

# Supporting Information: Conical Intersections Studied by the Configuration-Interaction-Corrected Tamm-Dancoff Method

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## Cartesian coordinates of molecules

We used the coordinates of planar NH<sub>3</sub> and C<sub>2</sub>H<sub>4</sub> indicated in Fig.1(a) and Fig.2(a), respectively, as reported in Ref.[1], corresponding to the optimized minimum-energy conical intersection (MECI) geometry by multi-state CASPT2/6-311+G(2d,p). The relevant xyz coordinates at MECI are given in Table S1 and Table S3. The coordinates of NH<sub>3</sub> with N–H bond stretching indicated in Fig.1(b) are given in Table S2. The optimized geometries of bithiophene molecule, *i.e.*, S<sub>0</sub>-min and two S<sub>1</sub> minimum structures, were reported in the Supporting Information of Ref.[2]. The corresponding coordinates are given in Table S4, Table S5, and Table S6. The optimized geometries of gas phase *cis*- and *trans*-azobenzene were reported in Ref.[3]. The corresponding coordinates are provided in Table S7 and Table S8. For the geometries of PSB11 discussed in main text, we used the coordinates of  $\beta$ -ionone ring frozen (PSB11<sub>frozen</sub>) structure reported in Ref.[4] and the xyz coordinates are given in Table S9. The bond lengths and torsion angles indicated in Fig.6(a) were digitalized and extrapolated according to the values in the Fig.2 of Ref.[3]. The corresponding numbers are listed in Table S10.

TABLE S1. The xyz coordinates of planar NH<sub>3</sub> optimized at MECI as reported in Ref.[1] with units in Å.

atoms	X	Y	Z
N	0.00	0.00	0.00
H	-0.38152359	0.94882791	0.00
H	-0.76127515	-0.68787230	-0.00019546
H	1.94065126	0.00	0.00

TABLE S2. The xyz coordinates of NH<sub>3</sub> with N–H bond stretching at  $r_1 = 2.0$  Å. Units in Å.

atoms	X	Y	Z
N	0.00	0.00	0.00
H	1.99970000	0.00	-0.03490000
H	-0.51942087	-0.89966335	-0.01813305
H	-0.51942087	0.89966335	-0.01813305

TABLE S3. The xyz coordinates of C<sub>2</sub>H<sub>4</sub> optimized at MECI as reported in Ref.[1] with units in Å.

atoms	X	Y	Z
C	0.00	0.00	0.00
C	1.39256669	0.00	0.00
H	-0.16311333	-0.86899057	-0.72061431
H	-0.15689386	-0.86646844	0.72855820
H	1.96657058	0.92903077	0.00000000
H	2.01361377	-0.90061491	-0.00046903

