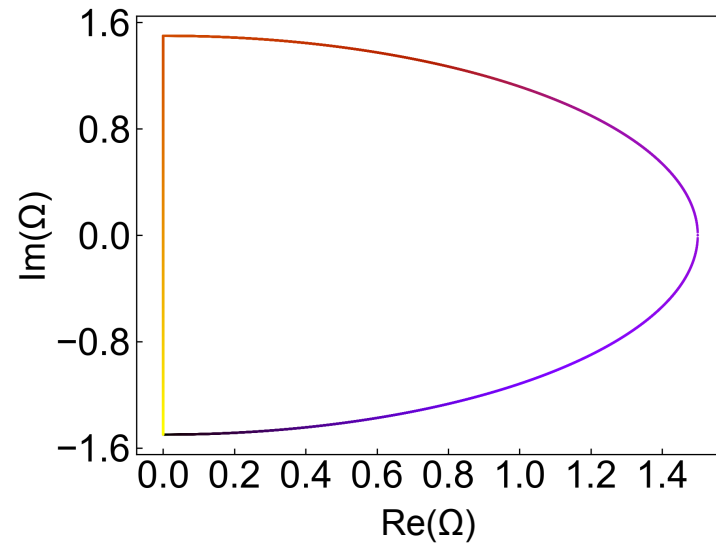


FIG. S2. Integration contour in the complex plane. The initial point of the contour is indicated in black and the last point is indicated in yellow.

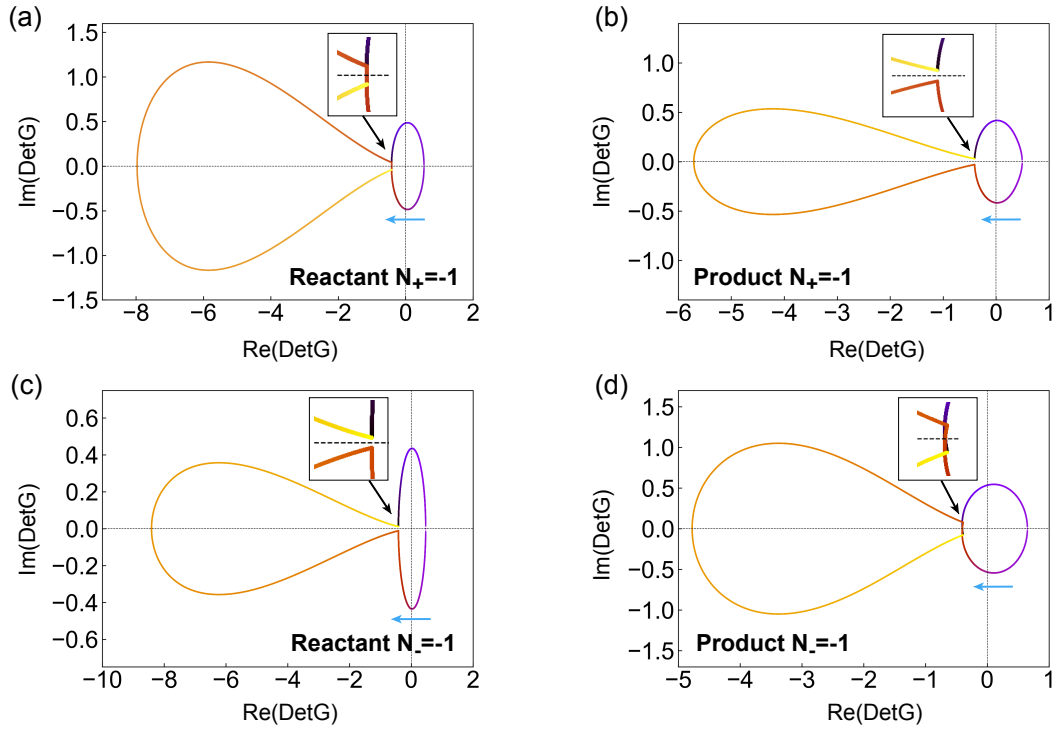


FIG. S3. Winding numbers of the conrotatory, symmetry allowed reaction for reactant and product geometries. $G^+(\omega|\mathbf{R})$ part: (a) reactant, (b) product. $G^-(\omega|\mathbf{R})$ part: (c) reactant, (d) product.

