Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Irreversible phototautomerization of *o*-phthalaldehyde through electronic relocation

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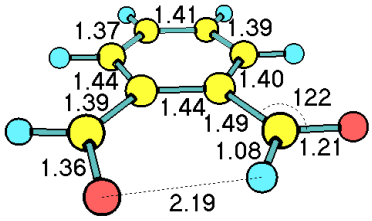
Supporting Information

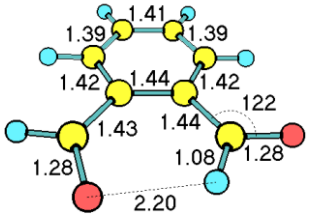
Table SI 1 Absolute and relative MS-CASPT energies of the critical points.

Structure	State	MS-CASPT2(Hartree)	MS-CASPT2(eV)
FC	S_0	-457.81157	0.00
	S_1	-457.70340	2.94
	S_2	-457.68755	3.37
$(\pi,\pi^*)_{Min}$	S_0	-457.80446	0.19
	S_1	-457.70408	2.92
	S_2	-457.68818	3.36
	S_3	-457.67084	3.83
$(\pi,\pi^*/ n,\pi^*)_X$	S_0	-457.79476	0.46
	S_1	-457.69124	3.27
	S_2	-457.66892	3.88
	S_3	-457.66078	4.10
$(n,\pi^*)_{Min\text{-}local\text{-}1}$	S_0	-457.78619	0.69
	S_1	-457.70354	2.94
	S_2	-457.67331	3.76
$(n,\pi^*)_{Min}$	S_0	-457.79916	0.34
	S_1	-457.71509	2.63
	S_2	-457.69932	3.05
$(n,\pi^*)_{Min\text{-}local\text{-}2}$	S_0	-457.78926	0.61
	S_1	-457.70784	2.82
	S_2	-457.66738	3.92
$(S_1/S_0)_{X\text{-}HT}$	S_0	-457.73758	2.01
	S_1	-457.71237	2.70
	S_2	-457.67075	3.83
$(S_1/S_0)_{X\text{-}Z\text{-}Ket}$	S_0	-457.73784	2.01
	S_1	-457.72857	2.26
	S_2	-457.65112	4.37
$(S_2/S_1)_X$	S_0	-457.73817	2.00
	S_1	-457.70518	2.89
	S_2	-457.69267	3.24
TS-S_1	S_0	-457.74775	1.74
	S_1	-457.72882	2.25
	S_2	-457.66548	3.98
TS-S_0	S_0	-457.74062	1.93
	S_1	-457.68831	3.35
	S_2	-457.65772	4.19
Bir	S_0	-457.74489	1.81
	S_1	-457.70281	2.96
	S_2	-457.65896	4.15
syn-Z-Ket	S_0	-457.75721	1.48
	S_1	-457.68440	3.46
	S_2	-457.59599	5.87

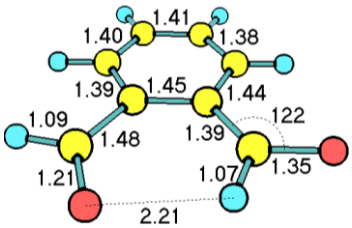
anti-Z-Ket	S_0	-457.76573	1.25
	S_1	-457.67644	3.68
	S_2	-457.64446	4.55



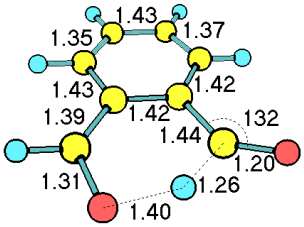
(a) $(n,\pi^*)_{Min\text{-}local\text{-}1}$



(b) $(n,\pi^*)_{Min}$



(c) $(n,\pi^*)_{Min\text{-}local\text{-}2}$



(d) TS-S_1

Figure SI 1 Structure of (a) $(n,\pi^*)_{Min\text{-}local\text{-}1}$, (b) $(n,\pi^*)_{Min}$, (c) $(n,\pi^*)_{Min\text{-}local\text{-}2}$, and (d) TS-$S_1$.