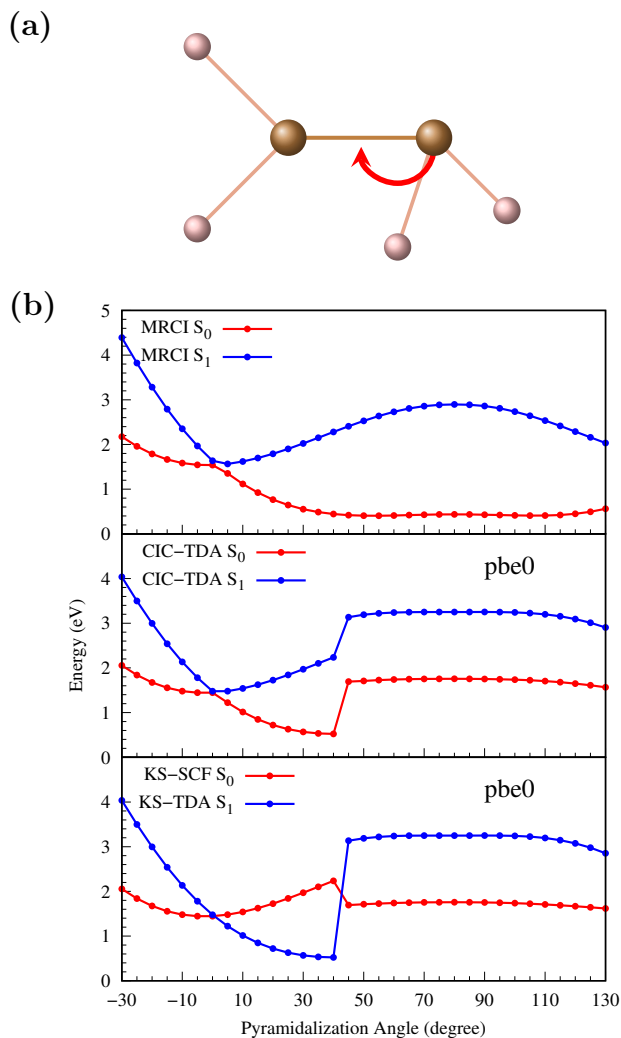


FIG. S1. (a) The geometry of pyramidalization with carbon and hydrogen atoms represented by brown and pink colors, respectively. (b) PESs of  $C_2H_4$  near  $S_1/S_0$  conical intersection along the pyramidalization angle as calculated by MRCI, CIC-TDA, and KS-SCF/KS-TDA methods. For the CIC-TDA and KS-SCF/KS-TDA calculations, PESs with PBE0 functional (the factor of Hartree-Fock exchange functional as 0.25) are not smooth.

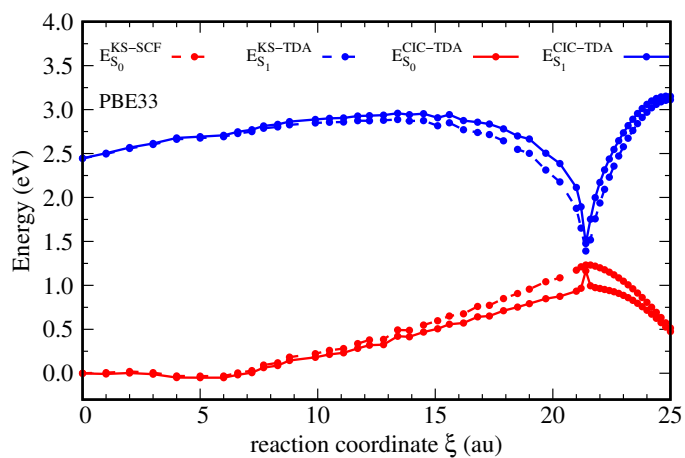


FIG. S2. The PESs of PSB11 along the reaction coordinate  $\xi$  as discussed in main text. In these CIC-TDA and KS-SCF/KS-TDA calculations, the PBE33 functional (the factor of Hartree-Fock exchange functional as 0.33) was used.

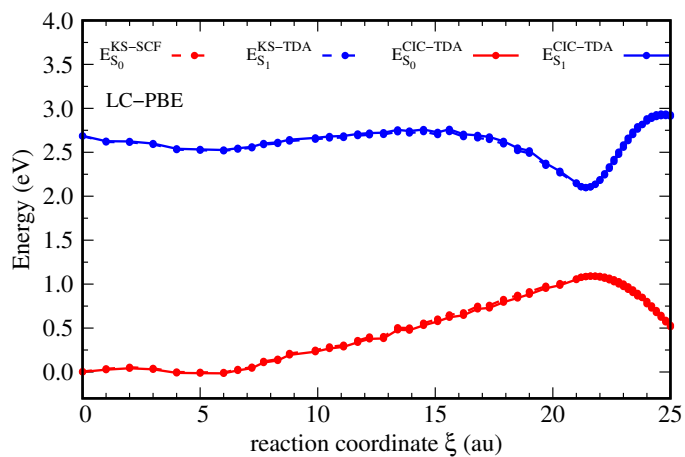


FIG. S3. The PESs of PSB11 along the reaction coordinate  $\xi$  as discussed in main text. In these CIC-TDA and KS-SCF/KS-TDA calculations, the long-range corrected PBE (LC-PBE) functional was used.

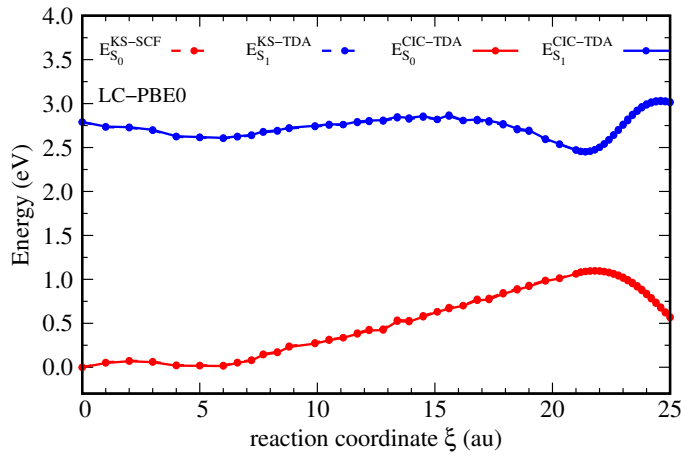


FIG. S4. The PESs of PSB11 along the reaction coordinate  $\xi$  as discussed in main text. In these CIC-TDA and KS-SCF/KS-TDA calculations, the long-range corrected PBE0 (LC-PBE0) functional was used.