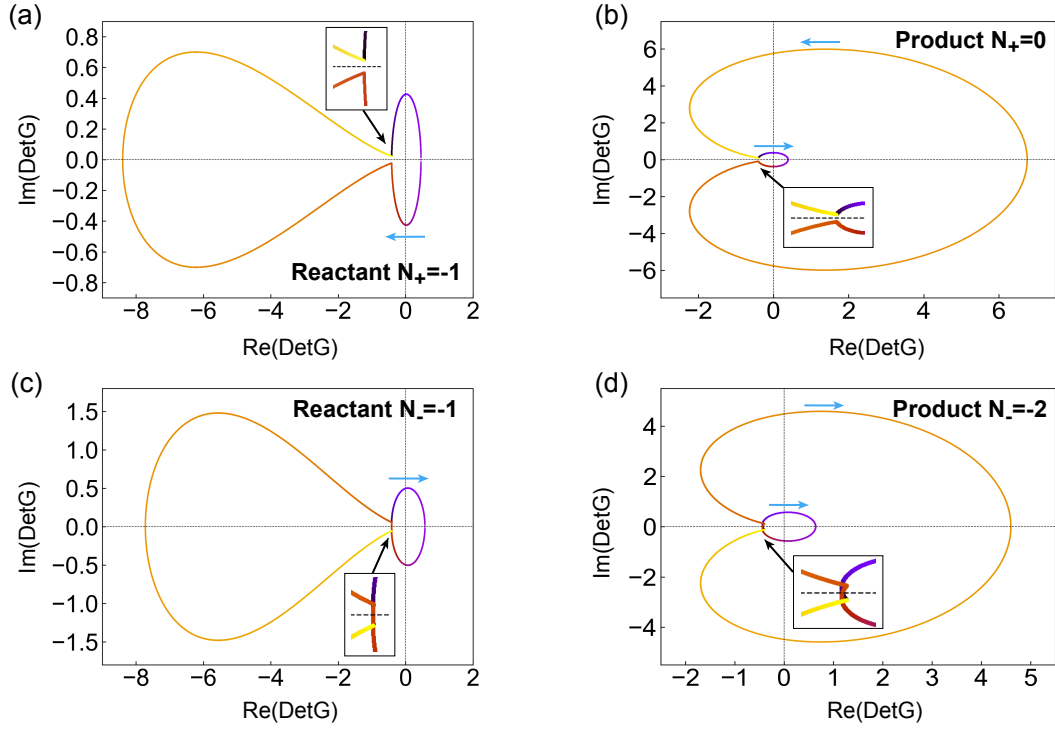


FIG. S4. Winding numbers of the disrotatory, symmetry forbidden reaction for reactant and product geometries. $G^+(\omega|\mathbf{R})$ part: (a) reactant, (b) product. $G^-(\omega|\mathbf{R})$ part: (c) reactant, (d) product.

