

Supplementary Data

for

Acceleration of the *Z* to *E* photoisomerization of penta-2,4-dieniminium by hydrogen out-of-plane motion: Theoretical study on a model system of retinal protonated Schiff base

submitted by:

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contents:

Potential energy surfaces with the interpolated point at $\theta_1 = 50^\circ$

The Cartesian coordinates of the stationary points in the S_1 and S_0 states and the S_1/S_0 degeneracy points (in Å).

I. RESULT OF LINEAR INTERPOLATION

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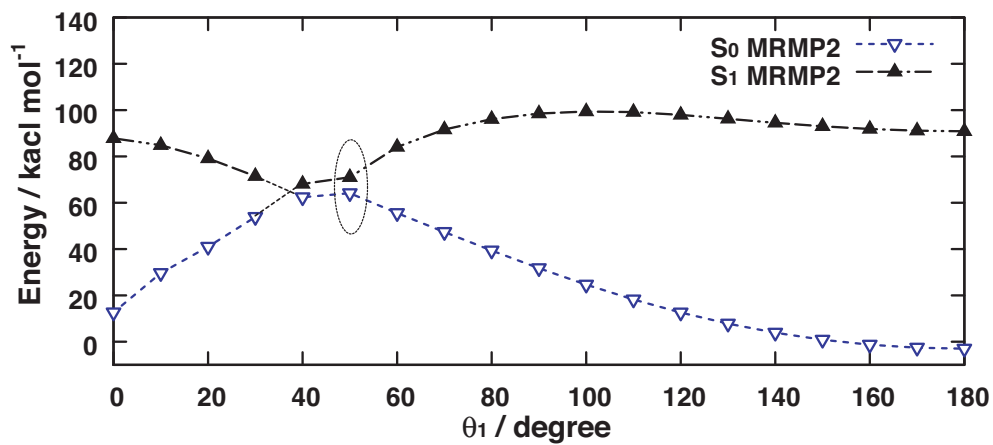


Figure S1: S₁/S₀ potential energy surfaces by MRMP2//CASSCF/6-31G*. The structure at $\theta_1 = 50^\circ$ is obtained by the linear interpolation between the relaxed structure at $\theta_1 = 40^\circ$ and $\theta_1 = 60^\circ$. The interpolated point is surrounded by ellipse. The other points are located by the relaxed scan.

II. THE RESULTS OF CAS/6-31G*

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Species: S₀ Z-PDI

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.418160
C	1.141120	0.000000	2.176530
C	2.516407	0.000000	1.744381
C	3.524528	0.000000	2.639622
N	-1.077806	0.000000	-0.714819
H	0.919440	0.000000	-0.552972
H	-0.953463	0.000000	1.915337
H	0.990584	0.000000	3.241813
H	2.749896	0.000000	0.695341
H	4.549827	0.000000	2.323627
H	3.341876	0.000000	3.698612
H	-1.043823	0.000000	-1.715586
H	-1.990158	0.000000	-0.298484

Species: TS₁

C	0.001432	-0.005796	-0.037636
C	-0.004545	-0.011174	1.380869
C	1.245348	-0.037113	2.168044
C	1.872553	1.116280	2.619757
C	3.032116	1.113713	3.391944
N	-1.082186	0.001618	-0.751746
H	0.932478	-0.004427	-0.574635
H	-0.960407	-0.016306	1.880519
H	1.626498	-1.008838	2.433457
H	1.441768	2.069350	2.360115
H	3.481137	2.031969	3.714419
H	3.504167	0.195675	3.687751
H	-1.049239	0.008146	-1.754499
H	-1.995430	0.000524	-0.333790