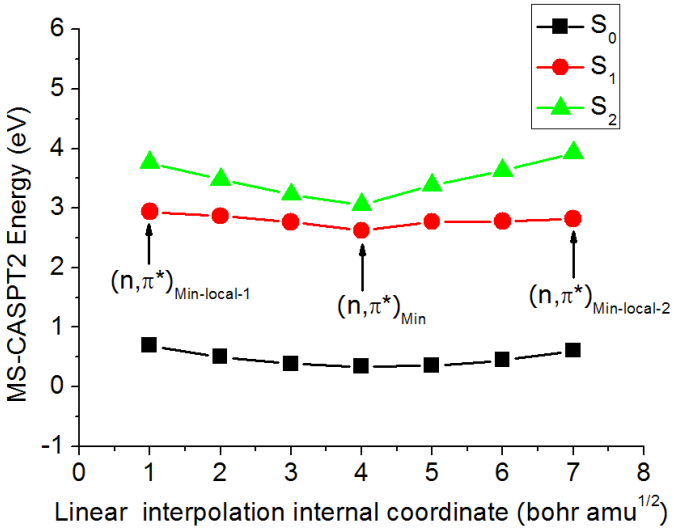


Figure SI 2 Relative MS-CASPT2 energies along the linear interpolation internal coordinate from $(n,\pi^*)_{\text{Min-local-1}}$ to $(n,\pi^*)_{\text{Min-local-2}}$.

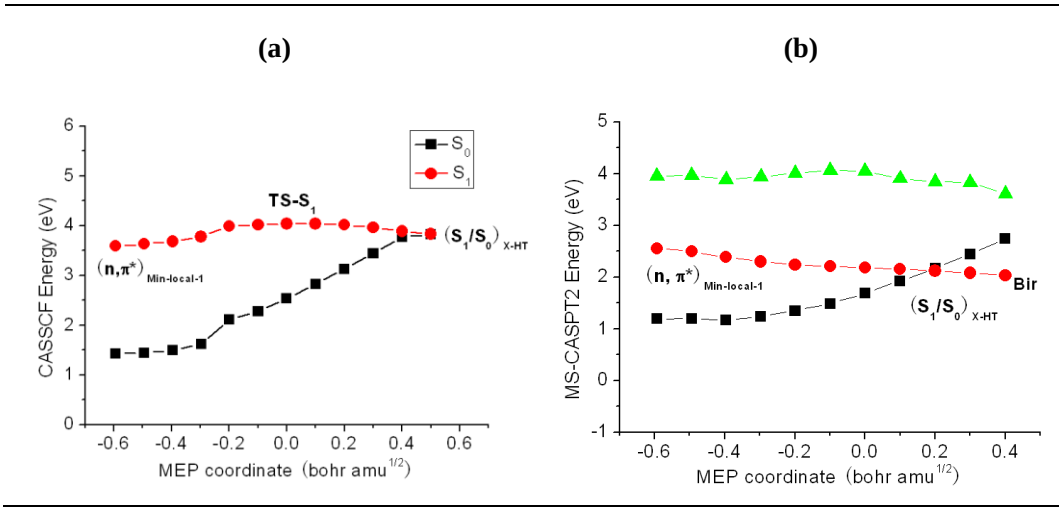


Figure SI 3 Energy profile along the MEP from $(n,\pi^*)_{Min\text{-}local\text{-}1}$ to $(S_1/S_0)_{X\text{-}HT}$: (a) at CASSCF level; (b) at MS-CASPT2 level.