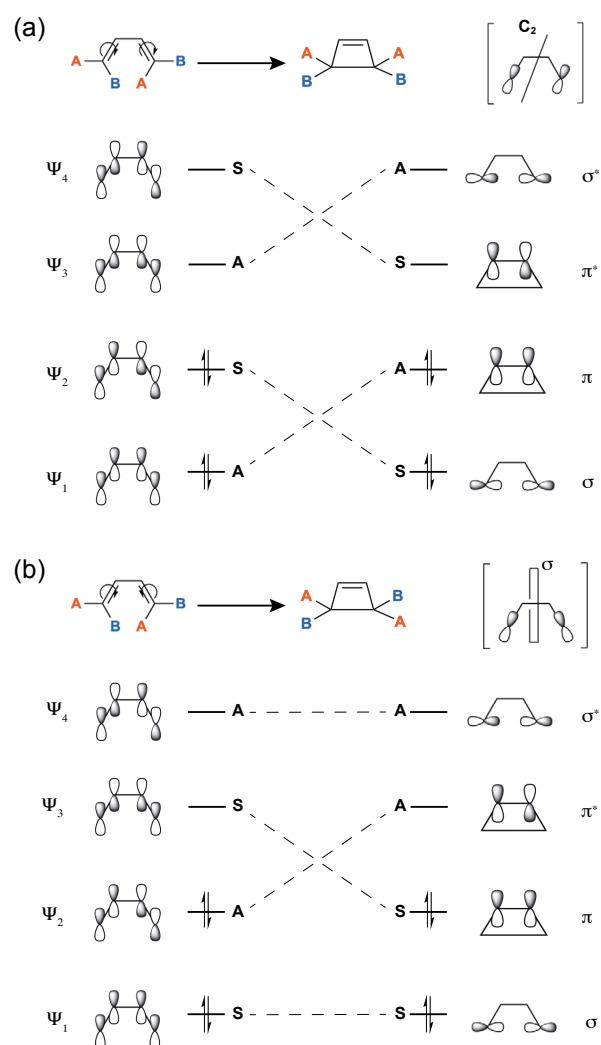


FIG. S5. Sketch of the molecular orbital correlation diagram of the (a) conrotatory pathway and (b) disrotatory pathway. The conserved symmetries are highlighted in the top right panel of each schematic.

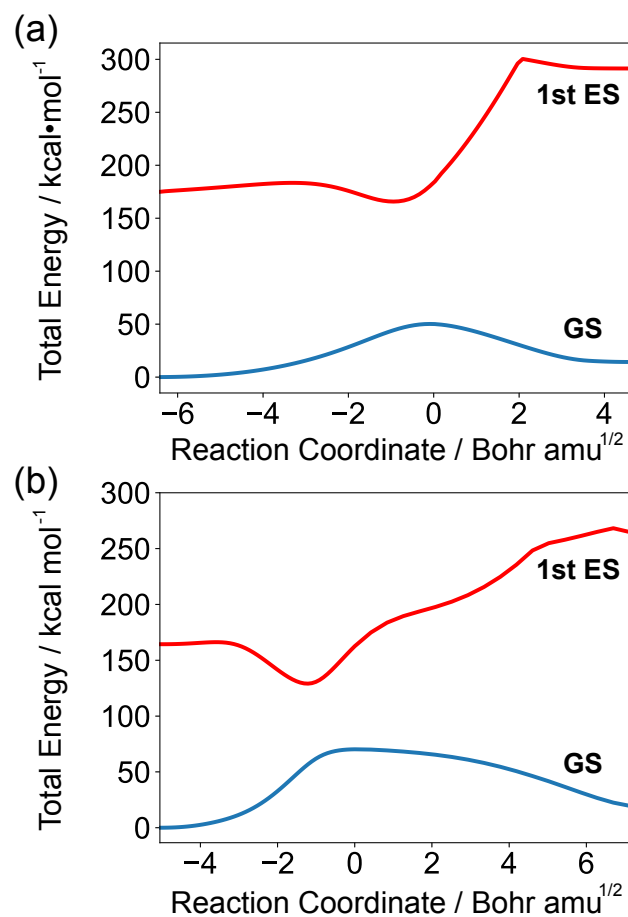


FIG. S6. Ground state and first excited state reaction coordinate plot at the CASSCF(4,4)/def2-SVP level. (a) The symmetry-allowed conrotatory ring closure of butadiene. (b) The symmetry forbidden disrotatory ring closure.

B. Cartesian Coordinates and active space orbitals

1. Butadiene to Cyclobutene

TABLE I. Cartesian coordinates of optimized TS for Butadiene to Cyclobutene (symmetry allowed pathway) calculated at the CASSCF(4,4)/def2-SVP level of theory

Atomic Symbol	x	y	z
C	-3.09698439	1.17951632	0.16758497
C	-2.06908488	0.52281088	-0.44725546
C	-3.20352459	0.57596689	1.49097860
C	-1.30338478	-0.09057832	0.60867476
H	-1.87494135	0.41670525	-1.50920999
H	-0.83910215	-1.06939566	0.49497187
H	-0.79861146	0.55856788	1.30909038
H	-3.69765520	2.00121927	-0.20634829
H	-3.44916940	1.16169369	2.37621284
H	-3.49097323	-0.46342605	1.55438280

TABLE II. Cartesian coordinates of product for Butadiene to Cyclobutene (symmetry allowed pathway) calculated at the CASSCF(4,4)/def2-SVP level of theory