Species: TS₂Supplementary Material (ESI) for PCCP
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C	-0.003491	-0.025093	0.004718
C	0.007419	0.035698	1.350967
C	1.240290	0.040684	2.146871
C	1.865329	1.194252	2.617790
C	2.996483	1.073107	3.379364
N	-1.106021	-0.163623	-0.776502
H	0.921921	-0.010899	-0.543789
H	-0.895206	-0.029248	1.940383
H	1.685891	-0.903661	2.426008
H	1.458536	2.158412	2.375086
H	3.515279	1.935547	3.755979
H	3.406061	0.110287	3.626533
H	-1.036314	0.074968	-1.739585
H	-2.010490	-0.036811	-0.379258

Species: S₁ Z-PDI*

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.378417
C	1.235440	0.000000	2.267232
C	2.541391	0.000000	1.844213
C	3.606425	0.000000	2.766115
N	-1.134231	0.000000	-0.743239
H	0.906599	0.000000	-0.572101
H	-0.937489	0.000000	1.902274
H	1.032281	0.000000	3.322195
H	2.785680	0.000000	0.798372
H	4.626896	0.000000	2.435101
H	3.425849	0.000000	3.824616
H	-1.096124	0.000000	-1.738270
H	-2.040033	0.000000	-0.326376

Species: Relaxed Structure at $\theta_1 = 40^\circ$ (RS₄₀)

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C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.397286
C	1.230284	0.000000	2.195417
C	2.387691	0.732853	1.905203
C	3.617424	0.331050	2.389851
N	-0.915433	0.596753	-0.733743
H	0.777087	-0.495013	-0.554315
H	-0.638947	0.813437	1.734367
H	1.440687	-0.929498	2.703949
H	2.330644	1.591439	1.259714
H	4.520966	0.793269	2.042416
H	3.711474	-0.494297	3.070145
H	-0.864001	0.582936	-1.730216
H	-1.699694	1.065882	-0.328839

Species: DP_{C40}

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.392799
C	1.249807	0.000000	2.178229
C	2.389726	0.735370	1.859530
C	3.643972	0.312630	2.273516
N	-0.890591	0.637847	-0.737486
H	0.759907	-0.522709	-0.552106
H	-0.612843	0.832390	1.726789
H	1.483041	-0.943282	2.649108
H	2.307877	1.608467	1.236904
H	4.532866	0.774872	1.890292
H	3.764574	-0.530336	2.927414
H	-0.836065	0.625608	-1.733320
H	-1.655886	1.137511	-0.334202

Species: DP_{H50}

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C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.391905
C	1.316516	0.000000	2.048036
C	1.591746	0.951183	3.033190
C	2.756097	0.885690	3.773030
N	-1.077028	-0.186029	-0.746853
H	0.879560	0.297562	-0.542849
H	-0.729567	-0.693799	1.782199
H	1.851155	-0.926029	2.209436
H	0.937572	1.797399	3.144582
H	3.011512	1.652333	4.479133
H	3.457168	0.081832	3.642919
H	-1.052142	-0.059774	-1.735411
H	-1.964360	-0.411027	-0.348171

Species: LEDP

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.375239
C	1.229234	0.000000	2.159732
C	1.862711	1.159625	2.616034
C	3.010697	1.087184	3.372198
N	-1.087047	-0.014715	-0.759014
H	0.928935	0.016775	-0.539917
H	-0.930640	-0.030344	1.919962
H	1.662226	-0.948944	2.438233
H	1.443145	2.117185	2.366754
H	3.504769	1.973551	3.721049
H	3.448174	0.142441	3.637235
H	-1.020648	-0.012670	-1.753517
H	-2.005868	-0.036468	-0.369422

Species: *E*-PDI

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C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.415516
C	1.186167	0.000000	2.095903
C	1.302540	0.000000	3.528499
C	2.503336	0.002581	4.141658
N	-1.066352	-0.000735	-0.732907
H	0.933483	0.000558	-0.533193
H	-0.939404	-0.000569	1.939447
H	2.104334	0.000615	1.531836
H	0.396177	-0.001460	4.107379
H	2.581879	0.003024	5.211646
H	3.424201	0.004224	3.587145
H	-1.014971	-0.000632	-1.732670
H	-1.985385	-0.001431	-0.332557