TABLE S4. The xyz coordinates of optimized  $S_0$ -min bithiophene structure as reported in Ref.[1] with units in Å.

atoms	X	Y	Z
C	0.12027495	0.71571272	0.05493598
C	-0.12027495	-0.71571272	0.05493598
C	1.28405149	1.39848545	0.31831287
C	-1.28405149	-1.39848545	0.31831287
C	1.14725255	2.81093789	0.22642491
C	-1.14725255	-2.81093789	0.22642491
C	-0.11806895	3.20124774	-0.10405096
C	0.11806895	-3.20124774	-0.10405096
S	-1.16742554	1.84040127	-0.32994087
S	1.16742554	-1.84040127	-0.32994087
H	2.20396213	0.90011764	0.59494876
H	-2.20396213	-0.90011764	0.59494876
H	1.95488123	3.50702862	0.41043484
H	-1.95488123	-3.50702862	0.41043484
H	-0.50356180	4.20093034	-0.23160591
H	0.50356180	-4.20093034	-0.23160591

TABLE S5. The xyz coordinates of optimized  $S_1$ -min-a bithiophene structure as reported in Ref.[1] with units in Å.

atoms	X	Y	Z
C	0.11152670	0.67910799	0.00
C	-0.11152670	-0.67910799	0.00
C	1.35854305	1.39188333	0.00
C	-1.35854305	-1.39188333	0.00
C	1.20054730	2.77778907	0.00
C	-1.20054730	-2.77778907	0.00
C	-0.14525417	3.16629087	0.00
C	0.14525417	-3.16629087	0.00
S	-1.22808900	1.82619831	0.00
S	1.22808900	-1.82619831	0.00
H	2.30497134	0.88846443	0.00
H	-2.30497134	-0.88846443	0.00
H	2.01071451	3.47941856	0.00
H	-2.01071451	-3.47941856	0.00
H	-0.53070359	4.16426731	0.00
H	0.53070359	-4.16426731	0.00

TABLE S6. The xyz coordinates of optimized  $S_1$ -min-b bithiophene structure as reported in Ref.[1] with units in Å.

atoms	X	Y	Z
C	0.15920037	0.31045414	0.11753307
C	0.01117539	-1.11654281	0.11760603
C	1.17195966	1.18365704	0.11728153
C	-1.17204183	-1.80712782	0.11724081
C	1.08380471	2.64822426	0.11728655
C	-0.99523942	-3.23130300	0.11736937
C	-0.00745488	3.47248692	0.11767141
C	0.31574076	-3.59409371	0.11785437
S	-1.66135095	2.99914200	0.11825485
S	1.37586054	-2.22042866	0.11813181
H	2.17868542	0.79137481	0.11696539
H	-2.12632155	-1.31722121	0.11690313
H	2.03849073	3.14655214	0.11700621
H	-1.80636944	-3.93357219	0.11710284
H	0.18395691	4.53058491	0.11763454
H	0.72141233	-4.58491083	0.11801480

TABLE S7. The xyz coordinates of optimized *cis*-azobenzene structure indicated in Fig.4(a) as reported in Ref.[3] with units in Å.

atoms	X	Y	Z
C	0.00	0.00	0.00
C	1.40778	0.00	0.00
C	2.12914	-1.20526	0.00
C	1.43609	-2.42458	0.09846
C	0.02765	-2.43644	0.13519
C	-0.68616	-1.22315	0.06504
N	2.16663	1.22177	-0.09950
N	1.96300	2.15411	0.75105
C	1.07163	1.91440	1.85850
C	0.05209	2.85556	2.07705
C	-0.84582	2.66582	3.14218
C	-0.68438	1.57323	4.01705
C	0.38451	0.67440	3.82705
C	1.26519	0.83900	2.74611
H	-0.04341	3.70716	1.39623
H	-1.66030	3.37971	3.30057
H	-1.37559	1.43417	4.85356
H	0.53109	-0.15866	4.52173
H	2.08654	0.13770	2.58452
H	3.22208	-1.17346	-0.04837
H	1.99357	-3.36609	0.12840
H	-0.51096	-3.38660	0.19814
H	-1.78068	-1.22969	0.06333
H	-0.54677	0.94446	-0.03962