Atomic Symbol	x	y	z
C	-3.17146349	1.11432397	0.06286150
C	-2.03004956	0.65461206	-0.47479331
C	-2.91020942	0.47780326	1.44256830
C	-1.56586814	-0.05285020	0.77611250
H	-1.58325458	0.74785513	-1.45692015
H	-1.49369264	-1.14043438	0.71065664
H	-0.65249038	0.33375841	1.23284853
H	-3.98674035	1.71433961	-0.32127821
H	-2.76802850	1.17809510	2.26703858
H	-3.61133671	-0.30175376	1.74432707

TABLE III. Cartesian coordinates of reactant for Butadiene to Cyclobutene (symmetry allowed pathway) calculated at the CASSCF(4,4)/def2-SVP level of theory

Atomic Symbol	x	y	z
C	-3.09340835	1.13042045	0.34887734
C	-1.98993051	0.41447654	-0.32534304
C	-3.62827516	0.80390429	1.54641604
C	-0.95083332	-0.18146992	0.28743789
H	-2.03468037	0.39101189	-1.40977716
H	-0.18817978	-0.69780713	-0.28123748
H	-0.82970405	-0.15841198	1.36363339
H	-3.50671363	1.97792351	-0.18947060
H	-4.42966700	1.39007092	1.97846949
H	-3.28690767	-0.05470822	2.11210203

TABLE IV. Cartesian coordinates of optimized TS for Butadiene to Cyclobutene (symmetry forbidden pathway) calculated at the CASSCF(4,4)/def2-SVP level of theory

Atomic Symbol	x	y	z
C	-0.66840178	-0.66103232	-0.00818259
C	0.67361021	-0.66141027	-0.00862591
C	-1.43289435	0.60805488	0.03538374
C	1.44137657	0.60566473	0.03363175
H	1.21823382	-1.61539078	-0.04042951
H	2.14264894	0.78695387	0.83953464
H	1.58068931	1.18977380	-0.86852658
H	-1.21529257	-1.60057521	-0.03935051
H	-2.13548136	0.78888953	0.83994591
H	-1.56158030	1.19736910	-0.86460614

TABLE V. Cartesian coordinates of product for Butadiene to Cyclobutene (symmetry forbidden pathway) calculated at the CASSCF(4,4)/def2-SVP level of theory

Atomic Symbol	x	y	z
C	-0.66984105	-0.79434568	-0.02512581
C	0.67388409	-0.79554427	-0.02875960
C	-0.79400730	0.71229649	0.04336154
C	0.80414504	0.71111393	0.04107838
H	1.41726863	-1.59610069	-0.06718586
H	1.26075172	1.11085021	0.94924062
H	1.25962353	1.19466817	-0.82582450
H	-1.41343272	-1.58071411	-0.05936407
H	-1.24933398	1.11309564	0.95151293
H	-1.25149596	1.19291830	-0.82399887

2. Planar 4π photoswitch

S1. Barca, G. M. J. et al. Recent developments in the general atomic and molecular electronic structure system. *J. Chem. Phys.* **152**, 154102 (2020).
S2. Sun, Q. et al. Recent developments in the PySCF program package. *J. Chem. Phys.* **153**, 024109 (2020).
S3. Helgaker, T., Jorgensen, P. & Olsen, J. *Molecular electronic-structure theory* (Wiley, 2000).
S4. Parcollet, O. et al. TRIQS: a toolbox for research on interacting quantum systems. *Comput. Phys. Commun.* **196**, 398415 (2015).
S5. Needham, T. & Penrose, R. *Visual Complex Analysis: 25th anniversary edition* (Oxford Univ. Press, 2023).

TABLE VI. Cartesian coordinates of reactant for Butadiene to Cyclobutene (symmetry forbidden pathway) calculated at the CASSCF(4,4)/def2-SVP level of theory

Atomic Symbol	x	y	z
C	-0.73492372	-0.56231099	0.04531593
C	0.74057925	-0.56246090	0.04784043
C	-1.54649913	0.51096493	-0.02430039
C	1.55419683	0.50651175	-0.02794648
H	1.20860767	-1.55056751	0.12000136
H	2.62945938	0.38468352	-0.01693699
H	1.18276739	1.52091098	-0.10236876
H	-1.19537926	-1.54244065	0.10699496
H	-2.62218237	0.39323509	-0.01903062
H	-1.17003775	1.52419770	-0.08757465

TABLE VII. Cartesian coordinates of optimized TS for planar 4π photoswitch reaction calculated at the CASSCF(8,8)/def2-SVP level of theory