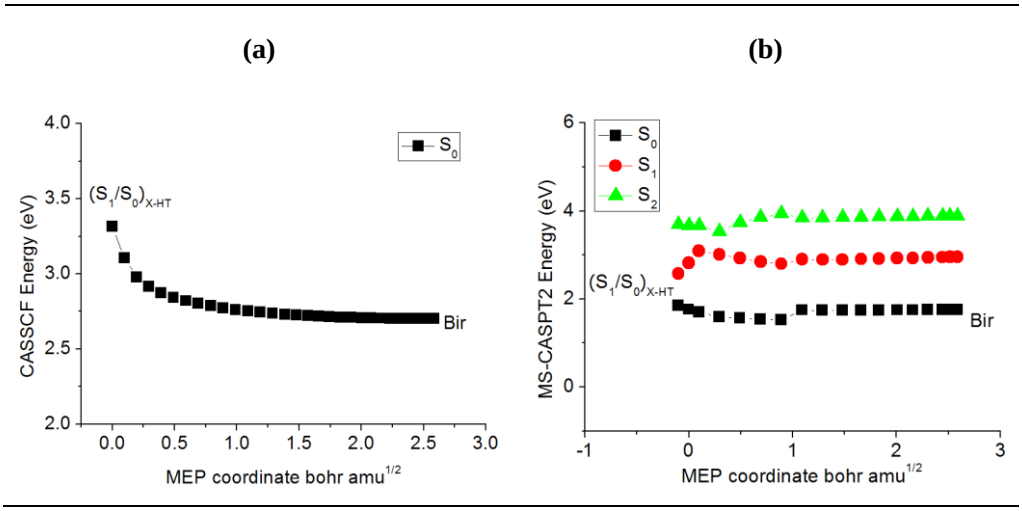


Figure SI 4 Energy profile along the MEP from $(S_1/S_0)_{X\text{-}HT}$ to Bir: (a) at CASSCF level; (b) at MS-CASPT2 level.

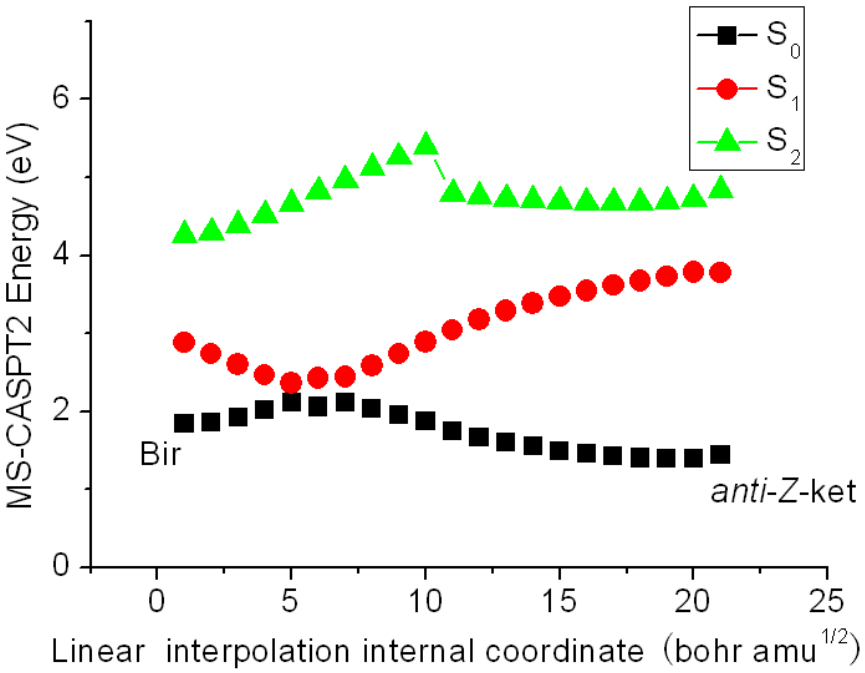


Figure SI 5 Relative MS-CASPT2 energies along the linear interpolation internal coordinate from Bir to *anti-Z*-Ket.