TABLE S8. The xyz coordinates of optimized *trans*-azobenzene structure indicated in Fig.4(b) as reported in Ref.[3] with units in Å.

atoms	X	Y	Z
C	0.00	0.00	0.00
C	1.41312	0.00	0.00
C	2.12973	-1.21332	0.00
C	1.43696	-2.43679	0.00
C	0.02907	-2.44482	0.00
C	-0.68280	-1.22494	0.00
N	2.22340	1.17081	0.00
N	1.54400	2.25707	0.00
C	2.35434	3.42797	0.00
C	1.63796	4.64138	0.00
C	2.33082	5.86476	0.00
C	3.73874	5.87267	0.00
C	4.45044	4.65269	0.00
C	3.76743	3.42788	0.00
H	0.54470	4.60292	0.00
H	1.77566	6.80791	0.00
H	4.28198	6.82257	0.00
H	5.54520	4.66192	0.00
H	4.30349	2.47707	0.00
H	3.22297	-1.17497	0.00
H	1.99203	-3.38001	0.00
H	-0.51402	-3.39483	0.00
H	-1.77756	-1.23459	0.00
H	-0.53629	0.95067	0.00

TABLE S9: The xyz coordinates of PSB11<sub>frozen</sub> structure reported in Ref.[4] with units in Å.

atoms	X	Y	Z
N	-0.029429	0.017858	0.074216
C	-0.007019	0.006393	1.415582
C	1.152627	0.039737	2.160031
C	1.267612	0.030386	3.620895
C	2.539165	0.069767	4.128204
C	3.050269	0.074779	5.517506
C	2.366786	0.040364	6.696459
C	2.955688	0.048606	8.026973
C	2.063313	0.007793	9.114704
C	2.429039	0.008279	10.448629
C	1.473708	-0.035053	11.573839
C	0.662629	1.017122	11.845135
C	-0.319136	1.004167	12.997569
C	-0.592171	-0.388087	13.553164
C	0.720525	-1.142561	13.720375
C	1.474984	-1.345128	12.393182
C	0.810497	-2.461087	11.563294
C	2.912919	-1.780869	12.732129
C	0.691213	2.332857	11.100932
C	4.444200	0.090461	8.252431
C	0.024985	-0.020705	4.482883
C	-1.227264	-0.016577	-0.740317
H	-1.285132	0.869481	-1.361060
H	-1.223652	-0.893139	-1.377016
H	-2.095529	-0.052669	-0.099332
H	0.843974	0.052242	-0.408107
H	-0.974738	-0.031302	1.873385
H	2.079562	0.076857	1.613587
H	0.022747	-0.906234	5.108585
H	-0.883916	-0.047273	3.900350
H	-0.038613	0.851258	5.124257
H	3.335130	0.103844	3.405621
H	4.122023	0.113104	5.554308
H	1.297166	0.002930	6.687250
H	5.007140	0.105221	7.333477
H	4.765959	-0.777628	8.818672
H	4.718229	0.973586	8.819785
H	1.011150	-0.000602	8.891182
H	3.473509	-0.053700	10.694917
H	-1.244989	1.471028	12.670558
H	0.073405	1.646974	13.784324
H	-1.259217	-0.928401	12.888414

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**TABLE S9 – continued from previous page**

atoms	X	Y	Z
H	-1.103055	-0.310756	14.507259
H	0.549361	-2.113099	14.176377
H	1.355574	-0.585071	14.405424
H	-0.217669	-2.223569	11.314930
H	1.343371	-2.631063	10.632593
H	3.471324	-2.089507	11.853689
H	0.814428	-3.395272	12.116111
H	2.887708	-2.630910	13.405623
H	3.463966	-0.985802	13.225725
H	1.509905	2.421781	10.400380
H	-0.238522	2.481465	10.557507
H	0.773155	3.152078	11.809492

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TABLE S10: The digitalized and extrapolated torsion angles [ $\Theta(C_6-C_7)$  and  $\Theta(C_{11}-C_{12})$  unit in degree] and bond lengths [ $d(C_{11}-C_{12})$  and  $d(C_6-C_7)$  unit in Å] indicated in Fig.6(a) along the reaction coordinate  $\xi$  according to the Fig.2 in Ref.[4].