Atomic Symbol	x	y	z
C	-0.68646049	0.74695677	-0.26518306
C	-0.73827797	-0.72022313	-0.19584633
C	-0.71085125	-3.55579734	0.31736165
C	-1.31871355	-1.62466264	-1.08968341
C	-0.16956536	-1.31195188	0.93895537
C	-0.15639506	-2.65334058	1.24435139
C	-1.27998984	-3.01678538	-0.83651161
H	-1.78895831	-1.26381147	-1.99523020
H	-1.72385740	-3.68402672	-1.56389070
H	-0.72922039	-4.61887884	0.51064384
H	-1.47488511	1.25954831	-0.80355763
C	0.28464389	0.76984793	2.05043721
C	0.65886915	1.40411985	-0.18743424
C	1.19861233	1.39390028	1.04021025
C	1.39995897	1.89838302	-1.38580012
O	2.46708703	2.40970922	-1.34519541
O	0.72253424	1.70862389	-2.50057220
C	1.31340802	2.12376046	-3.71306062
H	0.60278982	1.88054800	-4.49621964
H	1.50516236	3.19430184	-3.69939637
H	2.25073671	1.59839034	-3.88155103
H	2.21268296	1.70370245	1.26901102
N	0.28589794	-0.64505559	2.04045677
N	0.33208391	-2.81264448	2.52984500
C	0.56166804	-1.62683094	2.96074963
H	0.94901824	-1.39009523	3.94072556
C	-0.00107836	1.45962024	3.34928083
H	-0.21320437	2.51322961	3.16947246
H	-0.85843676	1.01205695	3.85135221
H	0.85915458	1.41035175	4.02701950

TABLE VIII. Cartesian coordinates of product for planar 4π photoswitch reaction calculated at the CASSCF(8,8)/def2-SVP level of theory

Atomic Symbol	x	y	z
C	0.13194802	0.02506223	-1.09168410
C	-0.36576492	-1.17663205	-0.41850802
C	-1.32690811	-3.60743833	0.76794356
C	-0.98295718	-2.17476368	-1.16612065
C	-0.24827439	-1.43162608	0.97211659
C	-0.70265645	-2.60211253	1.54609895
C	-1.46222675	-3.37571764	-0.58461285
H	-1.09523642	-2.02926564	-2.23253226
H	-1.93308270	-4.11443520	-1.21931565
H	-1.67700648	-4.51568985	1.23679578
H	-0.00438553	0.03394382	-2.16143703
C	0.86167991	0.60631412	1.99349451
C	0.74190885	1.10258996	-0.53969592
C	1.04051375	1.35354006	0.88409495
C	1.18740273	2.21943665	-1.44181168
O	1.70200074	3.21299028	-1.04911458
O	0.95879722	1.99752009	-2.72144365
C	1.35240567	2.99009442	-3.64379215
H	1.08100641	2.61502934	-4.62530088
H	0.83624667	3.92648840	-3.44466448
H	2.42547798	3.15932298	-3.59121442
H	1.48822224	2.31871080	1.05400848
N	0.29010919	-0.69277030	2.01553392
N	-0.45261529	-2.59635425	2.89602900
C	0.12038465	-1.47597969	3.12541842
H	0.44914326	-1.15470731	4.09897423
C	1.27664340	1.14159203	3.33980918
H	1.68955755	2.13991475	3.22737455
H	0.42801705	1.20167029	4.02360106
H	2.03912401	0.51237071	3.80258489

TABLE IX. Cartesian coordinates of reactant for planar 4π photoswitch reaction calculated at the CASSCF(8,8)/def2-SVP level of theory