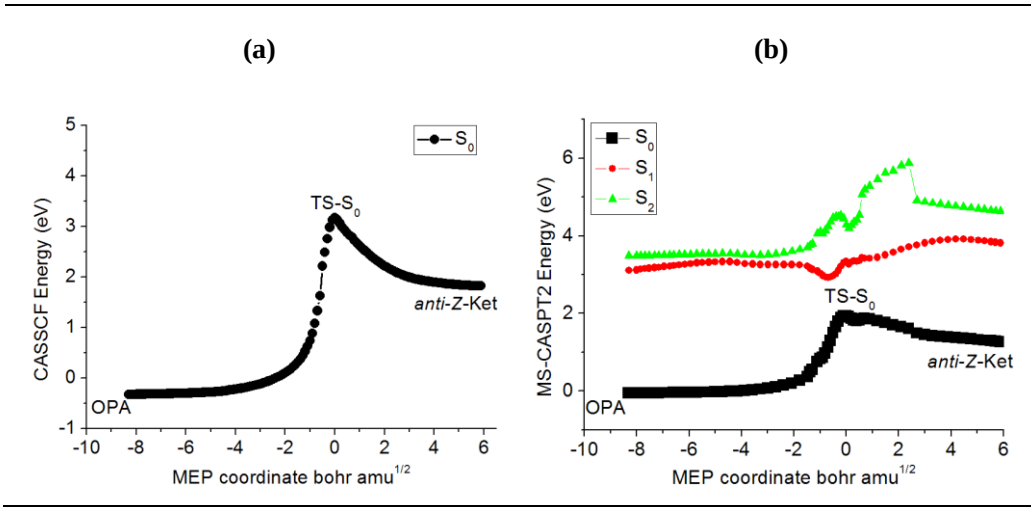


Figure SI 6 Energy profile along the MEP from OPA to *anti-Z*-Ket connected by TS-S_0: (a) at CASSCF level; (b) at MS-CASPT2 level.

Cartesian coordinates of the key structures

OPA-FC

6	-1.325006	-1.380602	0.000469
6	-2.436326	-0.539919	-0.000016
6	-2.249425	0.840650	-0.000253
6	-0.958273	1.366150	0.000059
6	0.167051	0.533948	0.000431
6	-0.021409	-0.868628	0.000586
1	-1.469739	-2.446624	0.000505
1	-3.426604	-0.957341	-0.000293
1	-3.096450	1.502256	-0.000736
1	-0.806223	2.427840	-0.000143
6	1.509703	1.198036	0.000343
6	1.065211	-1.887818	-0.000044
8	2.252155	-1.673447	-0.002455
1	2.388119	0.571129	0.000652
8	1.617251	2.402813	0.000179
1	0.710314	-2.918315	0.000798

$(\pi,\pi^*)_{Min}$

6	-1.344267	-1.407203	-0.001305
6	-2.474041	-0.545186	-0.000394
6	-2.282175	0.859765	0.000983
6	-0.960787	1.393574	0.000899
6	0.213111	0.543037	-0.000065
6	0.014727	-0.903013	-0.000344
1	-1.494686	-2.470912	-0.001980
1	-3.461358	-0.963437	-0.000571
1	-3.123452	1.524222	0.001846
1	-0.807291	2.452990	0.001356
6	1.524316	1.201486	-0.001965
6	1.078223	-1.902807	0.001637
8	2.271604	-1.676457	0.007783
1	2.408204	0.584233	-0.004427
8	1.622583	2.415495	-0.001161
1	0.735638	-2.935659	-0.002209

$(\pi,\pi^*/n,\pi^*)_X$

6	-1.433198	-1.443470	-0.011728
6	-2.571245	-0.554439	-0.011150
6	-2.384215	0.863734	0.007914
6	-1.051286	1.399306	0.017631
6	0.110378	0.515444	0.006824
6	-0.080090	-0.947082	0.000280
1	-1.599003	-2.510590	-0.018498
1	-3.565956	-0.960913	-0.018879
1	-3.230129	1.526796	0.012145
1	-0.879346	2.458081	0.024711
6	1.460432	1.164222	-0.014916
6	1.057759	-1.895868	0.012660
8	2.185270	-1.567147	0.018379
1	2.319202	0.512797	-0.028126
8	1.612320	2.363070	-0.019506
1	0.843944	-2.969156	0.022402

$(n,\pi^*)_{Min}$

6	0.00000000	0.00000000	0.00000000
6	1.38610000	0.00000000	0.00000000
6	2.08266458	1.22466200	0.00000000
6	1.38338512	2.42132579	0.00010886
6	-0.03398491	2.45624031	0.00026645
6	-0.74878972	1.20264410	0.00005667
1	-0.52969851	-0.93555304	-0.00009307
1	1.92263802	-0.93014697	-0.00000974
1	3.15653535	1.23258463	0.00000000
1	1.91747246	3.35069132	0.00023504
6	-0.69820101	3.72984203	0.00104472
6	-2.17494125	1.05474495	-0.00028546
8	-3.03748661	2.00453661	-0.00082017
1	-1.77101474	3.80137905	0.00390705
8	-0.05363203	4.83477579	-0.00116105
1	-2.58322727	0.05424564	-0.00043385