$\xi$	$\Theta(C_6-C_7)$	$\Theta(C_{11}-C_{12})$	$d(C_{11}-C_{12})$	$d(C_6-C_7)$
0.0	-68.75	-0.26	1.36371	1.49418
1.0	-65.98	-0.54	1.46112	1.47605
2.0	-63.24	-1.47	1.47406	1.47106
3.0	-59.56	-2.39	1.47711	1.46812
4.0	-50.97	-5.84	1.47512	1.45710
5.0	-48.78	-6.68	1.47518	1.45506
6.0	-46.41	-7.79	1.47419	1.45108
6.6	-44.10	-13.81	1.47619	1.44894
7.2	-42.89	-17.12	1.47714	1.44999
7.7	-42.60	-23.42	1.48298	1.44810
8.3	-41.53	-25.98	1.48209	1.44905
8.8	-40.87	-31.77	1.48304	1.44910
9.9	-39.13	-33.58	1.48505	1.45006
10.5	-38.90	-36.14	1.48705	1.45111
11.1	-38.57	-37.73	1.48610	1.45102
11.7	-37.02	-40.52	1.48706	1.44897
12.2	-36.65	-43.23	1.48711	1.44908
12.8	-36.18	-43.18	1.48711	1.44803
13.4	-34.16	-47.98	1.48921	1.44714
13.9	-34.86	-48.77	1.48712	1.44714
14.5	-33.55	-50.96	1.48818	1.44720
15.1	-34.62	-55.07	1.48818	1.44810
15.6	-32.19	-55.67	1.48724	1.44811
16.2	-33.91	-59.17	1.48634	1.45011
16.8	-32.56	-62.34	1.48714	1.45011
17.3	-32.74	-63.36	1.48595	1.45021
17.9	-32.22	-67.00	1.48630	1.45152
18.5	-32.36	-70.50	1.48466	1.45327
19.0	-31.61	-72.41	1.48417	1.45337
19.7	-31.65	-77.44	1.48267	1.45542
20.3	-31.65	-80.34	1.47933	1.45842
21.0	-30.99	-85.37	1.47585	1.46022
21.2	-30.70	-87.95	1.47508	1.46195
21.4	-30.55	-89.76	1.47400	1.46304
21.6	-30.40	-91.64	1.47286	1.46420
21.8	-30.25	-93.60	1.47165	1.46543
22.0	-30.08	-95.65	1.47039	1.46672
22.2	-29.91	-97.79	1.46907	1.46809
22.4	-29.73	-100.01	1.46768	1.46953
22.6	-29.55	-102.34	1.46622	1.47104
22.8	-29.35	-104.76	1.46470	1.47263

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**TABLE S10 – continued from previous page**

$\xi$	$\Theta(\text{C}_6\text{-C}_7)$	$\Theta(\text{C}_{11}\text{-C}_{12})$	$d(\text{C}_{11}\text{-C}_{12})$	$d(\text{C}_6\text{-C}_7)$
23.0	-29.15	-107.28	1.46311	1.47430
23.2	-28.94	-109.91	1.46144	1.47605
23.4	-28.72	-112.65	1.45970	1.47789
23.6	-28.49	-115.51	1.45789	1.47982
23.8	-28.25	-118.48	1.45600	1.48183
24.0	-28.00	-121.58	1.45403	1.48394
24.2	-27.74	-124.80	1.45197	1.48614
24.4	-27.47	-128.16	1.44984	1.48844
24.6	-27.19	-131.66	1.44761	1.49084
24.8	-26.89	-135.29	1.44530	1.49334
25.0	-26.59	-139.07	1.44290	1.49595

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## References

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- [1] Y. Shu, K. A. Parker, and D. G. Truhlar, “Dual–Functional Tamm–Dancoff Approximation: A Convenient Density Functional Method that Correctly Describes  $S_1/S_0$  Conical Intersections,” *J. Phys. Chem. Lett.* **8**, 2107–2112 (2017).
- [2] P. Kölle, T. Schnappinger, and R. de Vivie-Riedle, “Deactivation pathways of thiophene and oligothiophenes: internal conversion versus intersystem crossing,” *Phys. Chem. Chem. Phys.* **18**, 7903–7915 (2016).
- [3] F. Aleotti, L. Soprani, A. Nenov, R. Berardi, A. Arcioni, C. Zannoni, and M. Garavelli, “Multidimensional Potential Energy Surfaces Resolved at the RASPT2 Level for Accurate Photoinduced Isomerization Dynamics of Azobenzene,” *J. Chem. Theory Comput.* **15**, 6813–6823 (2019).
- [4] Cembran, A. and González-Luque, R. and Serrano-Andrés, L. and Merchán, M. and Garavelli, M., “About the intrinsic photochemical properties of the 11-cis retinal chromophore: computational clues for a trap state and a lever effect in Rhodopsin catalysis,” *Theor. Chem. Acc.* **118**, 173–183 (2007).