Atomic Symbol	x	y	z
C	-0.46316966	0.80869728	0.27256081
C	-0.70543504	-0.65206575	-0.07928471
C	-0.67484796	-3.52020717	0.21292190
C	-1.18891037	-1.44962764	-1.10089016
C	-0.24345320	-1.36385739	1.01594305
C	-0.17524883	-2.69788671	1.26026309
C	-1.16230154	-2.87462640	-0.92405868
H	-1.57645857	-1.03834307	-2.02346087
H	-1.54599094	-3.48445034	-1.73209500
H	-0.68561327	-4.59903717	0.28033912
H	-1.31754351	1.47265327	0.13959162
C	0.19265704	0.75756383	1.80498528
C	0.89137906	1.38201642	-0.09673298
C	1.43442523	1.31957614	1.13257849
C	1.46329761	1.83212495	-1.38748384
O	2.55850339	2.26127553	-1.51424849
O	0.60081214	1.70110857	-2.37491751
C	1.01657867	2.07770634	-3.67060304
H	0.17335097	1.88929164	-4.32692528
H	1.28376973	3.13187528	-3.69594288
H	1.87451267	1.48688281	-3.98344684
H	2.41375208	1.56759346	1.51765978
N	0.23903094	-0.68283510	2.07377291
N	0.37695351	-2.85369992	2.52078342
C	0.60777974	-1.65629160	2.95874429
H	1.04258657	-1.43401742	3.92175961
C	-0.44758344	1.56573653	2.91281414
H	-0.54921705	2.60872746	2.61249804
H	-1.43398023	1.16972673	3.15486050
H	0.16610944	1.53500116	3.81595373

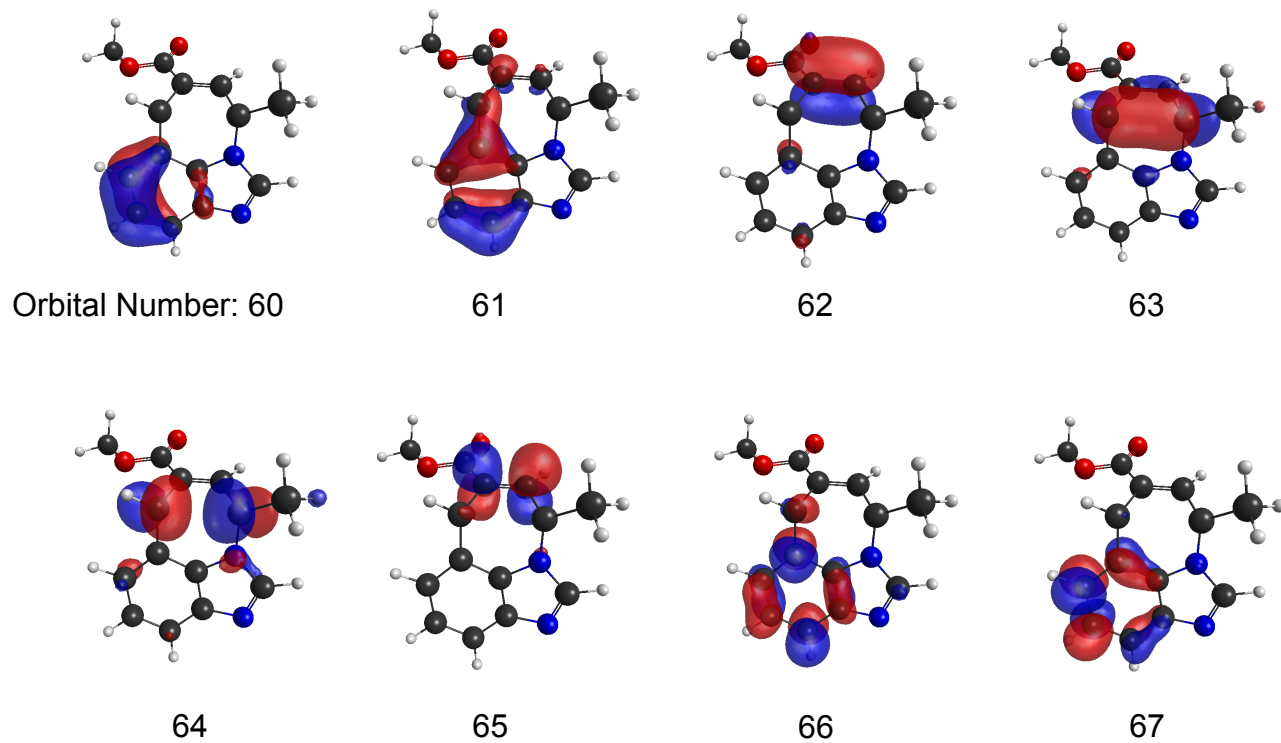


FIG. S7. The molecular orbitals in the active space (8,8) using def2-SVP basis sets in the optimized TS for the planar 4π photoswitch reaction.