$(n,\pi^*)_{\text{Min-local-1}}$

6	0.00000000	0.00000000	0.00000000
6	1.37410854	0.00000000	0.00000000
6	2.08223170	1.22078916	0.00000000
6	1.37794923	2.42193137	0.00021885
6	-0.02054228	2.46123972	0.00052982
6	-0.75922434	1.22405372	0.00011360
1	-0.53417799	-0.93212322	-0.00018581
1	1.90714631	-0.93286989	-0.00001693
1	3.15545554	1.22462198	0.00000000
1	1.90600462	3.35529358	0.00047252
6	-0.66828311	3.79784868	0.00214972
6	-2.14064382	1.07959201	-0.00055201
8	-3.05240693	2.08517903	-0.00168614
1	-1.74903080	3.84785163	0.00803940
8	-0.02997407	4.82639337	-0.00203958
1	-2.60786548	0.11531501	-0.00087115

$(n,\pi^*)_{\text{Min-local-2}}$

6	0.00000000	0.00000000	0.00000000
6	1.39815453	0.00000000	0.00000000
6	2.08318810	1.22849930	0.00000000
6	1.38885469	2.42074653	0.00000000
6	-0.04734466	2.45113895	0.00000000
6	-0.73830028	1.18129640	0.00000000
1	-0.52520961	-0.93898215	-0.00000000
1	1.93813252	-0.92732834	0.00000000
1	3.15763280	1.24051369	0.00000000
1	1.92896458	3.34611363	0.00000000
6	-0.72491205	3.66197634	0.00000000
6	-2.20925024	1.03002938	-0.00000000
8	-3.02250130	1.92411842	-0.00000000
1	-1.78945468	3.75475709	0.00000000
8	-0.07778613	4.84441027	0.00000000
1	-2.55584816	-0.00299984	-0.00000000

$(S_1/S_0)_{X\text{-}HT}$

6	1.027983	-1.651128	0.000000
6	2.261812	-1.093265	0.000000
6	2.407403	0.315172	0.000000
6	1.293911	1.132869	0.000000
6	0.000000	0.574753	0.000000
6	-0.141933	-0.838011	0.000000
1	0.915709	-2.720502	0.000000
1	3.136396	-1.716897	0.000000
1	3.389884	0.746557	0.000000
1	1.400938	2.200107	0.000000
6	-1.224820	1.392774	0.000000
6	-1.402759	-1.478690	0.000000
8	-2.536194	-0.880787	0.000000
1	-2.303334	0.209896	0.000000
8	-1.265282	2.593732	0.000000
1	-1.457372	-2.549558	0.000000

$(S_1/S_0)_{X\text{-}Z\text{-}Ket}$

6	1.044362	-1.641145	0.000000
6	2.283237	-1.070534	0.000000
6	2.428804	0.356238	0.000000
6	1.314028	1.153623	0.000000
6	0.000000	0.589196	0.000000
6	-0.170611	-0.849337	0.000000
1	0.946052	-2.712141	0.000000
1	3.161593	-1.690916	0.000000
1	3.409651	0.795202	0.000000
1	1.404130	2.224953	0.000000
6	-1.088067	1.485673	0.000000
6	-1.373609	-1.528920	0.000000
8	-2.616408	-1.015728	0.000000
1	-2.618631	-0.067780	0.000000
8	-1.325567	2.650995	0.000000
1	-1.395869	-2.600228	0.000000

$(S_2/S_1)_X$

6	1.009401	-1.686253	0.000000
6	2.241153	-1.155158	0.000000
6	2.415587	0.273617	0.000000
6	1.338239	1.110382	0.000000
6	0.000000	0.573497	0.000000
6	-0.164197	-0.850986	0.000000
1	0.876259	-2.753726	0.000000
1	3.107453	-1.790349	0.000000
1	3.410262	0.679815	0.000000
1	1.462147	2.176142	0.000000
6	-1.130063	1.415788	0.000000
6	-1.424788	-1.446828	0.000000
8	-2.540337	-0.800499	0.000000
1	-2.265625	0.279299	0.000000
8	-1.305942	2.615449	0.000000
1	-1.532252	-2.515126	0.000000

Bir

6	1.049716	-1.613723	-0.000040
6	2.301540	-1.036824	-0.000009
6	2.443409	0.364555	0.000047
6	1.303131	1.162548	0.000067
6	0.022208	0.596235	-0.000013
6	-0.147107	-0.825333	-0.000025
1	0.957172	-2.684720	-0.000070
1	3.175292	-1.662919	-0.000028
1	3.418585	0.814577	0.000044
1	1.390844	2.232837	0.000097
6	-1.136545	1.504000	0.000088
6	-1.367688	-1.521499	-0.000030
8	-2.610125	-1.017104	0.000047
1	-2.609620	-0.068033	0.000205
8	-1.162710	2.688757	-0.000334
1	-1.371932	-2.592261	-0.000044

***syn*-*Z*-Ket**

6	2.402457	-0.855694	0.000000
6	2.455218	0.604706	0.000000
6	1.318580	1.327575	0.000000
6	0.000000	0.669250	0.000000
6	-0.076345	-0.817105	0.000000
6	1.220397	-1.507122	0.000000
1	3.323240	-1.409785	0.000000
1	3.409443	1.098385	0.000000
1	1.346281	2.402188	0.000000
1	1.199420	-2.582327	0.000000
6	-1.192261	-1.581820	0.000000
1	-1.114065	-2.650369	0.000000
6	-1.067593	1.460281	0.000000
8	-2.492655	-1.205654	0.000000
8	-1.995068	2.157178	0.000000
1	-2.625242	-0.270710	0.000000

***anti*-*Z*-Ket**

6	2.393748	-0.905159	0.000000
6	2.452379	0.554870	0.000000
6	1.316344	1.282048	0.000000
6	0.000000	0.629298	0.000000
6	-0.073461	-0.848149	0.000000
6	1.208917	-1.554587	0.000000
1	3.313017	-1.462463	0.000000
1	3.409433	1.043246	0.000000
1	1.351422	2.356759	0.000000
1	1.181468	-2.630288	0.000000
6	-1.229748	-1.540619	0.000000
1	-1.265007	-2.613468	0.000000
6	-1.073611	1.422977	0.000000
8	-2.419589	-0.876005	0.000000
8	-1.931596	2.193529	0.000000
1	-3.148253	-1.478055	0.000000

TS-S_1

6	-1.428607	-1.391722	0.001542
6	-2.506248	-0.578046	0.000630
6	-2.351869	0.840532	-0.000324
6	-1.093906	1.393767	-0.000542
6	0.050588	0.560827	-0.000049
6	-0.101867	-0.855634	0.001063
1	-1.554116	-2.459487	0.002416
1	-3.494693	-0.999467	0.000665
1	-3.221816	1.468271	-0.000727
1	-0.963991	2.459335	-0.000852
6	1.391282	1.075323	-0.002166
6	0.997212	-1.713440	0.001268
8	2.248630	-1.330900	-0.000177
1	2.144702	0.066178	-0.001534
8	1.815393	2.198065	-0.004059
1	0.864146	-2.778816	0.002993

TS-S_0

6	-1.442178	-1.396655	-0.120573
6	-2.513371	-0.591258	-0.015374
6	-2.344692	0.831332	0.071798
6	-1.095732	1.384129	0.036990
6	0.054336	0.555694	-0.166614
6	-0.111314	-0.855572	-0.187154
1	-1.561617	-2.465415	-0.151626
1	-3.504446	-1.005381	0.022153
1	-3.211634	1.462251	0.144463
1	-0.959114	2.447913	0.101326
6	1.367982	1.136844	0.013702
6	1.008630	-1.683160	-0.041189
8	2.203306	-1.202114	-0.022012
1	2.121096	-0.105177	0.377093
8	1.884937	2.154249	-0.317655
1	0.898648	-2.712895	0.254820